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RÉPUBLIQUE ALGÉRIENNE DÉMOCRATIQUE ET POPULAIRE
MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE SCIENTIFIQUE
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FACULTÉ DE TECHNOLOGIE

DÉPARTEMENT DE GÉNIE DES PROCÉDÉS

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Préparée par :

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Titre :

Préparation des Matériaux Composites Argile-Nanoparticules pour la Dépollution de l'Eau

Soutenue le 29 novembre 2025 en présence des membres du jury d'examen :

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Abstract:

This doctoral dissertation explores the design and application of modified clay–nanoparticle composite materials for the removal of organic pollutants specifically phenol and methyl violet dye from contaminated water. The study addresses the growing environmental concern associated with persistent toxic pollutants released from industrial effluents, which conventional treatment technologies often fail to eliminate efficiently. The research focuses on the preparation of several types of modified bentonites, including inorganic (Hematite Nanoparticles), organo-modified (intercalated with quaternary ammonium surfactants), and hybrid inorganic–organic composites. Detailed procedures for purification, sodification, intercalation, and pillarization were performed to tailor the physicochemical properties of the clay materials. Advanced characterization techniques (TGA, FT-IR, XRD, SEM-EDX, and BET) confirmed successful structural and surface modifications, revealing improved porosity, enhanced interlayer spacing, and the presence of active adsorption sites. These structural changes directly contribute to the increased affinity of the modified clays toward organic contaminants. Adsorption experiments were conducted to evaluate the performance of the synthesized materials under varying conditions, including pH, contact time, pollutant concentration, temperature, and adsorbent dosage. Adsorption isotherms (Langmuir and Freundlich) and kinetic models (pseudo-first-order and pseudo-second-order) were applied to understand the interactions and mechanisms involved. The findings demonstrate that the hybrid inorgano-organo bentonite composites exhibit superior adsorption capacities compared to raw and singly modified clays. This improvement results from the synergistic effects of surfactant intercalation and hematite nanoparticle incorporation. The study concludes that these engineered bentonite-based materials represent cost-effective and environmentally friendly adsorbents suitable for water purification applications.

Keywords: Adsorption, modified Bentonite, nanoparticules, organic polluants

Résumé :

Cette thèse de doctorat porte sur la conception et l'utilisation de matériaux composites à base d'argile et de nanoparticules pour l'élimination de polluants organiques, en particulier le phénol et le colorant violet de méthyle, présents dans les eaux contaminées. Le travail répond à la problématique croissante liée à la présence de polluants toxiques et persistants dans les effluents industriels, que les méthodes de traitement classiques ne parviennent souvent pas à éliminer efficacement. L'étude s'intéresse à la préparation de différents types de bentonites modifiées : inorganiques (renforcées par l'hématite), organiques (intercalées avec des surfactants ammonium quaternaires) et hybrides inorgano-organiques. Les étapes de purification, sodification, intercalation et pilari-sation ont été réalisées afin d'améliorer les propriétés physico-chimiques des argiles. Les techniques de caractérisation (ATG, FT-IR, DRX, MEB-EDX et BET) ont confirmé la réussite des modifications structurales et superficielles, montrant une porosité accrue, un élargissement de l'espacement interfoliaire et la présence de nouveaux sites actifs. Ces modifications améliorent nettement la capacité d'adsorption des matériaux. Des essais d'adsorption ont été menés pour évaluer l'efficacité des matériaux préparés en fonction de plusieurs paramètres : pH, temps de contact, concentration initiale du polluant, température et masse d'adsorbant. Les isothermes de Langmuir et Freundlich ainsi que les modèles cinétiques du pseudo-premier ordre et pseudo-second ordre ont permis d'interpréter les mécanismes d'adsorption. Les résultats montrent que les composites hybrides inorgano-organiques présentent les meilleures performances d'adsorption, grâce à l'effet synergique entre l'intercalation organique et l'incorporation de nanoparticules d'hématite. L'étude démontre que ces matériaux à base de bentonite constituent des adsorbants économiques, efficaces et respectueux de l'environnement pour la dépollution des eaux.

Mots-clés : Adsorption, Bentonite modifiée, nanoparticules, polluants organiques.

الملخص:

تتناول هذه الأطروحة تطوير واستخدام مواد مركّبة مكوّنة من الطين والجسيمات النانوية بهدف إزالة الملوثات العضوية، وخاصة الفينول وصبغة الميثيل **البنفسجي**، من المياه الملوثة. وتستجيب هذه الدراسة للتحديات البيئية المتزايدة الناتجة عن الملوثات السامة والمستعصية التي تُطرح في المياه الصناعية، والتي غالبًا ما تفشل طرق المعالجة التقليدية في التخلص منها بشكل فعّال. يركّز العمل على تحضير عدة أنواع من البنتونيت المعدّل، بما في ذلك البنتونيت غير العضوي (المعزز بالهيماتيت)، والبنتونيت العضوي (المُدخل بمواد فعّالة سطحياً من نوع الأمونيوم الرباعي)، وكذلك المركّبات الهجينة العضوية-غير العضوية. وتم إجراء عمليات التنقية، التبديل بالصوديوم، الإدخال العضوي، والتدعيم لتعديل الخصائص الفيزيائية والكيميائية للطين. وقد أكدت تقنيات التحليل نجاح هذه التعديلات من خلال إظهار زيادة في المسامية، وتوسّع في المسافات بين الصفائح، وظهور مواقع نشطة جديدة المختلفة على السطح، مما عزّز قدرة المواد على الامتزاز. أُجريت تجارب امتزاز لدراسة أداء هذه المواد تحت مجموعة من الشروط مثل درجة الحموضة، وقت التلامس، تركيز الملوث، درجة الحرارة وكمية المادة المازة. وتم استخدام نماذج لانغمير وفرويندلِش بالإضافة إلى النماذج الحركية لفهم آليات الامتزاز. اظهرت النتائج نجاعة المواد الهجينة المعدّلة التي تجمع بين مزايا التعديل العضوي وغير العضوي، مما يمنحها مواد أعلى كفاءة في إزالة الفينول وصبغة الميثيل البنفسجي مقارنةً بالبنتونيت الخام أو المعدّل بشكل منفرد. وتخلص الدراسة إلى أن هذه المواد تمثل حلولًا منخفضة التكلفة وصديقة للبيئة لمعالجة المياه الملوثة.

الكلمات المفتاحية:الامتزاز،طين البنتونيت المعدل، الجسيمات النانوية، الملوثات العضوية

Publications and Conference Contributions

1. Publications

“Enhanced removal of phenol from aqueous media by organo modified bentonite using a cationic surfactant (tetraheptylammonium bromide)”, Hanane Alidra[1,2]. Faycal Djazi[1,2]. Bahadir Keskin[3]. Received: 29 September 2023 / Accepted: 22 November 2023 / Published online: 30 December 2023. The Author(s), under exclusive licence to Springer Nature B.V. 2023. publication\H.Alidra et al, Res_ Chem_Intermed_ published 30-12-2023.pdf

2. Communications

“**Adsorption Kinetics of an Organic Pollutant onto a Modified Clay.”,** Autor: ALIDRA HANANE, Co-Autor: Pr DJAZI FAYCAL. Participation in the First International Conference on Industrial Processes and Environmental Conservation, which was held at the University of Skikda on December from 7 to 9, 2021.

“Élimination d’un Polluant Organique dans l’eau par Adsorption sur une Argile Modifiée. ”, Autor: ALIDRA HANANE, Co-Autor: Pr DJAZI FAYCAL. Participation at the First International Conference on Industrial Processes and Environmental Conservation, which was held at the University of Skikda on December from 7 to 9, 2021.

“Phenol adsorption from Aqueous Solution on Modified Organo-Bentonite”, Autor’s: ALIDRA HANANE, Co-autor: Pr DJAZI FAYCAL. Involvement in the First International Conference on Materials Science and Engineering (ICMSE'21), held at the University of Khenchela on December 2021.

“Adsorption of Organic Compound from Aqueous Solution onto Modified Nano-Bentonite.”, Autor’s: ALIDRA HANANE, Co-Autor: Pr DJAZI FAYCAL. Participation in the International Conference on Advanced Engineering in Petrochemical Industry (ICAEPI'21), which was held at the University of Skikda on November 31 to December 02, 2021.

“Modification de la Bentonite Algérienne par le Bromure de Tetraphetyl Ammonium pour l’Elimination des Contaminants Organiques Dans L’Eau”, Autor’s: ALIDRA HANANE, Co-Autor: Pr DJAZI FAYCAL. Participation in the national Conference on the 3rd National Seminar of Applied Chemistry (SNCA24), which was held at the University of Guelma on November 14, 2024.

“Un Nouveau Matériau à Base d'Argile pour la Dépollution des eaux : Efficacité d'Elimination d'un Contaminant Organique”, Autor’s : ALIDRA HANANE, Co-Autor : Pr DJAZI FAYCAL. Participation in the national Conference: “Le Deuxième Séminaire National de Chimie (SNC’2025)”, which was held at the University of Guelma on May 13 and 14, 2025.

Abbreviations and Symbols List

COD: Chemical Oxygen Demand; WHO: World Health Organization; MV: Methyl Violet dye;

PAHs: Polycyclic Aromatic Hydrocarbons;

PCBs: Polychlorinated Biphenyls;

UNICEF: United Nations International Children's Emergency Fund;

MV2B: type of Methyl Violet dyes;

C.I: Color Index;

NIRS: National Institute of Research and Security;

TO: Tetrahedral-Octahedral, a type of mineral consists of an octahedral and tetrahedral layer;

T: Tetrahedral layer;

O: Octahedral layer;

$(Si)_2(Al)_2O_5(OH)_4$: Chemical formula of clay mineral;

CEC: Cation exchange capacity;

$(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}\ (OH)_2 \cdot n\ H_2O$: the general formula for montmorillonite clay;

HDTMA: refers to a chemical compound “Hexadecyl Trimethyl Ammonium”;

ENOF : the company « Entreprise Nationale des Produits Miniers Non Ferreux & des Substances Utiles »;

BWL: Burning Weight Loss

THPAB: refers to a chemical compound “Tetra-heptyl Ammonium Bromide”; CTAC: refers to a chemical compound “Cetyltrimethyl Ammonium Chloride” Na-Ben: in this work refers to “sodium bentonite”;

CTA-Ben: in this work refers to “Cetyltrimethyl Ammonium sodium bentonite”;

THPA-Ben organo-bentonite: in this work refers to “Tetra heptyl Ammonium Sodium Bentonite”;

α-Fe_2O_3- Ben: in this work refers to “Hematite Bentonite”;

α-Fe_2O_3-THPA-Ben: in this work refers to “Hematite Tetra heptyl Ammonium Bentonite”;

α-Fe_2O_3-CTA-Ben: in this work refers to “Hematite Cetyltrimethyl Ammonium Bentonite”;

$THPA^+$: Tetra heptyl Ammonium cation;

$CTA^{+:}$ Cetyltrimethyl Ammonium cations;

IUPAC: International Union of Pure and Applied Chemistry

SSA: specific surface area;

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General Introduction

General Introduction

Earth stands out among the solar system's planets as the only one endowed with a hydrosphere, which encompasses over 70% of its surface. Water transitions through three main sectors: the oceans (hydrosphere), the atmosphere, and the soil (lithosphere). The solar energy received by Earth heats the hydrosphere, causing evaporation and the subsequent presence of water vapor in the atmosphere. Upon cooling, this vapor condenses into droplets or ice crystals, resulting in precipitation such as rain, snow, or hail that descends onto the lithosphere [1]. This operational framework facilitates the identification of various water types, each characterized by different uses and compositions.

According to its important in earth equilibrium, water shouldn't not be perceived solely as a commercial entity; it should be recognized as a universal heritage that requires diligent protection and advocacy. This essential resource is fundamental to human survival, health, and nutrition, and it is intricately linked to agricultural and economic activities, as well as the quality of the environment. Nevertheless, it also serves as a universal repository for various pollutants.

Water, although it may seem inexhaustible, is distributed unevenly around the world. All nations will have to tackle the problem of water scarcity, both in the short and long term. The management of surface water resources has long been a key concern for public officials. In Algeria, water availability is estimated at 17 billion cubic meters per year, with 12 billion cubic meters located in the northern regions (comprising 2 billion cubic meters from groundwater and 10 billion cubic meters from surface water) and 5 billion cubic meters in the southern regions. It is important to note that over 70% of the surface water resources in the north are already being utilized [2]. The growing in industrialization decreases the water needs to its uses in all category of industries: chemical, petrochemical, pharmaceutical, agro-food, dyeing, …. and a lot of activities.

All that generate substantial pollution in natural water sources. The issue of water pollution constitutes a major risk to an imbalance in ecosystems and adversely impact human health, the environment, and aquatic systems, as pollutants originating from human activities contaminate water sources. Many of these pollutants are extremely toxic, and their presence, even in trace amounts, can result in harmful effects. Furthermore, water pollution exacerbates the scarcity of freshwater resources, a situation that is particularly acute in many developing countries.

The use of organic synthetic dyes spans multiple industrial sectors, including automotive, chemical, textile, leather, paper, printing, plastics, paints, cosmetics, pharmaceutical, and food industries use dyes extensively. The colored emissions of these dyes, causes a serious risk to

human health and environment, as contaminants from human activities infiltrate aquatic ecosystems. Many of these pollutants are notably toxic, and even low levels can result in adverse health effects.

Additionally, water pollution contributes to the diminishing availability of freshwater resources, a critical issue in many developing countries [3]. It is common to observe that during dyeing processes, approximately 15% to 20% of the dyes, and in certain cases up to 40% reactive dyes, are expelled with liquid effluents, which are frequently released into aquatic environments without prior treatment [4]. Similar to other organic substances, dyes are dangerous to human health, some synthetic pigments demand particular treatment strategies. However, the standard procedures used by wastewater treatment facilities are often poorly suited or entirely inadequate for the remediation of these biocidal pollutants.

Methyl violet (MV) has a crucial role due to its widespread application in textiles, paints, and printing inks, as well as in the dyeing processes of cotton, silk, paper, and leather, among other uses. Additionally, MV serves a purpose in the medical field as a key component of Gram's biological stain for the classification of bacteria. Although it can occasionally function as a subpar disinfectant, it has been identified as toxic to a majority of animal species. Inhalation of MV may lead to irritation of the respiratory system, while ingestion generally causes discomfort in the digestive tract [5].

Organic compounds polluted water, represents a significant environmental hazard owing to its intricate composition and elevated levels of persistent organic pollutants. Among these, the chemical oxygen demand (COD), exceeding 50,000 $mg.L^{-1}$, and phenolic compounds, approximately 5,000 $mg.L^{-1}$, are particularly concerning due to their stability, toxicity, and resistance to degradation. Elevated COD levels indicate a variety of contaminants, including phenols and other hazardous substances, which impose a considerable oxygen demand upon their release into aquatic environments, resulting in oxygen depletion and adverse impacts on aquatic life. Phenols, organics that are known for their high toxicity and potential for bioaccumulation [6].

Phenol represent is a hazardous substance prevalent in the wastewater effluents of numerous manufacturing sectors, including those involved in the production of polypropylene, cotton textiles, textile mills, refineries, coke ovens, iron and steel, insecticides, dyes, and intermediates. The unregulated release of these compounds into the environment poses significant risks to human health, manifesting both acute and chronic symptoms. In humans, exposure to phenolic substances can lead to irritation of the eyes, skin, and mucous membranes.

Repeated exposure has been associated with symptoms such as anorexia, weight loss, diarrhea, dizziness, excessive salivation, and darkened urine. In severe instances, such exposure may culminate in coma and respiratory failure [7].

The World Health Organization (WHO) highlights the necessity of purifying water to eradicate dangerous chemicals and other disease-inducing agents. Unfortunately, in some countries, water supplies are commonly compromised by microbiological contaminants, hazardous organic substances, industrial effluents, insecticides, and other anthropogenic influences [8].

Consequently, there is an urgent need to investigate appropriate methods, techniques, and materials for water decontamination to address this worsening issue that endangers both humanity and its environment.

Traditional approaches to water depollution, such as chemical precipitation, nano-filtration, and reverse osmosis, tend to incur high costs. As a result, it is essential to investigate cost-effective alternatives, like adsorption, that utilize eco-friendly inexpensive adsorbents produced from green sustainable substances for treating contaminated water [9]. In recent years, the employment of natural and modified clays for the removal of non-ionic organic compounds from contaminated water has become increasingly vital, primarily due to their high efficiency and low-cost. Modified clays have particularly piqued interest of many researchers because of their exceptional sorption properties, enabling them to modification and effectively adsorb organic compounds. The occupation of the interlayer space by an organic solvent leads to sorption mechanisms that involve the separation of solutes across the bulk volume, the aqueous phase, and the microscopic organic phase contained within the interlayer. Furthermore, solute retention may also take place through adsorption on surfaces [10].

Several scholarly works have examined the adsorption characteristics of modified-bentonites, investigating various factors affects adsorption mechanism. It is recognized that bentonite is integral to retention of hazardous water pollutants as phenol [11,12] and MV dye [13,14]. Our research work, study with selection of appropriate modified bentonite for the elimination of organic compounds, Phenol and MV from aqueous media that was realized in the Research on Physic-Chemistry of Surfaces and Interfaces Laboratory (LRPCSI) at the University of August 20, 1955 – Skikda. We suggest comparing the efficiency of different types of modified bentonites: Inorgano-Bentonites, Organo-Bentonites and the novel Inorgano-Organo-Bentonites on both phenol and MV adsorption mechanisms. The integration of the inorganic substances, Hematite nanoparticle “Fe_2O_3” into the interlamellar space of the studied modified bentonites enhance the adsorption characteristics. The sorption data provided in this thesis corroborate this theoretical framework with the Algerian bentonite under investigation.

This thesis is structured as following:

- Six chapters, the first one, is a theoretical overview of water pollution and practically causes by phenol and methyl violet dye. While the second chapter addresses water depollution techniques focusing on adsorption, bentonite and modified bentonites-based adsorbents. The third chapter is dedicated to a detailed preparation methods and materials of the modified-bentonites. The next fourth chapter of this manuscript resume all details of the characterization of the synthetize materials. The fifth chapter summarized the comparative investigation of both phenol and MV onto the studied adsorbents. We complete with the last part of our study presented in this thesis with the last sixth chapter that includes isotherms and kinetics of the performed adsorption mechanisms.

We finish, the manuscript with a general conclusion followed by the scientific research publications related to our thesis project.

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Chapter I: Water Pollution

I.1 Introduction

The issue of water pollution is a critical environmental challenge, as numerous organic and inorganic substances can be transported through surface and groundwater [1,2]. In our thesis work, we focus on organic pollution caused by contamination from aromatic organic compounds and dyes.

Phenolic compounds are prevalent contaminants found in wastewater, primarily produced by industries such as petroleum and petrochemicals, coal conversion, pulp and paper, and the production of phenol [3]. Given their detrimental effects on living organisms at minimal concentrations, phenols are designated as priority pollutants, with many classified as hazardous due to their potential risks to human health. The issue of water pollution caused by dyes becomes a prominent global challenge in recent years, garnering considerable attention from various stake holders [4]. The production of industrial organic dyes and pigments exceeds 100,000 distinct varieties, with total annual output amounting to several tons [5]. As a result, the discharge of dyes into water systems during manufacturing and usage further aggravates the environmental consequences, creating significant difficulties [4,6]. Methyl violet, along with various other basic dyes, is commonly polluted water.

Recently, there has been a growing interest this type of water pollution, caused by dyes and pigments to preserve aqueous environments. The focus of this chapter will be focus on the presence of phenol and methyl violet in water, and the resulting pollution.

I.2. Water Pollution

Water pollution, is the degradation of water quality, defined as well as the direct or indirect introduction of harmful substances into water, occurs when its physical, chemical, and biological properties are altered. This phenomenon has been the subject of considerable investigation regarding its detrimental effects on living organisms [7–9].

Figure I.1: Water Pollution and Discharge of Toxic Substances [10]

I.3. Origin of Water Pollution

Water pollution is basically resulting from human activities, which can threaten human health and the quality of ecosystems, both aquatic and terrestrial, that depend on these water systems. This can result in damage to physical property, a reduction in environmental quality, or limitations on other acceptable uses of the environment.

However, an examination of the various types of pollution indicates that, in addition to human influence, natural occurrences such as volcanic eruptions, severe weather, and earthquakes also contribute to this environmental challenge [9].

Besides, the origins of this pollution can be traced to multiple human-induced sources, the most significant of which include:

I.3.1. Domestic Pollution

It’s chiefly caused by the disposal of various materials from homes, including wastewater from cleaning, oil residues, and excrement.

I.3.1.1. Urban Activities

Urban water pollution primarily arises from the wastewater generated by residential and commercial establishments. This pollution is characterized by the discharge of domestic waste, collective washing waters, and various products discarded by the inhabitants of urban areas, including industrial effluents from small enterprises. The volume of wastewater released varies significantly depending on the size and activity level of the urban area. The term "sewer system" aptly captures this complexity. The contaminants present include human waste, food remnants, by products from slaughter houses, hospital discharges, laundry detergents, insecticides, hydrocarbons, small-scale industrial waste, and a range of toxic substances. Primarily due to domestic discharges: household chores, sewage systems, kitchen effluents.

I.3.1.2. Agricultural Activities

This sector employs nitrogen and phosphorus-based chemical fertilizers along with phytosanitary agents aimed at protecting crops and easing the workload of farmers.

However, the excessive use of these potentially harmful products can lead to the contamination of surface waters through leaching and runoff during rainfall, as well as the infiltration of groundwater. It is widely recognized that mineral fertilization can enhance crop yields; however, the application of high doses, which often surpass the actual requirements of the crops, can result in nitrogen excesses that may impede agricultural productivity through various pathways and lead to environmental degradation. Pesticides are utilized in agriculture to defend crops and harvests from adversaries, thereby increasing yields.

The leaching of these agricultural pesticides results in the pollution of water sources with toxic compounds, with their occurrence in aquatic ecosystems being exclusively attributed to diffuse pollution.

I.3.2. Industrial Pollution

It is significantly characterized by the discharge of liquid waste, which contributes to both organic and toxic contamination. These wastes originate from various industries, predominantly located along coastlines, where they dispose of waste directly and cool their machinery. Key sectors include food processing, agriculture, tanning and textiles, paper production, physical industries, chemical manufacturing, and petrochemicals.

This form of pollution poses toxic risks to living organisms and can impair the natural self- purification processes of water, potentially leading to the accumulation of harmful substances, such as heavy metals and radioactive materials, within the food chain. The impact of industrial discharges on water quality is influenced by their oxygen affinity, the concentration of suspended solids, and the levels of various substances present.: agro-food, chemical and pharmaceutical manufacturing, petrochemical processes, refining industries, dyeing.

I.4. Types of Water Pollution

There are three primary categories that define pollution:

I.4.1. Physical Pollution

Arises from various solid elements released through domestic and industrial discharges. It can be categorized into several types:

1. Solid Pollution: which originates from solid particles carried by industrial wastewater and runoff, as well as from open waste dumps.

2. Thermal Pollution: typically caused by water from industrial cooling systems, significantly alters the temperature of water bodies, thereby impacting the ecological balance of natural aquatic environments and the survival of living organisms.

3. Radioactive Pollution: is associated with the release of radioactive materials from nuclear facilities and radioactive waste treatment plants [10].

I.4.2. Chemical Pollution

Is caused by the presence of organic and inorganic pollutants that stem from a variety of human activities. This type of pollution includes a wide array of substances, such as solvents, metals (including zinc, lead, and cadmium), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pharmaceutical products, pesticides, and salts.

I.4.3. Microbiological Pollution

It arises from various sources, including hospital discharges, agricultural activities, and wastewater effluents. Consequently, water becomes contaminated with pathogenic microorganisms such as bacteria, viruses, and parasites, which pose significant risks to both environmental integrity and human health [11].

I.5. Water Pollution Impacts

Contaminated water sources cause irreversible harm to both health of living beings and integrity of ecosystems.

I.5.1. Environmental Impacts

The release of wastewater directly into the environment creates significant risks for the survival of various organisms and disrupts ecological equilibrium. For example, high levels of nitrogen and phosphorus can trigger eutrophication, which leads to rampant plant growth and a decrease in dissolved oxygen levels, ultimately resulting in the demise of numerous aquatic species, including fish and crustaceans. Furthermore, the presence of trace metals such as mercury and arsenic in these waters poses a serious threat to the most sensitive organisms, as their toxicity can induce dysfunctions and impairments in essential physiological processes such as nutrition, respiration, and reproduction [12].

The infiltration of contaminated water through soil layers can lead to a deterioration in the quality of groundwater, as it allows for the migration of contaminants found in the wastewater into the aquifers [13].

I.5.2. Human Health Impacts

Water is a vital resource for human existence. Insufficient access to clean water or the presence of contaminated water sources results in a wide array of health problems worldwide, especially in developing nations, where 80% of diseases are linked to water [7,14]:

- Water-related illnesses can be classified into six primary categories:
- Diseases that are transmitted via water (such as parasites, bacteria, and viruses);
- Skin and ocular infections caused by insufficient water supply;
- Diseases resulting from aquatic invertebrates;
- Illnesses associated with insects that proliferate near water.

The World Health Organization (WHO) estimates that each year, there are around 4 billion cases of diarrhea, in addition to millions of other health issues, linked to a lack of access to safe drinking water. Each year, 1.7 million people die from diarrhea, with the majority being children under five years old. The impact of waterborne diseases on human health is significant, compounded by pollution from chemical discharges into water bodies due to various human activities. UNICEF indicates that 60% of child mortality worldwide is due to infectious or parasitic diseases, primarily related to water pollution [15,16].

I.6. Water Pollution Caused by Organic pollutants

The extensive application of organic pollutants, particularly dyes and phenolic compounds, in industries such as textiles, paper, cosmetics, pharmaceuticals, paints, leather, food, and plastics has resulted in severe environmental pollution, especially in aquatic ecosystems.

Each year, the production of synthetic dyes exceeds 700,000 metric tons, with over 100,000 dye varieties available in the market. The textile sector is responsible for approximately 15% of the total global dye production, with nearly 97% of local dye wastewater being generated by the food, chemical, and textile industries. Regrettably, a significant portion of the leftover dyes from dyeing and finishing processes is released into the environment, often without any form of remediation. This situation raises critical concerns, as the discharged wastewater contains dyes that are known to be toxic, mutagenic, and carcinogenic, leading to detrimental effects on natural water bodies [17,18].

Methyl Violet 2B dye is recognized for his vivid and striking hues, making them a popular choice in the dyeing of various textiles, including cotton, wool, and silk. These dyes have facilitated the production of a diverse palette of colors, thereby assisting textile manufacturers in satisfying the increasing consumer demand for vibrant and colorful fabrics [19].

The swift advancement of the chemical and petrochemical sectors in recent decades has raised significant public apprehension regarding the extensive pollution of water bodies by numerous organic compounds produced during the manufacturing and processing phases of organic chemicals. Typically, organic constituents found in these wastewaters surpass the permissible limits for safe discharge [20].

Phenols, an organic product that frequently appear as contaminants in wastewater originating from petroleum and petrochemical industries, coal conversion processes, and facilities engaged in the production and processing of phenols for plastic manufacturing. Due to its high toxicity to living organisms, even at minimal concentrations, phenol is designated as a priority pollutant in wastewater. Furthermore, it is classified as a hazardous substance due to its potential adverse effects on human health [17,21].

I.6.1. Methyl Violet Dye

A dye is characterized as a substance that can permanently color another material. Historically, dyes were predominantly sourced from nature, including botanical, zoological, and mineral origins. The extraction process was frequently expensive, and the methods of application were often inconsistent and laborious. The first synthetic dyes emerged in the middle of the XIXth century. The progress of the dye industry has been intricately connected to the rise of synthetic dyeing and the overall development of chemical science. A genuine dye is defined by two independent characteristics: its color and its capacity to bond with a medium. Today, dyes serve as a fundamental material across various industries, including textiles, leather, paper, plastics, pharmaceuticals, and cosmetics, among others. The global production of dyes is approximately 7.105 million tons per year [22]. The release of dyes into the environment poses a significant issue. The presence of such contaminants in water is highly noticeable and undesirable, even in trace amounts. Numerous studies have demonstrated that exposure to dyes can lead to adverse effects on human health. This chapter will subsequently present the various families of chemical dyes, their environmental and biological risks, as well as the primary techniques for the remediation of industrial discharges [23]. Triphenylmethane dyes are used extensively in many industrial processes, such as textile dyeing, printing, papermaking, and in leather, food, and cosmetic manufacturing, these dyes may still persist in some environments [24].

I.6.1.1. Physic-Chemical Properties of MV2B

The Methyl Violet or triphenylmethane dyes, are known as MV2B and its Color Index Number (C.I. 42535), an organic compound soluble in water, ethanol, methanol, diethylene glycol and dipropylene glycol. It is a dark green powder dye stable under ordinary conditions and has a poor resistance towards light and to chemical bleaches [25,26].

The chemical formula is $C_{24}H_{28}N_3Cl$, and the molecular weight is 393.96 $g.mol^{-1}$ [27]. The MV is a water-soluble; it becomes yellow in the pH range of 0.13 to 0.5 and green to blue in the pH range of 2.0 to 3.0 [28]. Dyes are organic compounds that dissolve in solvents used for coloring and dyeing. They are generally categorized into three types: anionic, non-ionic, and cationic. Among these, cationic with their cyclic structures, have a lot of properties that makes them strong adhesion, and stability in products [29]. Some Physic-Chemical properties of the MV2B dye are organized in table I.1 [30,31].

Table I.1: Physic-Chemical Properties of MV2B

	Properties	
Methyl Violet Dye « MV2B »	Molecular formula	$C_{24}H_{28}N_3Cl$
	N° CAS	C.I. 42535
	Molar mass, g/mol	393.96
	Appearance	Crystalline solide, Green powder
	Odor	Odorless
	Melting point	137 °C
	Absorption(λmax),nm	583-587 nm
	Solubility	50 g/l in water; at 25 °C 60 g/l in alcohol

I.6.1.2. Hazards, Toxicity and Safety of MV2B

Organic dyes owing to their limited biodegradability and the potential carcinogenic risks they pose to human health and environmental. Exposure to these substances may result in a range of health complications, such as dermatitis, pain, significant respiratory tract irritation, nasal septum perforation, skin ulcers, and acute diarrhea [32].

Like Dyes, are extensively utilized across various industries for the purpose of imparting color. However, these compounds can present significant long-term environmental risks. Dyes are generally categorized into three types: anionic, non-ionic, and cationic. Among these, MV2B cationic dyes are particularly hazardous due to their cyclic structures, which contribute to their toxicity. Despite their dangers, cationic dyes are favored in industrial applications due to their ease of use, strong adhesion, and stability in products, that’s why it’s necessary to keep attentive when using, storage and transportation [33]. This particular dye is extremely hazardous to human health, possesses carcinogenic and mutagenic properties suspected of causing cancer in humans and is recognized as an irritant that can harm the eyes, skin, and both the gastrointestinal and respiratory systems. Besides, dangerous for aquatic environment, MV restricts the growth of microorganisms and interferes with photosynthetic activities in aquatic organisms [27,29]. The table I.2, present the Hazards, Toxicity and Safety concerns of MV2B [30].

Table I.2: Hazards, Toxicity and Safety of MV2B

Methyl Violet "2B"		Causes severe skin burns and significant eye injuries	Stringent preventive measures are necessary when storing and using phenol and its aqueous solutions
		Very hazardous in case of skin contact (corrosive and irritant),	Using standard safety protocols of use.
		Carcinogenicity, and mutagenicity penetrating	Limit exposure, controlled handling
		Soil and groundwater contamination, biodegradable, slow photodegradation, toxic for aquatic organisms	Never dispose of it down the drain, collect waste of the hazardous chemical

I.6.1.3. Applications

Dyes are organic compounds that dissolve in solvents and are extensively utilized across various industries, including textiles, paper, leather, printing, food, and pharmaceuticals. Methyl violet 2B dye, used for the purpose of imparting color as a coloring material in dyeing. Because it is a cationic basic dye used as a pH indicator. However, these compounds can present. With its favorable properties, the cationic dye is various industrial applications due to the ease of use, strong adhesion, and stability in products [29]. It's also used in clinical diagnosis for microscopy, bacteria staining according [30].

I.6.2. Phenol

I.6.2.1. Physic-Chemical Properties of Phenol

Phenol, an aromatic compound classified as an acidic alcohol, is also referred to carbolic acid, hydroxybenzene, hydroxyl benzene, and benzo-phenol.

This compound, exhibits a strong reactivity towards oxidizing agents. The reactions it undergoes with several substances, including formaldehyde, aluminum chloride, nitrobenzene, sodium nitrate, and 1,3-butadiene, can be quite explosive. Furthermore, when heated, liquid phenol can damage certain metals like lead, zinc, and aluminum, as well as specific types of plastics, notably polyethylene. At normal temperature and pressure, phenol is found in a solid state, appearing as either a crystalline mass or colorless needles. This compound is hygroscopic and has a characteristic odor that is both sharp and slightly sweet (with an olfactory limit of 0.05 ppm). The presence of impurities, moisture, or light can cause phenol to take on a pink or red hue. It can liquefy when mixed with a small amount of water, approximately 8%. Products containing over 10% water are sold as liquid phenol [34].

Phenol appears as a translucent, colorless crystalline substance and a white powder at ambient temperature; however, when combined with water, it transforms into a viscous liquid. The Phenolic crystals exhibit hygroscopic properties, allowing them to readily absorb moisture from the atmosphere, resulting in a color change from pink to red upon exposure to air. This compound possesses a sweet, tar-like odor and demonstrates solubility in alcohol, glycerol, petroleum, and water. Noted that phenol appears as a colorless crystalline solid, characterized by a sweet, tarry scent reminiscent of a clinical environment, and is highly toxic [17].

Table I.3: Physic-Chemical Properties of Phenol

	Properties	
Phenol	Molecular formula	C_6H_6O
	N° CAS	108-95-2
	Molar mass, g/mol	94.11
	Density, g/cm3	1.07
	Appearance	Transparent crystalline solide
	Odor	Odorless
	Melting point, °C	40.5
	Boiling point, °C	181.7
	Absorption(λmax),nm	270
	Solubility	8.3 g/100 mL in water at 20 °C

I.6.2.2. Hazards, Toxicity and Safety of Phenol

Phenol’s status is given as priority pollutants that can be highly toxic, even in low concentrations [17].

Many research works were performed in the reason of study hazards, toxicity of phenol and to publish the safety concerns to protect exposures, according to the investigations executed on phenol by the national institute of research and security “NIRS” in France, the findings are presented in Table I.4 [34].

Table I.4: Hazards, Toxicity and Safety of Phenol

	Pictogram	Hazards	Safety
Phenol		Causes severe skin burns and significant eye injuries	Stringent preventive measures are necessary when storing and using phenol and its aqueous solutions
		Toxic upon: inhalation, skin contact and if ingested	Using PPE when handling.
		Susceptible to the induction of genetic mutations.	Using PPE when handling. Minimize exposure frequency.
		Highly toxic to aquatic and soil organisms, causes groundwater contamination and air pollution.	Handling in a fume hood,

I.6.2.3. Applications

Phenol serves primarily as an intermediary in various industrial applications. It is utilized in the plastics industry for the production of bisphenol A, which is essential for creating phenolic resins. Additionally, phenol is involved in the synthesis of alkylphenols, caprolactam, salicylic acid, chlorophenols, nitrophenols, picric acid, and adipic acid. It also plays a role in the manufacture of plasticizers, adhesives, hardeners, solvents, and insulators. In the pharmaceutical sector, phenol is employed as a disinfectant, antipruritic agent, and local anesthetic. It has been banned in cosmetics since 2005, however, since 2006, its use as a biocidal active substance has been prohibited [34].

I.7. Conclusion

At the end of this chapter, we conclude that the important of water as a natural resource, put a huge responsibility on us minimize and control harmful and hazardous substances discharges in utilized water. Some industrial activities are the most important causers of water pollution. Chemical, petrochemical, dyeing, automotive, … generates a significant quantity of organic pollutants that are rejected in water. Organic pollutants are considered as the most toxic water contaminants according to their properties that affects human health, environment and eco- system. Removing those pollutants from water is the interest of the recent scientific research works. That aims to develop new low-cost eco-friendly solutions, techniques and materials for water depollution.

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Chapter II: Water Depollution

II.1. Introduction

Water is a vital resource for human health and development, but with increasing consumption by individuals and pollution problems caused mainly by the uncontrolled and untreated discharge of wastewater, which contributes considerably to the contamination of groundwater and the increase in its rise, it's essential to think about purifying this water. That's why, since ancient times, big scientific interests are focused on elimination of a category of water pollutants that are organic contaminants from water. In this chapter, we present the various methods used in water depollution, and principally adsorption to remove organic pollutants from aqueous solutions with the use of a local material, such as clay and modified clay, to treat wastewater is a promising technique for purifying this water.

II.2. Water Depollution

A numerous methods and techniques are used to reduce water pollution, some of them are recuperative methods and its strategy is to reclaim and enhance the pollutant for diverse applications, and others are destructive method that facilitate the removal of pollutants through their degradation. Other classification existed also:

II.2.1. Chemical Oxidation

The Chemical oxidation techniques are generally applied for the treatment of wastewater containing non-biodegradable pollutants and also for hazardous organic pollutants present in low concentrations. There are two types oxidation:

II.2.1.1. Classical Oxidation

It consists of adding an oxidizing agent to the water to be treated. Among the most commonly used oxidants are chlorine, hydrogen peroxide (H_2O_2), oxygen (O_2) and ozone (O_3). It has been found that this process is sometimes insufficient to remove some persistent pollutants [1].

II.2.1.2. Advanced Oxidation

Is based on the generation of an •OH radical which is a very strong oxidant (($E° = 2.8$ V/ESH at 25°C) and very reactive capable of oxidizing contaminants organics that are refractory. Below are the main methods of generating this radical:

1. **Fenton process ($Fe^{2+/}H_2O_2$):** This process is a combination of H_2O_2 and Fe^{2+} (reagent fenton). This results in the formation of the hydroxyl radical. According to many studies this process has a high efficiency for the removal of water pollutants [2,3].

2. **Peroxonation (O_3/H_2O_2):** The decomposition of ozone (O_3) in the presence of peroxide hydrogen promotes the formation of the hydroxyl radical. But its effectiveness depends on the nature of the pollutant [4].
3. **Photolysis of hydrogen peroxide (UV-H_2O_2):** this process consists of irradiating the peroxide hydrogen by UV rays in order to generate the hydroxyl radical. The effective use of this technique was proven in reducing water pollution [5].
4. **Photocatalysis of hydrogen peroxide (TiO_2/UV/H_2O_2):** Several factors are at the origin of the wide use of TiO_2 as a photocatalyst such as its low cost and stability both in acidic and basic media. It has successfully applied to remove water [6].

II.2.2. Biological Techniques

These methods involve breaking down organic pollutants present in water by microorganisms. There are two modes for this type of treatment:

II.2.2.1. Aerobic Technique

It takes place in a basin made up of active sludge on which organic pollutants will undergo biodegradation by bacteria and others microorganisms. This operation is characterized by its effectiveness against certain organic pollutants by biodegradation [7,8].

II.2.2.2. Anaerobic Technique

It is based on the degradation of organic pollutants by microorganisms in the absence of oxygen, but for certain pollutants, anaerobic degradation causes the formation of amines which are more toxic than the initial compounds [9].

II.2.3. Physic-Chemical Techniques

II.2.3.1. Precipitation and Co-precipitation

The principle of this method is to react contaminant with precipitating agent (based on iron or aluminum, … salt), resulting in the formation of a precipitate. So that the ions can be effectively removed. Sometimes, pre-treatment by oxidation is necessary [10].

II.2.3.2. Coagulation-Flocculation

This method is used to reduce the percentage of organic pollutants in wastewater. Many researchers applied this method to treat polluted water, many coagulants are used effectively industrial ones as: $MgCl_2$ [11], and ferric chloride [12] as natural coagulant extracted from the plants [13].

II.2.3.3. Ionic Exchange

Ion exchange is a commonly employed technique for the removal of charged contaminants, including both anions and cations. The fundamental principle of this method involves passing contaminated water through a series of resins that can exchange harmless ions for the charged contaminants present in the water [14].

II.2.3.4. Membrane Technology

We distinguish four types of membranes used for the removal of water contaminants. They are applied in microfiltration, nanofiltration, reverse osmosis and ultrafiltration. Microfiltration is generally used for the retention of disperse insoluble in water [15–17]. Reverse osmosis is the most widespread technique [14,18].

II.2.4. Adsorption

In the context of terminology, “Adsorption” this term was first refers the condensation of gases on surfaces from the process where gas molecules penetrate into the bulk. Subsequently, the adsorption process and the reverse phenomenon of desorption appears. In science and technology, adsorption is a surface phenomenon in which atoms or molecules adhere to the solid surface of an adsorbent through various mechanisms. Desorption, conversely, refers to the process by which adsorbed molecules or atoms are released from the substrate [19]. It consists in attaching molecules to the surface of solids by covalent bonds or specific interactions. It is largely and effectively used as depollution techniques and, by being a subject that has garnered the interest of numerous research studies, and it is essential to articulate our work efficiently.

Figure II.1: Adsorption Principle [20]

This technique is widely used to trap both organic and inorganic pollutants. However, the problem of regeneration and its high cost were behind the search for other alternatives. Numerous studies have been performed to discover effective economic adsorbents for removing water pollutants as organic compounds [20–27] and dyes as well [28,29]. Natural Clays were the object of many research works, the important capacity of adsorption of those minerals was improved also in reducing water pollution [30,31]. Their low-cost and abundance have led to numerous studies focusing on their modification to advance their ability to retain water pollutants [32,33].

II.3. Principles Regarding Adsorption

Adsorption in closed systems, like any transfer process, is governed by an exchange mechanism between the contacting phases. This mechanism is influenced by operational conditions and the physicochemical properties of the adsorbent and adsorbate.

II.3.1. Adsorption Mechanism

During the adsorption process, the pollutant is transferred from the adsorbate phase to the adsorbent phase. Clays serve as excellent adsorbents due to their porous properties. Depending on the mechanisms involved, two distinct types of adsorptions can be identified:

II.3.1.1. Physical Adsorption

Is due to electrostatic forces between the solute and the solid surface. It involves low energies. Characterized by interactions of the Van der Waals type between molecules and surfaces. These interactions encompass London dispersion forces, as well as dipole-dipole and induced dipole- dipole interactions. In the case of ions, the adsorbed species retain associated water molecules. This process can lead to the deposition of multiple layers of atoms or molecules, particularly at the solid-gas interface. Physical adsorption is typically easily reversible and exothermic.

II.3.1.2. Chemical Adsorption

Involves the adherence of a molecule to a surface through ionic or covalent or hydrogen bonds between the adsorbate and the adsorbent. Unlike physical adsorption, chemisorption is often more difficult to reverse and is limited to a monomolecular layer. The bonding in chemical adsorption is frequently specific by its irreversibility due to the significant energies, occurring only between elements with compatible electronic configurations.

Figure II.2: Adsorption Mechanism [34]

II.3.2. Adsorption Isotherms

Various theoretical and empirical models have been proposed to elucidate the relationship between the equilibrium adsorbed amount (q_e) and the equilibrium concentration (C_e). An adsorption isotherm is defined as the collection of equilibrium points that represent qe by an as a function of the remaining C_e, expressed as qe = f (C_e). In the closed system residual method, the concentration of the adsorbate retained by the adsorbent is determined by the difference between the initial concentration of the solute (C_0) and C_e. The computation expression of (q_e) is detailed in part (IV.2.2.1). In the liquid phase, four distinct types of adsorption isotherms can be identified, as proposed by Giles in 1974 [35]:

- **The S Isotherm,** is characterized by an increasing slope as the concentration of the solute in solution rises. This behavior typically indicates the presence of interactions among molecules within the adsorbed phase, often referred to as "lateral interactions." Conversely;
- **The L Isotherm,** also known as the Langmuir isotherm, exhibits a decreasing slope with increasing solute concentration. This type of adsorption occurs at specific sites where lateral interactions are minimal. In the Langmuir model, it is assumed that all adsorption sites possess identical energy levels.
- **The H Isotherm,** represents an extreme case of the L curve, indicating a very high affinity of the solid phase for the adsorbed substance.
- **The C Isotherm,** which is linear, is characterized by a constant slope regardless of the concentration of the species involved, up to the maximum adsorption capacity. This is rarely observed and may also indicate an absorption phenomenon, leading to a partition coefficient between two phases.

Figure II.3: Types of Adsorption Isotherms in Liquid Phase [36]

II.3.3. Modeling of Adsorption Isotherms

The modeling adsorption isotherm is a graphical representation of the amount adsorbed by unit of mass or unit of surface area as a function of the concentration of the solute at equilibrium. This representation makes it possible to characterize the adsorbent/adsorbate interactions by studying the effect of initial solute concentration on the adsorption capacity of adsorbents.

Several mathematical models have been developed for the characterization of adsorbent- adsorbate interactions. For our study, we used two models most requested empirical models, the Freundlich model and Langmuir model. These models give in most cases a correct representation of the isotherm's adsorption.

II.3.3.1. Freundlich Model

The Freundlich model assumes that the adsorbent surface is heterogeneous with a non-uniform energy distribution of adsorption sites on the surface [33]. The nonlinear form of this model is expressed by the equations detailed in part (V.2).

II.3.3.2. Langmuir Model

According to this model, the solid surface is assumed to be uniform, the heat of adsorption does not vary with the degree of surface coverage, adsorption occurs in a localized manner leading to the formation of a single layer, and interactions between adsorbates are considered insignificant [33]. The Langmuir model is expressed with the equations detailed in part (V.2).

The Langmuir model is based on the following approximations:

- The surface of the adsorbent is ideally uniform, that is to say that all the sites adsorption has the same adsorption properties;
- There are no interactions between the adsorbed solute and that in solution;
- Adsorption is limited to the monolayer.

II.3.4. Adsorption Kinetics

Adsorption kinetics allows us to determine the time required for the balance between the solute and the adsorbent. It also allows us to have an idea of the mechanism adsorption and the transfer mode between the two liquid and solid phases. Several models' kinetics have been developed to describe the kinetics of adsorption and to specify the nature interactions at the solid-liquid interface.

In the present work, two kinetic models were selected to study the kinetic behavior of pollutants on the surface of clays, namely the kinetic model pseudo first order, the pseudo second order kinetic model.

II.3.4.1. Pseudo-First Order Kinetic Model

This kinetic model was proposed by Lagergren and assumes that the adsorption rate at a time t is proportional to the difference between the quantity adsorbed at equilibrium and that at time t [37]. This model is expressed by Lagergren Equations detailed in part (V.3). This model is characterizing with the quantity adsorbed at equilibrium qe and the rate constant K1 can be obtained from the slope and the y-intercept.

II.3.4.2. Pseudo-Second Order Kinetic Model

This model allows to characterize the adsorption kinetics by admitting a rapid adsorption of solute on high energy sites and relatively slow adsorption on low energy sites. The pseudo- second order kinetic model is expressed by Lagergren Equations detailed in part (V.3).

II.4. Factors Affects Adsorption Process

The adsorption process depends on several factors that can influence the capacity and the kinetics of the retention of a solute on an adsorbent.

II.4.1. Adsorbents

The structure and nature of the adsorbents play an important role in trapping different organic and inorganic compounds present in water. The size of the particles, Specific surface area and porosity are the main properties that affect the affinity of an adsorbent with respect to the solute [36].

Among the natural adsorbents that have been the subject of numerous adsorption studies, clays are found. Their fine particle size, their layered structure and their large specific surface area are the main properties that give them a significant capacity adsorption.

II.4.2. Adsorbate

The physicochemical properties of the adsorbate are decisive and play a role essential during its adsorption on a solid surface of the adsorbent.

The structure molecular is one of the main parameters that influences the retention of adsorbates. More the molecular structure is bulky plus its retention by certain solid phases is difficult. Furthermore, the adsorption of solutes is conditioned by the composition of solution since the simultaneous presence of several species generates competition with respect to adsorption sites especially for those with a similar structure [19,39].

II.4.3. Adsorption Medium

The adsorption process can be affected by the adsorption medium conditions through [39]:

II.4.3.1. Potential Hydrogen

The pH is a predominant parameter in the adsorption process. It affects directly the charge state of the adsorbent and the adsorbate. Its effect on the retention of contaminants is often studied. In most cases, low pH favors adsorption anions while the alkaline environment favors that of cations.

II.4.3.2. Temperature

Adsorption is a global process resulting from several processes at the interface solid-liquid. It can be exothermic, endothermic or athermic. It is therefore conditioned by temperature. Thus, the increase in temperature promotes the chemisorption process while its lowering favors physical adsorption.

II.5. Clay minerals

II.5.1. Definition

Clays can be defined in various ways, and the interpretation of the term "clay" varies across disciplines such as soil mechanics, rock mechanics, and soil physics. It may denote a collection of mineral species, a type of rock family, a soil category, or a grain size classification that encompasses particles smaller than 2 micrometers in diameter. Generally, clays are crystalline in nature and are frequently encountered in sedimentary soils and rocks. Conversely, minerals like illite and chlorite are commonly found within the siliceous components of igneous and metamorphic rocks [38]. They are, hydrated aluminosilicates belonging to the phyllosilicate family. These minerals serve as the primary components of clay rocks following any potential refinement processes. Especially Bentonite is classified as a member of the phyllosilicates, with montmorillonite being its primary constituent, possess two categories of sites that could interact with ions found in solution [39].

II.5.2. Origin and Composition of Clay Minerals

Come from the erosion of silicate rocks, in particular from the disintegration of the minerals that make up granite: mica and feldspar. The most common clay minerals - kaolinite, halloysite, montmorillonite, illite and vermiculite - are very fine particles, which can either remain in place (residual clays, e.g. flint clays, decalcification clays) or be transported over long distances by rivers to the seabed (e.g. ocean floor clays). Depending on the source rock (granite, gneiss or shale) and climate, the resulting clay minerals are different. In cold climates, there is little alteration, and the clay minerals are identical or only slightly different from the rock minerals (illite and chlorite), inherited from the original rock. In hot, humid climates, hydrolysis is extensive, with kaolinite forming in drained environments and smectites in confined environments. In temperate, humid climates, alteration is moderate, with the appearance of interlayers, illite and degraded chlorites, and vermiculite. The Clays are of considerable technical interest and are used in a variety of fields: as raw materials in ceramics and drilling

muds, as mineral adsorbents in the purification of water polluted by noxious waste, whether metallic or organic, and as gelling agents in paints and pharmaceuticals. More recently, they have been used as watertight barriers in the construction of technical landfill sites (geomembranes) and in the containment of radioactive elements. These many applications depend on clay properties such as plasticity, adsorption capacity, ion exchange capacity and thixotropy.

II.5.3. Mineralogy, Structure, and Chemical Properties of Clays

Clay is a natural material composed mainly of minerals with very fine crystallites (generally less than 2µm). Its formation is linked to the physical, chemical and biological alterations that affect massive parent rocks. The chemical composition of clays is very similar to the average decomposition of the earth's surface. It is composed of at least 50% more or less hydrated alumina silicates, with the presence of a few associated minerals such as iron oxides and hydroxides, carbonates and quartz Clays are also often associated with organic matter in the form of clay-humus complexes. Clays are characterized by a layered structure (phyllosilicates) or a fibrous structure (sepiolite and palygorskite). Because of various physic-chemical properties such as high specific surface area, plasticity, water adsorption and swelling capacity, and low permeability, clays can be applied in many fields such as the manufacture of construction materials, cosmetics, water decontamination or waste storage, including nuclear waste.

II.5.4. Clay Mineral's Structure

Most clay minerals are characterized by a sheet-like structure, hence the name phyllosilicate. These sheets are made up of two types of layers, octahedral and tetrahedral, whose vertices are occupied by O-2 and OH- ions. These negatively-charged ions tend to repel each other, forming a framework for the cations that ensure the electrostatic stability of the entire structure. The structural representation of clay minerals can be schematized as a unit associating a sheet and an interfoliar space. Generally speaking, the sheet is made up of two types of layers:

II.5.4.1. Tetrahedral Layer

Formed by a central atom A, normally silicon, surrounded by four oxygen atoms. Each tetrahedron is linked to its neighboring tetrahedrons by sharing three corners. The combination of six tetrahedra forms a hexagonal cavity. The thickness of the tetrahedral layer is 4.6 Å.

II.5.4.2. Octahedral Layer

Is formed by a central atom A, often aluminum, surrounded by oxygen atoms and hydroxyl groups. Each octahedron is connected to the other neighboring octahedra, sharing only the stops between them. The thickness of this octahedral layer is 5.05Å.

Figure. II.4: Representation of Tetrahedral and Octahedral Clay Layers [40]

Figure II.5: Clay Structure [41]

II.5.5. Clay Minerals Classification

The classification of clay minerals is generally based on the following two criteria: sheet type and overall sheet charge.

1. **Sheet type:** Depending on the thickness of the sheet or its composition, there are three main families of clays.
    - ❖ **Minerals at 7Å or type 1:1 (TO)**, the elementary sheet of these phyllosilicates is formed by the combination of a tetrahedral layer (T) and an octahedral layer (O), and is around 7Å thick. Kaolinite, one of the most common clay minerals, corresponds to this type. Clays rich in this type of mineral are often used in ceramics, notably in the manufacture of porcelain. The kaolinite sheet is often neutral dioctahedral and aluminous, with a composition of $Si_2Al_2O_5(OH)_4$. The distance between the sheets is small due to the strong attraction between the hydrogen of the hydroxyl groups in the octahedral layer and the oxygen in the tetrahedral layer, in addition to Van der Waals bonds, making the sheets difficult to separate. Kaolinite is classified as a non-swelling clay. Isomorphic substitutions are low, resulting in no charge deficit. Cation exchange capacity (CEC) is therefore low, since it derives solely from the amphoteric nature of the surface groups. Kaolinite is one of the few clays that can develop appreciable anion exchange capacity, depending on pH. Its isoelectric point is generally between pH 2 and 3. This family of clays is characterized by the following reflections: d001

around 7.14 Å and d002 around 3.57 Å, and their derived lines. The former corresponds to the interlamellar distance.

- **Minerals at 10 Å or type 2:1 (TOT),** this type of mineral consists of an octahedral layer sandwiched between two tetrahedral layers. The basic thickness of the layer is 10Å. This thickness generally varies according to the nature of the interfoliar cation and its sphere of hydration. There are two main families of this type of mineral: illite and smectites.
- **The Illite,** the aluminum in illite's octahedral layer is partially substituted by Mg^{2+} or Fe^{2+} ions. The often-significant charge deficit created by this substitution is compensated for by K^+ ions. The presence of potassium, an anhydrous cation, in the interfoliar space ensures rigidity of the bond between the sheets, preventing these minerals from swelling in the presence of water. These potassium ions are difficult to exchange, resulting in low CEC. Among the chemical formulas proposed, we accept the following:
  - The d001 reflection is around 10 Å. This corresponds to the thickness of the foil.
  - Reflection d002 at around 5 Å.
  - Reflection d003 at around 3.33 Å. This reflection is often confused with that of quartz, which is omnipresent in most clay samples.
- **The Smectites,** this type of mineral is characterized by a very high cation exchange capacity due to isomorphic substitutions. This negative charge is compensated by cations in the interfoliar space. The electrostatic attraction between the sheets is weak, enabling this type of clay to incorporate water molecules into their interfoliar space. Smectites are therefore swelling clays. Thickness therefore depends on the hydration rate of the compensating cations. The most important minerals in this family are montmorillonite and steven site. Montmorillonite is a dioctahedral clay with a negative surface charge, essentially due to the substitution of silicon Si in the tetrahedral layer by aluminum Al, and of aluminum in the octahedral layer by Mg, Fe, Zn or Ni. The charge defect created by this substitution will be neutralized by mobile and easily exchangeable cations such as Na^+, Ca^{2+}. The general formula for montmorillonite is: $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n\ H_2O$. Bentonite is a natural clay consisting essentially of montmorillonite. It is either sodic or calcic. It is characterized by a high capacity for adsorption, ion exchange and swelling.
- **Minerals at 14 Å or type 2 :1 :1 (TOTO),** the 2:1:1 sheet consists of alternating T-O-T sheets and an octahedral interfoliar layer. The characteristic equidistance is around 14 Å. The chlorite family belongs to this type of mineral. Chlorites are subdivided into two layers: a hydroxide layer forming an octahedron $[(Mg, Fe) (OH)_6]$ and a TOT layer. The charge deficit of the TOT

sheet is compensated for by cations that lodge in the hexagonal cavities beneath the hydroxide sheet, causing water molecules to penetrate between the two types of sheets and thus increasing the fundamental equidistance.

2. **Fibrous Clays:** In addition, there is a fifth category of clays that is not listed among the phyllosilicate clays. These are fibrous clays such as sepiolite and palygorskite.

Table II.1: Clays Types Characteristics

	Type	*Number of sheets per particle*	*Particle diameter (µm)*	*Particle thickness (µm)*	*Specific area (m^2/g)*	*C.E.C (meq/100g)*
Kaolinite	1:1	100-200	0.1-4	1-10	10-20	3-15
Illite	2:1	1-10	0.1-1	0.003-0.01	65-100	10-40
Montmorillonite (smectite)	2 :1	1	0.1	0.001	700-840	80-150
Chlorite	2:1:1	1	0.1	0.005	800	10-40

II.5.6. Clay Minerals Characteristics

Isomorphic substitutions in the crystalline part of montmorillonite are responsible for the negative charge on the surface of the sheets. This negative charge, known as the permanent charge, enables montmorillonite to exchange cations (cation exchange capacity, CEC) and adsorb water molecules (swelling capacity). Montmorillonite has a number of other interesting characteristics, which can be summed up by its high specific surface area, low cost and colloidal state [33].

II.5.6.1. Cation Exchange Capacity (CEC)

The essential property of phyllosilicates is that they disperse on contact with water to form more or less stable suspensions. Interfoliar cations are generally exchangeable with organic or inorganic cations found in solutions in contact with phyllosilicate [24]. Each phyllosilicate is then characterized by its cation exchange capacity, defined as the number of monovalent cations that can be substituted for compensating cations to offset the charge of 100 g of calcined mineral.

In clays, there are two main reasons for the existence of an ionic exchange capacity, one internal and the other external:

- **The presence of isomorphic substitutions (internal CEC):** the most frequent is the substitution of Al3+ by Mg2+ in the octahedral layer. This is the exchange mechanism for montmorillonite. According to Caillere et al. (1982) [42], the distance between the negative sites in the octahedral layer and the exchangeable cation on the surface of the sheet is such that the forces of attraction are weak. Substitution of Si by Al in the tetrahedral layer is also possible,
- **Edge phenomena (external CEC):** at the edges of a sheet, the valences of silicon and oxygen in the tetrahedral layer, on the one hand, and aluminum and oxygen in the octahedral layer, on the other, are not saturated.
- **To compensate for these valences**, water molecules hydrolyze and silanol (Si-OH) or aluminon (Al-OH) groups are formed, which, depending on the pH, can capture or release protons. These protons can then be exchanged with other cations. The number and nature of sheet-edge charges are directly related to pH.

II.5.6.2. Specific Surface Area

The fine size of clay particles gives them a high surface area in relation to their volume. Specific surface area increases with decreasing diameter. The surface area of clays is greater than that of minerals of the same size but different shape.

The properties of clays are mainly controlled by their internal and external surfaces. The total surface area comprises the outer surface, between the clay particles, and the inner surface, corresponding to the interfoliar space. According to Elsinger et al., (1988) [43], smectites have the highest total surface area compared with illite and kaolinite.

II.5.6.3. Hydration Degree

The degree of hydration varies from one clay family to another. Some clay minerals are able to incorporate water molecules into their structure. This water modifies the size of the layer, causing it to swell. These clays are known as swelling clays. Smectites, illite and interlayered minerals offer much greater expansion capacities than other clay species [40].

Water incorporation is reversible at atmospheric pressure and depends on temperature and vapor pressure. The more humid the air, the more water the clay will be able to incorporate. Swelling minerals have a sheet structure at 1 nm. Depending on hydration, a water layer 0.25 or 0.52 nm thick develops. This hydration leads to a volume increase of up to 95%. Note that there are minerals with adsorbed water but no swelling properties.

II.5.6.4. Charge Clay Surfaces

Clay minerals are characterized by a non-neutral electrical surface. There are two types of charge:

- A permanent or structural charge linked to ionic substitutions (Al^{+3} for Si^{+4} in the tetrahedron, Mg^{+2} or Fe^{+2} for Al^{+3} in the octahedron), with a negative sign;
- A surface charge that varies according to the pH of the medium, linked to chemical reactions taking place on the surface of minerals or following the adsorption of surfactants, with a positive or negative sign.

In 1982, Caillere et al. [42], demonstrate that surface charge is linked to the hydrolysis of broken Si-O and Al-O bonds along surfaces (at the edge of the sheet). At low pH values, clay is characterized by an anionic exchange capacity, as a positive charge is developing. At high pH, a cation exchange capacity develops, as a negative charge appears. At equilibrium or zero charge, there is no exchange capacity. The study of cation distribution on the surface of clay particles is modeled by the double layer theory. These models explain the interactions between the clay surface, interfoliar cations, interfoliar water and surrounding solutions.

II.5.7. Clay Minerals-Based Adsorbents

The alteration of clay through the incorporation of chemical molecules species between its layers. Besides, the clays possessing of a number of physic-chemical properties that generally give them a high adsorption capacity, without missing their large specific surface area, high cation exchange capacity and ability to trap water molecules in the interfoliar space. In addition, the presence of associated minerals such as iron, aluminum and calcium oxides can increase its adsorption capacity, because of that many studies are rounding clay minerals [38].

The enhancement of modified clays-based adsorbents was demonstrated by the effective phenolic compound's removal from water onto modified clay and that in 1999, by R. Wibuls was and al. [44]. In 2004, R.-S. Juang and al. [45] confirmed that when studied the phenolic compound's sorption from water onto organo modified montmorillonite. In 2012 also, M. C. Di´az-Nava and al. [46] successfully modified bentonite with organic surfactants and used them in Phenol adsorption in order to eliminate water pollution. The studies continued until these last year's where the researchers Ran Haijie He and al. (2022) [47], as well as Wei and al. (2023) [48] used efficiently the modified of montmorillonite and bentonite by organic surfactants for Phenol adsorption. The elimination of methyl violet dye from waste water by adsorption was the goal of many investigation

[27,49–51]. S. S. Mohammed and D. T.A. Al-Heetimi (2019) worked together to refine adsorption capability of Iraqi Bentonite and that to remove methyl violet organic dye [10].

All this makes them the interest of a lot of scientific research works. In our study, we have been concentrating on studying the Bentonite-based adsorbents and their efficiency in organic compounds and dyes removal via adsorption from contaminated water.

Figure II.6: Molecular Model of MV Adsorption onto Clay Mineral (Halloysite Nanoclay) [48]

II.6. Bentonite Based Adsorbent

II.6.1. Bentonite

Clay materials were first named tyrolite, after William Taylor's studies of their deposits in the USA. The term bentonite was first used by Knight used the because the first site discovered was near Fort Benton in the Wyoming/Montana region of the USA. Bentonite is a volcanic rock that was deposited as volcanic ash in fresh or salt water millions of years ago. This ash chemically modified into bentonite. Sodium bentonite is formed from ash deposited in seawater, while calcium bentonite is formed from ash deposited in freshwater. Bentonite also comes from the weathering of siliceous rocks such as basalt and granite. The term bentonite is currently used to designate the trade name of a mineral that essentially contains smectites, the most common geological form of which is montmorillonite, a name derived from a deposit in Montmorillonite, southern France. Depending on the nature of the deposit, bentonite may contain a variety of minerals other than montmorillonite [33].

Algeria's most economically valuable bentonite deposits are found in the Oran region (western Algeria). In particular, the Maghnia quarry (Hammam Boughrara) is estimated to hold reserves of one million tons, while the Mostaghanem site (M’zila) has reserves of two million tons [53].

II.6.2. Modified Bentonite-Based Adsorbents

Modified clays fall into three broad categories: organoclay complexes, inorgano-clays and inorgano-organo-clays. In the field of adsorption, and despite their thermal instability, hydrophobic and organophilic organoclay complexes have been widely used in the depollution of water contaminated by certain organic pollutants.

Figure II.7: Bentonite Structure [50]

II.6.2.1. Organo Modified Bentonite-Based Adsorbents

Organoclay complexes natural or synthetic clays are hydrophilic minerals which, through chemical treatment made organophilic by chemical treatment. Among organophilic modification methods, cation exchange is the most commonly used.

The most frequently used cations are alkylammonium ions. Substitution is carried out in aqueous media, as the swelling of the clay facilitates the insertion of alkylammonium ions into the interfoliar galleries. After filtration of the suspension and drying of the clay, the presence of alkylammonium ions on the surface of sheets, primary particles and aggregates gives the clay an organophilic character. Moreover, their intercalation between the platelets leads to an increase in the interfoliar distance, the entropic contribution of adsorption energy increases and more Van der Waals interactions are developed.

The binding of organic cations also depends on the size and shape of the polar head, according to Rowland and Weiss (1963) [55]. The results of Mc Atee's work (1959) showed that ions from primary amines did not adsorb in sufficient quantities to reach CEC, unlike quaternary ammoniums. It was also shown that the bond strength of amino derivatives decreases sharply from primary to secondary and tertiary compounds [56].

On the other hand, Choi et al. (2004) [57] showed that clay treated with a quaternary ammonium salt containing a hydroxy ethyl function enabled good dispersion in polar polymers. Chavaria et al. (2006) [58], speculate that thermoplastic polyurethanes have an affinity for the hydroxide function of organophilic clay with hydroxy ethyl functions.

Indeed, such affinity is favored by a hydrogen bond between the organophilic clay hydroxide and the polymer matrix, resulting in an exfoliated system. The groups carried by the ion's carbon chain also influence the quality of ion exchange. In fact, cationic exchange is favored when the ammonium cation has a group capable of interacting with the surface hydroxides of the layers via hydrogen bonds.

Figure II.8: Mechanism of Phenol Adsorption onto Bentonite [54]

II.6.2.2. Inorgano Modified Bentonite-Based Adsorbents

Inorganic-clay complexes numerous studies have shown that there are two groups of compensating cations: those that enable maximum dispersion for all phyllosilicates with hydration properties: Na^+, Li^+, H^+ and Ag^+; those that only allow hydration limited to a few water layers: Cs^+, Ca^{+2}, Mg^{+2}, Ba^{+2}. In 1954, Norrish linked the swelling of clay particles to the hydration of cations, ranking the latter by decreasing value of their reduced hydration energy. He obtained the following ranking for the alkali series and calcium: $Li^+ > Na^+ > Ca^{+2} > K^+ > Cs^+$ [60]. This classification gives a good idea of the behavior of Li^+ and Na^+, which allow the material to swell, and Ca^{+2} and Cs^+, for which limited hydration is observed. However, it does not explain the special case of K^+, which behaves like Na^+ or Ca^{+2}. With regard to potassium, Faisandier (1997) [61] has shown that its main effect is to provoke the formation of heterogeneous systems in which hydrated and collapsed smectite sheets coexist within the same particle (distance to 1nm).

II.6.2.3. Inorgano-Organo Modified Clay-Based Adsorbents

The first published works on the application of organo-inorgano-clay complexes or mixed bridged clays demonstrated the highly hydrophobic character of this new generation of adsorbent materials. Zielke and al. [62]; Michot and al. [63]; Montarges and al. [64] devoted their initial research mainly to adsorption tests of certain phenol compounds on aluminum-bridged smectites co-adsorbed with cationic surfactant molecules.

Through the various results obtained, they have shown that co-adsorption of all these bridged clays with long-chain molecules increases the hydrophobicity of these materials in the same way as the activated carbons used, and that the longer the hydrocarbon chain, the higher the hydrophobicity and organophilic. In another laboratory, Shu et al. used three different adsorbent materials for the adsorption of certain chlorophenols and nitrophenols and found that zirconium-bridged montmorillonite co-adsorbed with a non-ionic surfactant adsorbed significant quantities of these organic micropollutants, compared with silicalite and zeolite beta. For their part, Jiang et al. showed that a montmorillonite intercalated with aluminum polycations and modified by co-adsorption with hexadecyl trimethyl ammonium HDTMA adsorbed significantly more phenol than the other organo- and inorgano montmorillonite matrices prepared. In 2008, Angela de Mello et al. [65] grafted a smectite with (3-mercaptopropyl) trimethoxy silane. In June 2009, Tao Xu et al. [66] intercalated a meta kaolinite with potassium acetate by grinding et Miguel de Araújo Medeiros et al. impregnated vermiculite with glycerol to remove oils spilt in water: diesel et motor oil. In July 2009, Hikaru Uno et al. [67] modified mica with a dodecyl ammonium salt (DDA) by ion exchange. In the same context, other research has shown that modified clays can remove pollutants such as phenol, toluene, 2-mercaptobenzothiazole and chlorobenzene.

II.7. Conclusion

This chapter present an overview of the different techniques of water depollution. According to the interest of our work, we focused on adsorption of pollutants onto solids.

Adsorption, is largely and effectively used as depollution techniques and, by being a subject that has garnered the interest of numerous research studies, and it is essential to articulate our work efficiently.

Clays are considerable demonstrates a big interest to be used as adsorbents applied in purification of polluted water, especially organic pollution. Bentonite is a type of clays that presents a very good adsorption property. That’s why numerous researches work studied aimed improving those properties by various modifications of these clay mineral.

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Chapter III: Preparation and Characterization of Modified Bentonites

III.1. Introduction

A great deal of scientific research has gone into the development of modified bentonites using both organic and inorganic modifiers. Bentonite-based composite nanomaterials are the focus of much research, and several synthesis techniques have been used.

This chapter presents and describes the various techniques, methods and products used to synthesize and characterize new bentonite-based materials that are inorganically modified with inorganic nanoparticles and organic surfactants.

The synthetized materials were tested to determine their thermal properties and also more characteristics at several scales: molecular, atomic, structural and textural. In this part of our study, the characterization of our samples was carried out by appropriate methods: Thermal Gravimetric Analysis (TGA), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy coupled with X-ray Diffraction (SEM-EDX) and the Brunauer, Emmett & Teller (BET) analysis to determine the specific surface area measurement.

III.2. Modified Bentonites Preparation

III.2.1. Bentonite Modifications

A series of modifications were carried out on purified Algerian bentonite to produce new clay materials based on modified bentonite.

The diagram in Figure III.1 summarizes the steps followed in the preparation of modified bentonites:

Figure III.1: Descriptive Diagram of Bentonite Modification Steps

III.2.2. Materials and Products

III.2.2.1. Materials

All the experiments in this work were carried out on the same batch of bentonite which is the subject of this study, originating from the M'Zila deposit located in Mostaganem (North-West Algeria) and marketed by the ENOF company; the main characteristics of this bentonite are grouped together in Table III.1[2].

This creamy-colored bentonite is finely ground and purified before use. It has undergone a series of modifications by organic and inorganic chemical agents using several techniques.

This was done to create new materials and test their ability to adsorb organic pollutants in aqueous solution.

Table III.1: Chemical Composition of M'Zila Raw Bentonite.

Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	TiO_2	P_2O_5	BWL
% weight	64,22	11,62	4,88	9,33	3,47	0,46	3,38	1,06	0.03	1,55

BWL* : Burning weight Loss

III.2.2.2. Products

Tetra-heptyl Ammonium Bromide (THPAB) has the chemical formula $C_{28}H_{60}N^+Br^-$ and a molecular weight of 490.69 g/mol, supplied by Fluka. Cetyltrimethyl Ammonium Chloride (CTAC), a product of Aldrich Co, its molecular weight equals 320 g/mol and chemical formula: $C_{19}H_{42}N^+Cl_-$. Both products are organic cationic surfactants, organic quaternary ammonium salts composed of long-chain alkyl ammonium cations and a halogen anion (Bromide, Chloride). THPAB and TCAC are used in this work as surface modifiers, their structures presented in Figure III.2 and Figure III.3 respectively.

Figure III.2: THPAB Chemical Structure

Figure III.3: CTAC Chemical Structure

All other chemicals used in this study: iron chloride ($FeCl_3.6H_2O$), ammonia (NH_3), sodium chloride ($NaCl$), hydrogen chloride (HCl), silver nitrate ($AgNO_3$), … were of analytical quality and were used as supplied without further purification. Demineralized and distilled water were used in our experiments.

III.2.3. Raw Bentonite Purification

Raw bentonite is a mixture of minerals and fragments of crystalline impurities. Purification is a technique applied to remove these impurities [2]. The following experimental protocol defines the steps carried out to obtain purified bentonite:

III.2.3.1. Sedimentation

This technique is based on the relationship between particle size and the speed at which they fall in a given liquid, and enables the removal of water-insoluble matter. To begin purification, 10 g of crude bentonite were dispersed in a beaker containing one (01) liter of distilled water, under stirring at room temperature for 20 minutes; the suspension was left to stand for 24 hours. The solid fraction, comprising particles smaller than 2 micrometers (< 2 µm), was collected, filtered and dried at 80°C for 12 hours; after cooling in a desiccator, it was ground, sieved and mixed [2,3].

III.2.3.2. Neutralization

In this step, 10 g of sieved bentonite is immersed in 500 ml of a 0.5 N HCl solution (pH range 2 to 3) under magnetic stirring for 4 h at room temperature, in order to remove carbonates $(CO_3)^{-2}$. The clay is then filtered and washed several times with distilled water until neutralization and disappearance of chloride ions (Cl^-), proved by a negative test with silver nitrate. $AgNO_3$ [2,4] then leave to stir with hydrogen pyroxide (H_2O_2) at 60°C for one night. [5]. The purified clay is then dried, crushed and sieved, making it ready for modification.

Figure III.4: Pictures of Raw Bentonite Purification

III.2.4. Purified Bentonite Modification

Purified bentonite underwent a series of chemical treatments to achieve its modification while improving its properties and developing new clay materials. The steps involved in preparing modified bentonites are described below.

III.2.4.1. Sodification

The sodification of bentonite consists in increasing the sodium content in the bentonite. This method is based on the principle of sodium homo-ionization by replacing all the exchangeable cations of various types (calcium (Ca^{+2}) and magnesium Mg^{+2} ...) in the bentonite with sodium ions (N_a^+) [6,7]. Purified bentonite (Ben) was homogenized in a solution of sodium chloride (NaCl. 1 M) by stirring at room temperature for 24 hours until saturated with sodium (Na^+). Residual salts were then removed by centrifugal decantation; the paste obtained was washed several times with distilled water to remove excess NaCl salt and cations exchanged from the clay, until filtrate Cl^- ions tested negative (with $AgNO_3$ test, 0.1 N) [8,9].

The sodium bentonite (Na-Ben) obtained was dried at 70°C, then ground and stored for use in the following steps.

Figure III.5: Pictures of Purified Bentonite Sodification.

The resulting organo-bentonites: CTA-Ben and THA-Ben were recovered, ground and stored in glass vials for characterization and further use.

III.2.4.2. Intercalation

The chemical modification of clay minerals by ammonium salts results in the best possible spacing between the mineral clay sheets and also creates pores in the new organophilic clays exhibiting a remarkable affinity for organic compounds. Organic bentonites were prepared by intercalation according to the procedures described in the literature, by exchanging the inorganic cations of sodium bentonite (Na-Ben) with quaternary ammonium cations: Cetyltrimethyl Ammonium Chloride (CTAC) and Tetra-heptyl Ammonium Bromide (THPAB). The quantities of these organo-modifiers were determined for 100% of the CEC [9,10]. In this work, the Na-Ben was intercalated while going through a series of operations.

III.2.4.2.1 THAB Intercalation

Intercalation of Na-Ben sodium bentonite was carried out using a quantity equivalent to 100% of the CEC value of the THPAB cationic surfactant; this quantity is required to saturate the cation exchange capacity of Na-Ben.

To achieve this, A suspension of Na-Ben was generated by dispersing it in a surfactant solution. Where, 100 mL of the prepared THAB solution was placed in a 500 mL beaker, and then 10 g of Na-Ben was introduced with the prepared solution under stirring at 70°C for 24 hours. The suspension was then rested and decanted, and the solid phase was washed with distilled water until a negative bromide (Br^-) test was obtained (with $AgNO_3$ test, 0,1 N) The paste was then recovered, washed, centrifuged, dried at 70°C and finally ground. After preparation, the new THPA-Ben organo-bentonite was stored for further characterization and use.

III.2.4.2.2. CTAC Intercalation

Intercalation of Na-Ben sodium bentonite was carried out using a quantity equivalent to 100% of the CEC value of the cationic surfactant CTAC; this quantity is desired to saturate the cation exchange capacity of Na-Ben. First, 100 mL of a 4% aqueous solution of CTAC was prepared by dissolving in distilled water, then 10 g of Na-Ben sodium bentonite was dispersed in the solution. The suspension was stirred for 24 hours at 70°C. The modified clay was recovered by centrifugation, washed until the supernatant solution was free of chloride ions (Cl^-), as indicated by the $AgNO_3$ assay, then dried at 60 °C [9,11–13]. The solid was crushed and sieved, then stored in glass vials for further characterization and use. The resulting organo-bentonite, symbolized here after as CTA-Ben.

Figure III.6: Pictures of Na-Ben Intercalation

III.2.4.3. Pillarization

Bentonite bridging is a chemical modification technique used to produce new materials with increased surface area and porosity, good thermal stability and the ability to adsorb and/or degrade contaminants. In recent years, there has been considerable interest in their use as adsorbents and also as catalysts [15]. There are several publications in recent literature on different aspects of iron oxide-containing materials, due to their low cost they are generally used as adsorbents for the removal of contaminants such as organic compounds and dyes from aqueous media [16].

In our work, the modified bentonites: Na-Ben, THPA-Ben and CTA-Ben, were bridged by inorganic nanoparticles, they are the iron oxides of Hematite (α-Fe_2O_3). These bridging particles were synthesized by the chemical precipitation method, where the precipitating agent was an aqueous solution of 2 M ammonium hydroxide (NH_4OH); an aqueous ferric solution with a concentration of 0.05 M was prepared at room temperature by dissolving a quantity of hydrated hexa iron (III) chloride ($FeCl_3,6H_2O$) in deoxygenated deionized water prepared by nitrogen degassing.

The solution was immediately put under nitrogen atmosphere and magnetic stirring for 30 minutes at 80°C; under the same conditions (stirring and T°), suspensions of Na-Ben, THPA-Ben and CTA-Ben were prepared by dispersing 10g of each of the three modified bentonites separately. A mixture of the iron chloride solution and the suspensions already prepared, stirred at 80°C, was titrated with an ammonium hydroxide solution added dropwise while controlling the hydrogen potential until pH 11 was maintained, then stirred for 3h; according to literature, hematite particles within the interfoliar spaces are of the order of 2 Nm [17,18]. Hematite form α-Fe_2O_3 of iron oxide was formed according to the following reaction:

$$2\ FeCl_3 + 6\ NH_3 + 3\ H_2O \rightarrow Fe_2O_3 + 6\ NH_4Cl \ .... I.1$$

Sodium and organic bentonites were bridged by wet impregnation in a hematite suspension. The resulting precipitates were filtered, the solids were collected and centrifuged, then washed with distilled water and ethanol several times and finally dried at 60ºC for 24 hours [19].

The three nano-composites obtained by bridging Hematite nanoparticles in the interfoliar space of sodified and intercalated bentonites are here after named: α-Fe_2O_3- Ben, α- Fe_2O_3-THPA-Ben and α- Fe_2O_3-CTA-Ben. These are then recovered and stored in glass bottles for characterization and use.

Figure III.7: Pictures of Modified Bentonites (Na-Ben, THPA-Ben and CTA-Ben) Pillarization

III.3. Modified Bentonite Characterization

III.3.1. Thermogravimetric Analysis « TGA »

III.3.1.1. TGA Test Method

Thermogravimetric analysis (TGA) is a technique used to provide information on the thermal behavior and stability of materials by means of a thermal analysis curve of the clays studied, giving the variation in weight loss for each change of state of the samples and this is done continuously as a function of temperature increase with a constant heating rate. This analysis is based on the thermal reactions that occur when a compound is heated. The curve obtained highlights water loss, oxidation of organic matter, recrystallization and recombination [20].

III.3.1.2. Test Handling

In our study, the analysis of the six modified bentonites: Na-Ben, THPA-Ben, CTA-Ben, α-Fe_2O_3-Ben, α-Fe_2O_3-THPA-Ben et α-Fe_2O_3-CTA-Ben was carried out by the SDTQ600 analyzer equipped with TRIOS software at the Yildiz Technik University in Turkey; where 60 mg samples were placed in aluminum crucibles while being accurately weighed, the program provides for a linear temperature rise with a rate of 5°/min from room temperature to 1200°C followed by cooling with a rate of 20°C/min, as shown in figure III.8.

Figure III.8: Pictures of ATG Analysis

III.3.2. Fourier Transmission Infrared « FT-IR » Analysis

III.3.2.1. FT-IR Test Method

Fourier Transform Infrared Spectroscopy (FT-IR), a spectral method resulting from changes in the vibrational and rotational states of a molecular bond, provides valuable information on absorbed water molecules and structural hydroxyl groups in clay minerals. It enables us to detect organic compounds and mineral structures.

Infrared absorption bands correspond to rotational energy transitions of molecular vibrations. Two types of vibrational modes are identified: interatomic elongation (γ with variation in distance) and angular deformation (δ with variation in angle between two adjacent bonds. FT-IR is also a technique for characterizing materials by determining their chemical characteristics, enabling us to identify clay minerals. It consists on the position of the bands of certain groups characteristic of clay minerals [21,22].

III.3.2.2. Test Handling

In this work, this test was carried out using Thermo Scientific spectrometer at the Yildiz Technik University in Turkey. As shown in figure III.9, the samples were pressed and the IR-TF spectra were recorded with a resolution of 2 cm^{-1} and tested between 4000-400 cm^{-1}.

Figure III.9: Pictures of FT-IR Analysis

III.3.3. The X-ray Diffraction Analysis « XRD »

III.3.3.1. XRD Test Method

X-ray diffraction is a technique widely used to identify the nature and structure and mineralogy of crystallized products (crystals, minerals, clays...) due to the fact that their atoms are arranged according to specific crystal planes. Bragg's law (equation III.1) establishes the essential condition for diffraction:

$$2d \sin\Theta = n\lambda \quad \text{...} \text{I.1}$$

Where:

λ: is the wavelength of the incident X-ray beam.

n: is the diffraction order (integer).

d: distance between reticular planes of the same family conventionally designated by Miller indices
h, k, l θ: diffraction angle (°) Indexing.

III.3.3.2. Test Handling

In our work, the preparation conditions for all samples were identical: the sample to be analyzed was lightly pressed and deposited on a slide to obtain a thin clay film of uniform thickness adhering to the slide wall.

The slides were analyzed at the PTAPC lab of Laghouat in Algeria, by a PANanalytical EMPYREAN type analyzer shown in figure III.10, the diffractometer with a Cu anticathode X-ray tube (wavelength K_α = 1.54Å); powered by a current of 40 mA at 45kV. Analyses were performed in an angular range between 3 and 90° for all samples.

Figure III.10: Pictures of XRD Analysis

III.3.4. Scanning Electron Microscope SEM / X-ray Energy Dispersive Analysis EDX

III.3.4.1. SEM-EDX Test Method

The principle of XRD involves applying radiation of X-ray wavelength (0.1 nm < λ < 10 nm) oriented at an angle ϴ to the incident beam onto the clay sample. The radiation penetrates the sample. There is absorption of part of the energy i.e. radiation and excitation of atoms with emission of radiation in all directions. Radiation emitted by atomic planes that are in phase will generate a coherent beam that can be detected. This is reflected in the diffractogram, representing intensity as a function of diffraction angle ϴ [23,24].

The morphology of the clays was observed using a scanning electron microscope. Working voltages are generally between 10 and 20 kv. This gives a magnification of up to 20,000 times.

The principle of this technique is based on the interaction between electrons emitted by a tungsten filament and the surface of the sample. By analyzing the intensity of the secondary electrons, the morphology of the observed surface can be reconstructed. The Scanning Electron Microscope produces three-dimensional images of the surface of samples with a resolution of up to a few nanometers (nm) and a very high depth of field. It also enables elemental chemical microanalysis of the object's surface using EDS or EDX (Energy Dispersive X-ray spectrometry).

It has three detectors: a secondary electron detector, a backscattered electron detector and a photon detector. Its principle, consists in scanning the sample surface with an electron beam in successive lines, and transmitting the detector signal to a cathode-ray screen whose scanning is perfectly synchronized with that of the sample.

III.3.4.2. Test Handling

The scanning electron microscopy (SEM) used for observing the morphology and the organization of the solid particle’s aggregates; the SEM analysis was performed by PHILIPS XL 30S microscope at the University of Gibza in Turkey, as shown in figure III.11.

Figure III.11: Pictures of SEM-EDX Analysis

III.3.5. Brunauer, Emmett & Teller « BET » Analysis

III.3.5.1. BET Test Method

The specific surface or mass area of a powder is the total surface area per unit mass. It governs exchange properties of the clay and adsorption phenomena. Experimental determination of specific surface area is based on the principle of low-temperature nitrogen adsorption. This technic is based on the quantity of adsorbate, the size of the adsorbed molecules and their possible arrangements, it is possible to estimate the surface area on which the adsorbate molecules are bound, using the BET calculation model (Brunauer, Emmett and Taller). This method requires sample pretreatment (degassing and dehydration between 150 and 300°C) to remove all previously adsorbed gases [22].

III.3.5.2. Test Handling

The specific surface areas of the solids in the study were measured using nitrogen physisorption experiments. The BET model (Brunauer, Emmett and Teller) was used to calculate the specific surface area of the clay materials. The instrument presented in figure IV.5 was an ASAP 2420 analyzer from Micromeritics at the PTAPC lab of Laghouat in Algeria; it was used for a minimum surface area of 15 to 20 m2 is required in the cell (the sample mass should be chosen according to this parameter).

Pre-treatment at 250°C for 3h under vacuum (~ 10-6 Torr) is performed prior to analysis. Relative pressure is measured at four points, in order to refine the specific surface measurement, giving an accuracy of ± 5%.

Figure III.12: Pictures of BET Analysis

III.4. Characterization Results and Discussion

III.4.1. TGA Analysis

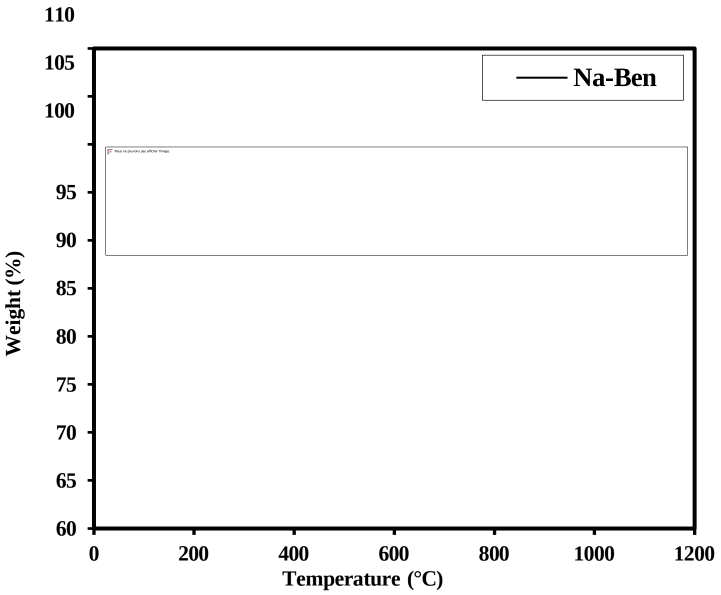
TGA is a universal useful tool to evaluate the thermal stability of the synthetized materials by giving valuable regarding chemical modifications [25].

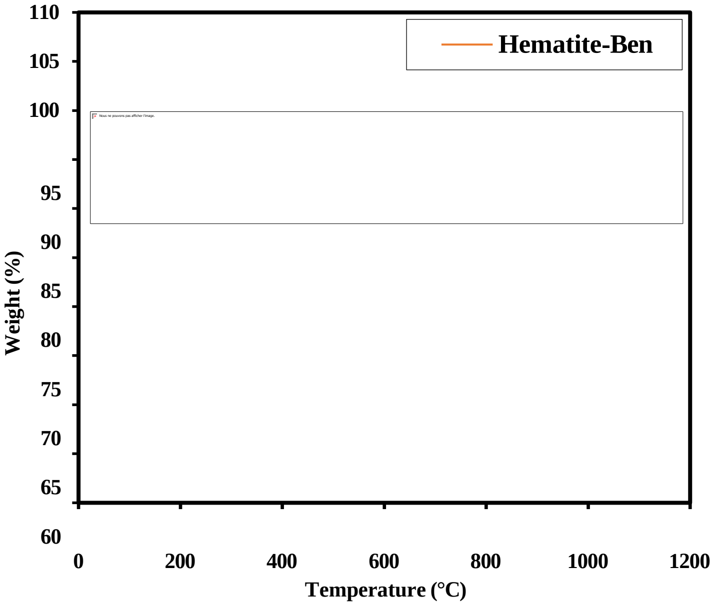
The TGA analysis results are summarized in the thermograms presented in Figure III.13, where the curves interpret the thermal behavior of the modified bentonites.

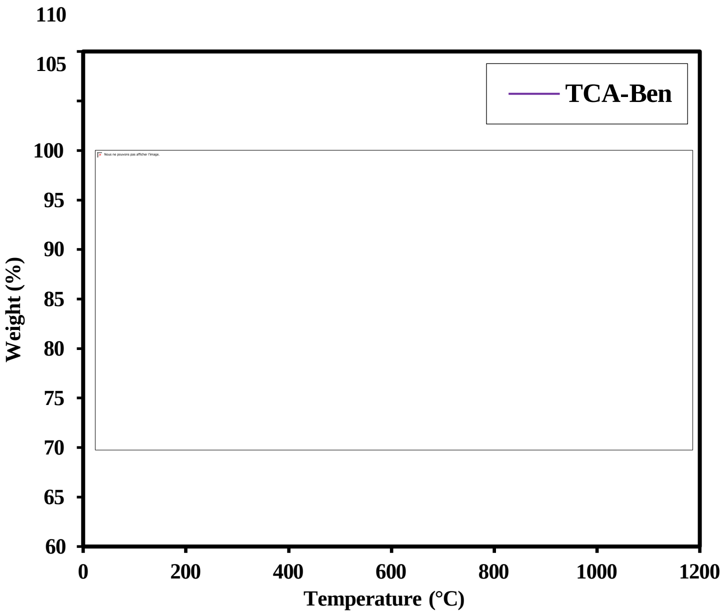
The obtaining phases are related with formation and decomposition of the modified bentonites: Na-Ben, THPA-Ben, CAT-Ben, Hematite-Ben and both Hematite-THPA-Ben and Hematite-CAT-Ben through heat treatment, they are in good agreement with Thermo Gravimetric Analysis TGA results. The modified bentonites were analyzed under the T changes from room temperature to 1200°C where the samples have undergone decomposition due to water loss until the stability of the rest of the material [18].

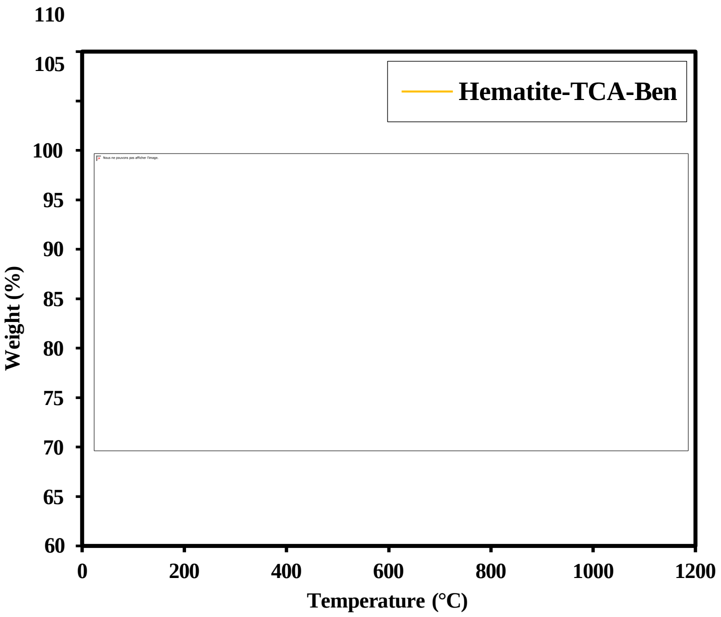
From Figure III.13 the thermal analysis TGA of the synthesized bentonites with different modifications. About Na-Ben, Hematite-Ben there are three distinct mass loss steps in the temperature ranges. The first weight loss step occurred gradually between [38°C – 90.56°C], [41.9°C – 119.08°C] and the mass loss was of 7.01%, 6.01%, and this loss of weight is attributed to the removal of water existing on the surface of the sodic bentonite. The second step corresponds to a mass loss of 2.98%, 3% occurring at [90.56°C - 643°C], [606.52°C – 896.89°C], which is due to the combustible organic products present in our prepared sample. The third step stands for a minor weight loss (1.01%) occurring in the range of [643°C - 907°C], [119.08°C – 606.52°C], which is due to the transition phase of synthesized compounds. Finally, after 907°C, the curve becomes parallel to the temperature axis, which emphasizes high stability of the sodic bentonite. Concerning organo modified bentonites CTA-Ben, THPA-Ben, there are three distinct mass loss steps in the temperature ranges. The first weight loss step occurred gradually between [40.16°C – 105.98°C], [49.38°C – 118.05°C] The mass loss was of 5.8%, 1.04% and this loss of weight is attributed to the removal of water existing on the surface of the sodic bentonite. The second step corresponds to a mass loss of 26.89%, 18.62% occurring at [105.98°C – 639.57°C], [118.05°C – 595.08°C] which is due to the combustible organic products present in our prepared sample. The third step stands for a minor weight loss (0.34%), (4.5%) occurring in the range of [639.57°C – 872.6°C], [595.08°C – 1025.57°C], which is due to the transition phase of synthesized compounds. Finally, after 872.6°C, 1025.57°C the curve becomes parallel to the temperature axis, which emphasizes high stability of the sodic bentonite.

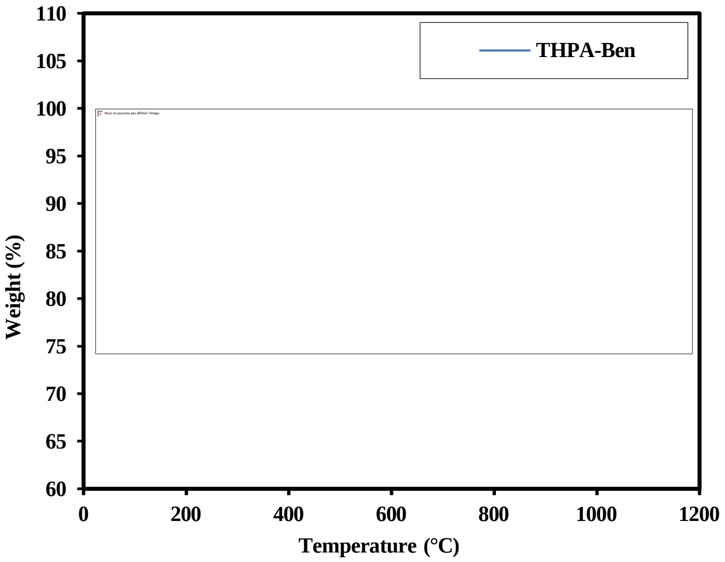
The new composites-based bentonite: Hematite-CTA-Ben and Hematite-THPA-Ben are characterized by three distinct mass loss steps in the temperature ranges. The first weight loss step occurred gradually between [41.12°C – 109.74°C], [38.97°C – 109.79°C]. The mass loss was of 5.32%, 5.32% and this loss of weight is attributed to the removal of water existing on the surface of the sodic bentonite. The second step corresponds to a mass loss of 18.69%, 2.71% occurring at [109.74°C – 623.66°C], [38.97°C – 109.79°C]. which is due to the combustible organic products present in our prepared sample. The third step stands for a minor weight loss (5.99%, 0.14%) occurring in the range of [623.66°C – 725.89°C], [557.71°C – 725.23°C] which is due to the transition phase of synthesized compounds. Finally, after 725.89°C, 725.23°C the curve becomes parallel to the temperature axis, which emphasizes high stability of the sodic bentonite. There are signals related with the mass loss which are similar to those they stand for the dehydration of the free water, degradation of organic compounds and the transition phase of the synthesized materials. The positions of the latter differ according to the nature of the base [18].


Na-Ben
Weight (%)
110
105
100
95
90
85
80
75
70
65
60
0
200
400
600
800
1000
1200
Temperature (°C)


Hematite-Ben
Weight (%)
110
105
100
95
90
85
80
75
70
65
60
0
200
400
600
800
1000
1200
Temperature (°C)


TCA-Ben
Weight (%)
110
105
100
95
90
85
80
75
70
65
60
0
200
400
600
800
1000
1200
Temperature (°C)


Hematite-TCA-Ben
Weight (%)
110
105
100
95
90
85
80
75
70
65
60
0
200
400
600
800
1000
1200
Temperature (°C)


THPA-Ben
Weight (%)
110
105
100
95
90
85
80
75
70
65
60
0
200
400
600
800
1000
1200
Temperature (°C)

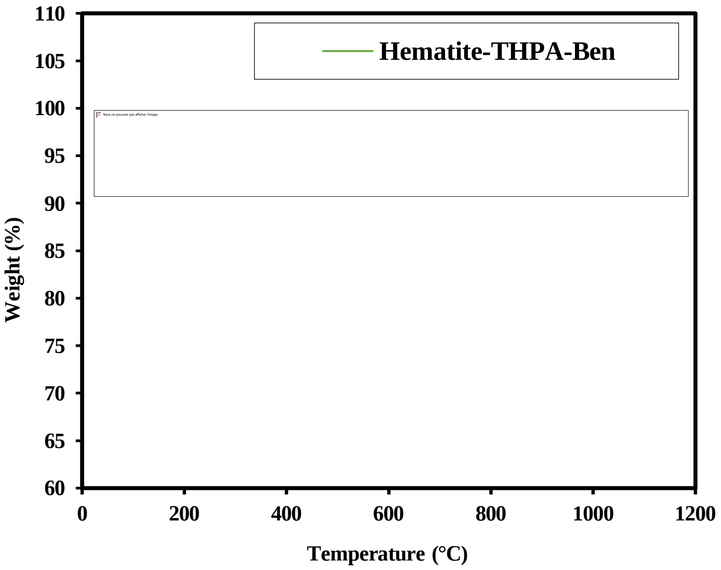

Hematite-THPA-Ben
Weight (%)
110
105
100
95
90
85
80
75
70
65
60
0
200
400
600
800
1000
1200
Temperature (°C)

Figure III.13: Thermograms of Modified Bentonites

III.4.2. FT-IR Analysis

FT-IR spectroscopy was utilized to detect the presence of the functional groups absorbed on the surface of the six synthesized materials after different chemical modifications. Figure III.14 presents the FT-IR spectra of the six (06) modified bentonites Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben, prepared with organic and inorganic chemical modifiers.

The results of the FTIR analysis that were applied on the modified bentonites indicates the different modification done on the Algerian bentonite. The FTIR spectrums of the six modified bentonites Na-Ben, THPA-Ben and CTA-Ben indicate a characteristic peak at 3622 cm^{-1} bands attributed to stretching vibrations of the structural hydroxyl group –OH in the interlayer bonded to aluminum and/or magnesium of the mineral bentonites (Mg-OH-Al, Al-OH-Al, and Fe-OH-Al units) the same groups stretching and bending vibration bands of the adsorbed water are seen respectively around 3425 and 1630 cm^{-1} for Na-Ben also at 3423 and 1631 cm^{-1} for THPA-Ben, which they occupy the sites of the modified bentonites layers and their octahedral and tetrahedral surface, respectively. A Si–O–Si bending nearly at 1000 cm^{-1}. The band at 1622 cm^{-1} is corresponding to H–O–H bending vibrations of water, at 910 and 833 cm^{-1} two weaker bands are also detected. The bands near 510 and 410 cm^{-1} are attributed to Si–O–Si, and Al–O–Si bending vibration respectively [26]. The gradual transformation of the silicate layer to a three-dimensional framework of protonated amorphous silica can be observed in the region of the stretching vibrations of Si–O groups within the 1630 cm^{-1} layer [27]. In both of organo-modified (THPA-Ben and CTA-Ben) and inorgano-organo-bentonite (Hematite-THPA-Ben and Hematite-CTA-Ben), the characteristic absorption bands of THPA and CTA cations corresponding to: C–H bending bands of methylene and methyl groups $–CH_2$, $–CH_3$ at nearly 1460 cm^{-1}; 1560 and 1365 cm^{-1} large band for N=O, large bending bend of 1860cm^{-1} of O=N and aromatic C=C stretching at 1500 cm^{-1}, which was a vibration of the aromatic cycle and an alkyl group, that cause penetration of an organic compound into the interlayer space of bentonite as organic cation, when cation exchanging. Surfactant’s cations can interact with bentonite through electrostatic interactions, π interactions, and van der Waals forces [28]. The characteristic peaks of the organo modified clays with two additional peaks in range 2920 and 2850 cm^{-1}, which are attributed to the υCH_2 antisymmetric stretching vibration of intercalated surfactants molecules with the bentonite layer [29]. The presence of the pillared Hematite nano particles in nano modified bentonites: Hematite–Ben, Hematite–THPA–Ben and Hematite–CTA–Ben, is characterized a strong band below 694 cm^{-1} is assigned Fe–O stretching mode. The band corresponding to Fe–O stretching mode of Fe_2O_3 is seen at 540 cm^{-1} [30].

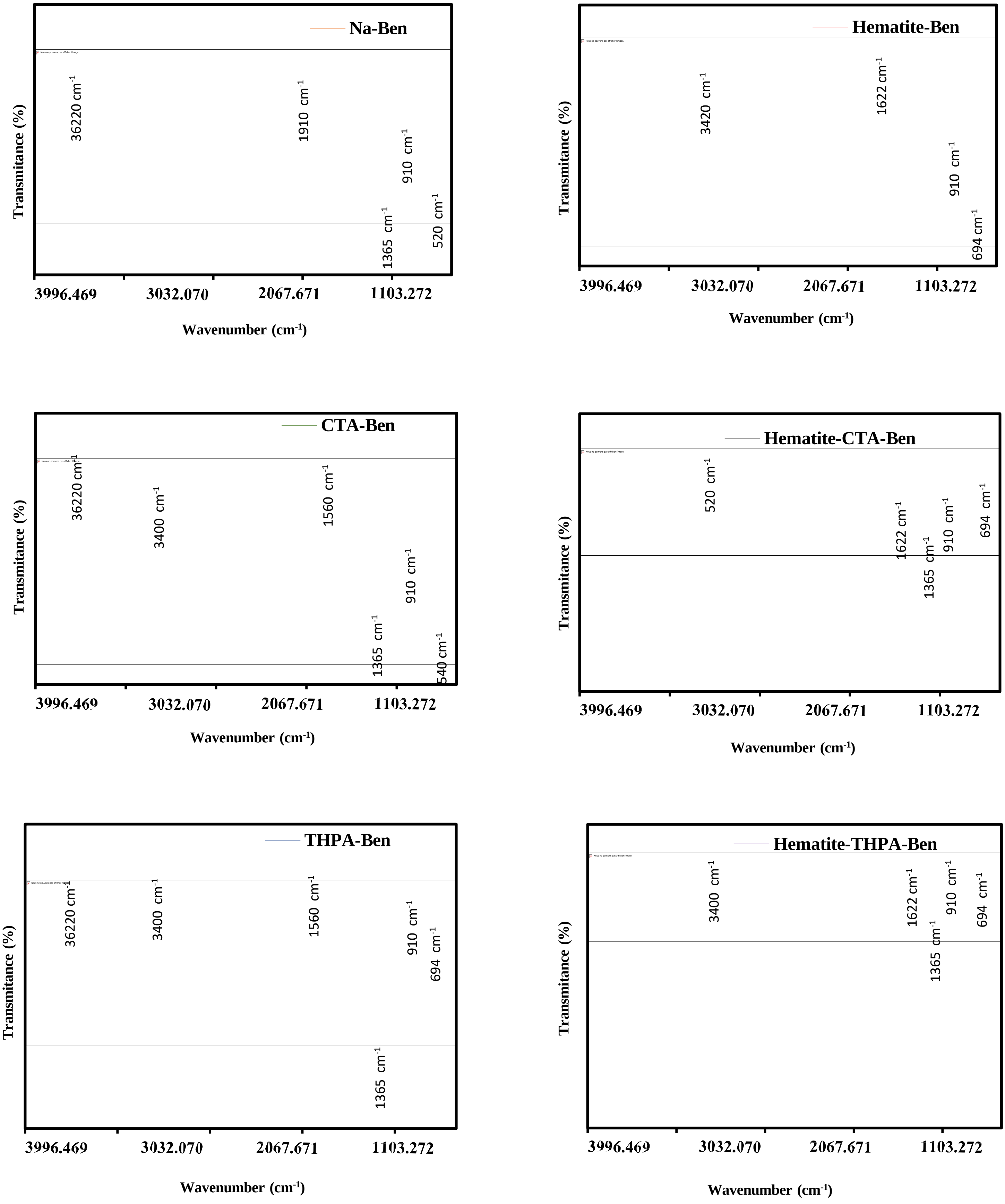


Figure III.14: IR Spectrum of Modified Bentonites

III.4.3. XRD Analysis

The mineralogical compositions of the organo and inorgano modified bentonites were determined from the XRD analysis results performed on their samples using PANanalyse EMPYREAN automated diffractometer (Cu-Kα) with λ=1.54 Å in 2Ɵ range of 3-90° (45kV, 40 mA). The X-Ray patterns of the modified bentonites are illustrated in Figure III.15.

When X-ray irradiates, the bentonite particles scattering occurs and can be described by the Bragg Law. According to this law, the layer spacing of the modified Bentonites: Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben, and Hematite-CTA-Ben can be calculated [31].

The diffractogram shows the difference between the six analyzed bentonites, it is clear that the chemical modifications that was done by addition of the organic surfactants as intercalant agents: THPAB and CTAC or the inorgano nanoparticle hematite α-Fe_2O_3 as pillaring agent, into the bentonite has a remarkable effect comparing with the sodium bentonite case. The main peaks of the Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben, and Hematite-CTA-Ben phases are presented in the diffractograms, they are composed almost entirely of natural clay which is the principal mineral: montmorillonite and a few impurities such as the rest of the phases are considered as non-clay minerals: Illite, quartz, Muscovite [2,32]. With surfactant chemical modification, the structure of the clay's layers is changed, the layer spacing d001 increased from d=12.44 Å (2Ɵ = 7.22°) for Na-Ben to d=22.72 Å (2Ɵ = 3.89°) and d=20.39Å (2Ɵ = 4.34°) for THPA-Ben and CTA-Ben respectively. The increase in the basal spacing of Na-bentonite by adding the quaternary ammonium surfactants THPAB and CTAC demonstrate the intercalation of the surfactants molecules into the interlayer space of the sodic bentonite and this with the replacement of the inorganic interlayer cations and their hydration water with $THPA^+$ and CTA^+ cations, as proper with literature; regarding the orientation and the number of molecular layers in the interlamellar spacing of clay minerals, and considering the molecular sizes of both THPAB and CTAC, the increases in the basal spacing point to a bilayer arrangement for the organo surfactants molecules [33,34].The results, confirm the modification of bentonite minerals by the organic surfactants that introduces some changes into the crystal structure of bentonite minerals in the resulting organo modified bentonites THPA-Ben and CTA-Ben. The orientation and the number of molecular layers in the interlamellar spacing of clay minerals, and considering the molecular sizes of both THPAB and CTAC, the increases in the basal spacing point to a bilayer arrangement for the organo surfactants molecules. With the chemical inorgano modification, by addition the hematite nanoparticles the structure of the sodic and organo bentonite's layers are changed, the layer spacing d001 increased from d=12.44 Å (2Ɵ = 7.22°), d=22.72 Å (2Θ = 3.89°) and d=20.39Å (2Θ = 4.34°) for Na-Ben, THPA-Ben and CTA-Ben to d= 13.72Å (2Θ = 8.12°), d= 22.98 Å (2Θ = 3.90°) and d= 24.39Å (2Θ = 5.62°) for Hematite-Ben, Hematite-CTA-Ben and Hematite-THPA-Ben respectively. The increase in the basal spacing of Na-Ben, THPA-Ben and CTA-Ben by adding the inorgano modifier: Hematite (α-Fe_2O_3) prove the successful pillaring of this inorganic nanoparticle into their interlayer spaces and that by replacement of some inorganic interlayer cations and their hydration water with α-Fe_2O_3; the hematite coats a specific plane of bentonite in the nano scale, while the coating of the bentonite plane [19].

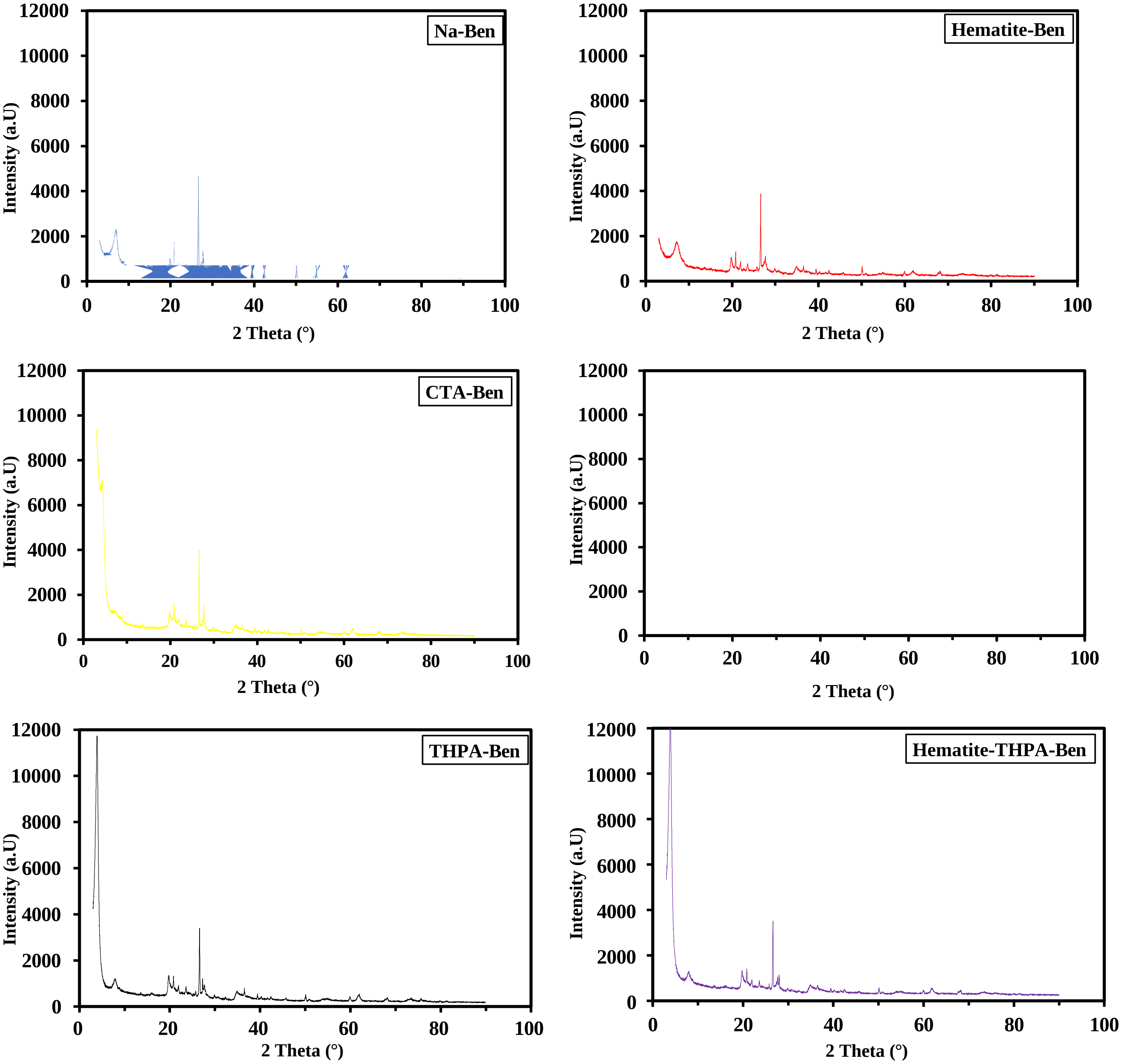


Figure III.15: Diffractograms of Modified Bentonites

III.4.4. SEM/EDX Analysis

SEM and EDX analysis results were obtained, the SEM images of the modified bentonites: Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben presented in Figure III.16. Average particle size of the prepared materials was measured at high resolution, microscopic analysis was carried out to confirm their growth pattern and the distribution of the crystallites [30]. The comparison between the six images allow to remarque a laminated structure for the six materials, they show also a micro-morphology of clays surfaces.

The sodic bentonite Na-Ben has a flake morphology however the Organo Bentonites: THPA-Ben and CTA-Ben has an enormous heterogeneous pores variable in size [35], clearly seen the granular particles shapes that contribute to trapping and adsorbing organic compounds [36].

The new inorgano materials: Hematite-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben prepared by pillaring the Hematite (α-Fe_2O_3) nanoparticles in the structure of Na-Ben, THPA-Ben and CTA-Ben, have successfully prepared with formation of clusters nanocrystals where the formed α-Fe_2O_3 nanocrystals were agglomerated in the structure of the resulting inorgano modified bentonites and this as proper in literature [30].

Na-Ben **Hematite-Ben**

CTA-Ben **Hematite-CTA-Ben**

THPA-Ben **Hematite-THPA-Ben**

Figure III.16: SEM Photomicrograph of Modified Bentonites

The major element in the clays structure: Si with 41.9, 30.2, 28.53, 32.25, 27.27 and 25.5 wt% for : Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben receptively, along with the Al, Si and O elements of SiO_2 and Al_2O_3 present the aluminosilicates structure, as proper in literature [30,37].

The chemical composition of the modified bentonites samples was investigated by EDS; the quantitative analysis results are listed in a Table. 1. The values of weight percentage of the compositional elements describe the changes of the chemical composition after each modification.

The intercalation of the Na-Ben by cationic surfactants surfactant's molecules THPAB and, CTAC was successfully done and that was confirmed by:

- The appearance of new elements: C, N in the structures of the organo modified bentonites: THPA-Ben, CTA-Ben and also in both of the tow composites: Hematite-THPA-Ben and Hematite-CTA-Ben.
- The appearance of Br and the increase of Cl in the structure of THPA-Ben and CTA-Ben respectively due to their presence originally in the surfactant's structures (Br in THPAB and Cl in CTAC);
- The decrease in weight percentage of Mg and K of the Na-Ben indicate their cation exchange with $THPA^+$ and CTA^+.

The nanoparticles Hematite (α-Fe_2O_3) pillared Bentonites: Hematite-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben were well prepared and this was confirmed by the increase of Fe and O weight percentages in their structures comparing with the sodic and organic bentonites: Na-Ben; THPA-Ben and CTA-Ben.

Table III.2: Modified Bentonites Elementary Analysis obtained by EDS

Element		C	N	O	Na	Mg	Br	Al	Si	Cl	K	Fe
Wt %	Na-Ben	0	0	31.6	3.4	1.2	0	12.5	41.9	0.2	3.1	6.1
	THPA-Ben	18.5	2.9	29.8	0.04	0.8	9.1	3.3	30.2	0.36	1.1	3.9
	CTA-Ben	21.43	2.62	28.04	0.15	0.64	0	2.21	31.25	10.07	1.02	2.57
	Hematite-Ben	0	0	34.3	1.06	0.71	0	5.3	32.53	0.19	2.12	23.79
	Hematite-THPA-Ben	17.01	1.5	31	0.34	0.61	0.08	2.07	30.2	0.13	0.04	17.02
	Hematite-CTA-Ben	17.21	2.6	30.32	0.05	0.32	0	2.03	30.14	0.17	0.06	17.1

III.4.5. BET Analysis

III.4.5.1. Specific Surface Measurement

The use of BET technic in this study aims to determine the specific surface area (S_{BET}), average pore diameter (D_a) and total porous volume (V_t) of the modified bentonites. The analysis results are presented in Table III.2, The S_{BET} of our studied materials: Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben, and Hematite-CTA-Ben are: < 50.9203, 10.9998, 10.8365, 44.3097, 2.8625 and 2.41278 m²/g respectively where a notable decrease after Na-Ben modifications in the order Na-Ben >Hematite-Ben >THPA-Ben > CTA-Ben > Hematite-THPA-Ben > Hematite-CTA-Ben; in the other side, a similar trend is also found for the V_t values of Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben, and Hematite-CTA-Ben that are respectively: 0.053126, 0.020916, 0.03674, 0.052419, 0.0036456 and 0.007078 m^3/g; however, after modification the D_a of our bentonite gets a slight increase seen for Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben, and Hematite-CTA-Ben respectively : 4.1178,7.6058, 7.0021, 6.0438, 8.7959, and 8.9294 nm.

The decrease in S_{BET} and V_t of the modified bentonites after by intercalation of cationic surfactants and the pillared Hematite nanoparticles can be explained by the fact that bentonite has the ability to expand the interlamellar space when ion exchange occurs with the modifier's molecules. As a result, relatively large cations can be compactly charged and packed into the bentonite interlamellar spaces, leading to a significant pore blocking and a reduction in total porous volume, and BET specific surface area; all this can explain the results obtained after bentonites intercalation and/or pillaring of the organic and nano molecules in their interlamellar space when ion exchange occurs. Additively, it is widely known that organic cations and especially organic surfactants increase the spacing between tetrahedral sheets; this has led to increased packing density of organoclays by increasing surfactant loading in clays and altering the arrangement of surfactant molecules from parallel to surfactant chains oriented at certain angles to the silicate surface; this can also be attributed to the blocking effect of porous aggregates and increased particle [38]. The notable decrease of S_{BET} is possibly due to the block of some structural channels by organic or inorganic ligands grafted on the edge of the clay sheets, resulting in less access to nitrogen. Meanwhile, the decrease of porous volume may also be caused by the modifier's molecules existed on the external surface and that is consistent with the results of Anirudhan and Ramachandran [39] and Rathnayake [40] Therefore, some of the grafted molecules ligand may graft on the external surface of the clay (bentonite) instead of intercalating into the clay interlayer after modification [41]. The decreases of S_{BET} of the clay is also due to organophilization, this observation aligns with prior findings.

It should be noted that the average pore of the sodic bentonite Na-Ben is less than that of the other modified bentonites. These results suggest that surfactants and Hematite molecules are present in the interlayer domain and on the surface of resulting modified bentonites. During the phenomenon of nitrogen adsorption, the molecules of Nitrogen gaseous N_2 occupy the geometric outer surface and penetrate the capillaries also. The surface area of the clay decreases

due to organophilization, This observations aligns with prior findings [42–44]. The increase in porosity can be due to the presence of the modifiers molecules in the interlamellar space of the clay [45].

Table III.3: BET Analysis Obtained DATA (S_{BET}, BET, D_a, V_t)

Materials	S_{BET} (m^2/g)	D_a (nm)	V_t (cm^3/g)
Na-Ben	< 50.9203	4.1178	0.053126
THPA-Ben	10.9998	7.6058	0.020916
CTA-Ben	10.8365	7.0021	0.03674
Hematite-Ben	44.3097	6.0438	0.052419
Hematite-THPA-Ben	2.41278	8.0021	0.003645
Hematite-CTA-Ben	2.8625	8.9294	0.007078

III.4.5.2. Nitrogen Adsorption Isotherms

The Nitrogen adsorption-desorption of the study applied on the modified bentonites: Na-Ben, THPA-Ben, CTA-Ben, Hematite-Ben, Hematite-THPA-Ben, and Hematite-CTA-Ben are presented in Figure III.17.

The isotherms of the analyzed samples are found to be of classical as type IV for particles condensation of according to the IUPAC classification which are typical for mesoporous materials, furthermore, the hysteresis loop of H3 type in a wide p/p_0 range of 0.05–1.0 indicates a wide pore size distribution plot of the six studied samples, this results was in good agreement with other in literatures (Ying Xu [41] ; Milan Kragović [46] ; Dehmani [47]).

These isotherms show that the clay material has little affinity for N_2 adsorption. Similar observations have been previously reported by Jiang [48].

Na-Ben

Hematite-Ben

THPA-Ben

CTA-Ben

Hematite-THPA-Ben

Hematite-CTA-Ben

Figure III.17: BET Isotherm Linear Plot of the Modified Bentonite.

These isotherms show that the clay material has little affinity for N_2 adsorption. Similar observations have been previously reported by Jiang [48].

III.5. Conclusion

In this chapter we present a part of our work, where we were interested on the different characterization technics to use to determine the properties of the synthetized materials.

The results obtained confirm the success of the intercalation and pillaring modifications described in Chapter IV that aims to prepare new materials based on an Algerian bentonite from M’Zila. XRD and EDS results proved presence of Hematite nanoparticles (α-Fe_2O_3) and surfactants molecules ($THPA^+$ and CAT^+) in the surface of the modified bentonites: Na-Ben, THPA-Ben, CAT-Ben, Hematite-Ben and both Hematite-THPA-Ben and Hematite-CAT-Ben. The SEM and BET results show the good properties of the synthetized materials so that we want curiously to test their ability to adsorb some pollutants from aqueous solution for environmental applications.

Also at the end of this part of our study, we were able to conclude that: the techniques used to modify M'Zila bentonite are characterized by their simplicity and low cost, and the products used are inexpensive and less hazardous to humans and the environment.

All this has enabled us to develop a new THPA-Ben organo-bentonite by intercalation using the cationic surfactant tetraheptylammonium bromide THPAB, as well as two new nano-composite materials: α-Fe_2O_3-THPA-Ben and α-Fe_2O_3-CTA-Ben by pillaring the hematite nanoparticles « α-Fe_2O_3 » in the interfoliar space of the intercalated organo-bentonites using CTA-Ben also. The six synthetized materials: Na-Ben, THPA-Ben, CTA-Ben, α-Fe_2O_3-Ben, α-Fe_2O_3-THPA-Ben and α-Fe_2O_3-CTA-Ben will be analyzed by several characterization techniques to determine the influence of chemical modifications on their properties.

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Chapter IV: Organic Pollutants Adsorption

IV.1. Introduction

After synthesizing and characterizing the various adsorbent materials, we will focus on their adsorption ability and efficiency towards removing organic pollution from aqueous media.

Due to their divers' chemical properties and functionalities, organic compounds are extensively used in various industries such as: pharmaceuticals, chemicals manufacturing, petrochemicals, agrochemicals, automotive, aerospace without missing cosmetics and textiles and other domains. Nonetheless, they effect widely both environment and human health [1,2].

Adsorption is the most effective method selected to eliminate organic pollution from water, for this first approach, we chose methyl violet (MV) a cationic synthetic dye studied as an organic pollutant model to evaluate and compare the synthetized adsorbents, and also we selected Phenol which is an aromatic product with a benzene ring and hydroxyl group (OH-).

This chapter is edited for the purpose of presenting the adsorption studied that examinates the capacity of the purified and modified bentonites to remove MV and Phenol from aqueous solutions, the experiments performed to investigate the effect of various parameters on this adsorption process.

IV.1. Technics and Reagents

IV.1.1. Adsorbents

The unmodified and modified bentonites were chosen as adsorbents of two organic compounds: phenol and methyl violet from aqueous solutions. The unmodified bentonite is a purified Algerian bentonite named in this work "Ben"; the modified bentonites as we precedent cited are: Na-Ben, Hematite-Ben, CTA-Ben, THPA-Ben, Hematite-CTA-Ben and Hematite-THPA- Ben are synthetized by a chemical modification of the purified bentonite that is described in chapter IV and presented in Figure IV.1.

Figure IV.1: The Synthetized Modified Bentonites-Based Adsorbents

IV.2.2. Adsorbates

Methyl Violet (MV), known as MV2B, is a basic organic powder dye, highly toxic to aquatic organisms and suspected of causing cancer in humans. Its chemical formula is $C_{24}H_{28}N_3Cl$ its molecular weight is 393.96 g/mol [3]. The MV is a water-soluble, it turns yellow in pH range of 0.13 to 0.5, and from green to bleu in pH range of 2.0 to 3.0; its structure is depicted in Figure IV.2 [4].

Figure IV.2: Methyl Violet MV Structure.

Before the use of the MV dye supplied by Panreac, it was first dried at 60 ° C for four hours to remove the moisture. Amount of colorant powder was dissolved in distilled water to prepare stock solution for MV (by dissolving 410.1 mg of MV in 1000mL of distilled water, for a cation exchange capacity (CEC) equal to 100%); it was stirred for 24 hours, allowed to rest for 72 hours, then filtered and stored.

Studies on the methyl violet's adsorption on modified bentonites were conducted using colorant solutions diluted to various concentrations.

Phenol, also known as carbolic acid or Monohydroxy benzene, is a toxic organic compound that can cause genetic abnormalities and have serious adverse effects on organ function with repeated exposure or a prolonged exposure. Its chemical formula is C6H5OH with a molecular weight of 94,11 g/mol. [5]. The phenol used in this work is an analytical reagent supplied by China Chemistry Co. Ltd (Shanghai, China), with a purity of 98%, its chemical structure is illustrated in Figure IV.3.

Figure IV.3: Phenol Structure

A stock solution of phenol was prepared for a cation exchange capacity (CEC) equal to 100%, by dissolving 285 mg of MV in 1000mL of distilled water; after stirring for 24 h, diluted solutions were prepared and then used so that phenol would be an adsorbate in adsorption on modified bentonites.

Due to their harmful effects, phenol and MV were chosen as pollutant in this study to be eliminated by adsorption on new synthetized adsorbents (nano materials composites based on bentonite).

A stock solution of phenol was prepared for a cation exchange capacity (CEC) equal to 100%, by dissolving 285 mg of MV in 1000mL of distilled water; after stirring for 24 h, diluted solutions were prepared and then used so that phenol would be an adsorbate in adsorption on modified bentonites.

Due to their harmful effects, phenol and MV were chosen as pollutant in this study to be eliminated by adsorption on new synthetized adsorbents (nano materials composites based on bentonite).

IV.2.3. Ultraviolet Visible (UV-Vis) Spectrophotometer

The apparatus consists of several components integrated into a single equipment; witch’s the UV-Vis spectrophotometer. The UV-Vis instrument investigates the interaction of light radiation with matter in the ultra violet (200-400) and visible (400-800) range [6]. Figure IV.4 shows a real pick of the used UV-Vis spectrophotometer from LANGE marque type DR 6000.

Figure IV.4: Ultraviolet Visible instrument (DR600)

As presented in Figures IV.5, standard working solutions of phenol and MV were prepared at different concentrations (0.5, 1, 2, 3, 5, 8, 10, 15, 25, 35, 50 mg.L-1) by dilution of the stock solution with deionized water for, and then used to realize the calibration curve of a spectrophotometer and to determine the maximum wavelengths (λ max) of absorption of both of the two studied solutions [6].

Figure IV.5: Phenol Stock and Standard Working Solutions.

UV-Vis's spectrophotometer was used after calibration, Figures IV.6 (a.b) present the calibration curves of both phenol and MV. The determination of adsorbates concentrations was in UV-Vis domain at λ max of 275 and 588 nm for phenol and MV respectively, that were determined by the maximum wavelength (λ max) spectra presented in Figure IV.7 (a. b).

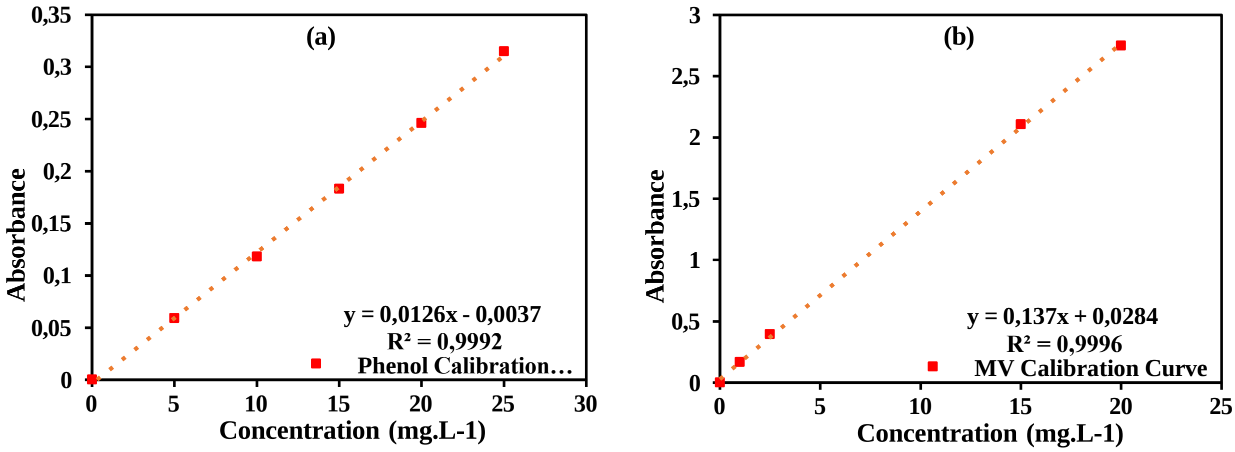


Figure IV.6: Calibration Curve of Phenol (a) and MV(b)

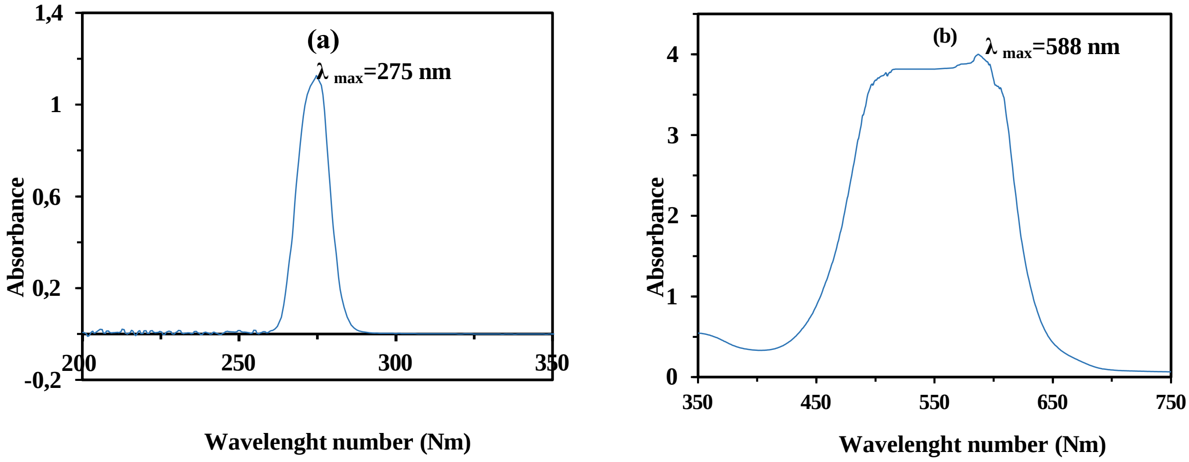


Figure IV.7: Maximum Wavelength Spectra (λ max) of Phenol (a) and MV(b)

IV.3. Adsorption Experiments System

Adsorption experiments were applied on the prepared modified bentonite: Na-Ben, THPA-Ben, CAT-Ben, Hematite-Ben and both of Hematite-THPA-Ben and Hematite-CAT- Ben, and that to test their ability of pollutants retention and to determine the time needed to reach the equilibrium, we studied also the kinetics and isotherms of adsorption. For this purpose, samples of 0.04 g of modified bentonites (adsorbents) were used and stock solutions (adsorbates) were already prepared by dissolving separately phenol and methyl violet (MV) in double distilled water.

All adsorption experiments were realized in batch equilibrium system. For each adsorption experiment the identified adsorbent mass was mixed with 100 mL of the adsorbate aqueous solution (Phenol or MV) in an Erlenmeyer flask of 250 ml volume, the mixture was shaken at 200 rpm. At predetermined time intervals the same samples volume was collected from the shaken solutions and then centrifuged, the collected centrifuged samples were filtered the solids were separated and the solution supernatant was used to determine the residual adsorbate concentration determined using spectrophotometer.

Figure IV.8: MV Adsorption Experiments

For the optimization of experimental parameters of the Phenol and MV adsorption onto our synthetized adsorbents (Na-Ben, Hematite-Ben, CTA-Ben, THPA-Ben, Hematite-CTA-Ben and Hematite-THPA-Ben we studied the:

- **Effect of adsorbent dose:**

  To observe the effect of the adsorbent dose on dye adsorption, different amounts of adsorbent (varying from 10 to 60 g) were respectively added into initial concentration of 5 $mg.L^{-1}$. the mixture was shaken at ambient and nature pH until the equilibrium time was reached.

- **Effect of initial concentration and contact time:**

  Initial concentration of the studied solution and contact time have an important role on the driving force that compensates for all the mass transfer resistance between the aqueous phase and the adsorbent surface [7]. In order to study the effect of the dye initial concentration and the contact time on the adsorption uptake. The adsorbates (Phenol and MV) solutions with initial concentrations of 5 to 25 mg.L^{-1} were agitated with 0.04 g of each adsorbent (Na-Ben, Hematite-Ben, CTA-Ben, THPA-Ben, Hematite-CTA-Ben and Hematite-THPA-Ben) at ambient temperature and natural pH, the residual adsorbates concentrations were determined in UV-Vis until the equilibrium time was reached.

- **Effect of pH:**

  To study the effect the pH media, pH measurements of phenol and MV solutions at 5 mg.L^{-1} initial concentration was carefully adjusted between 1 and 9 using NaOH and HCl solutions [8]. The solutions were stirred using a magnetic stirrer at room temperature. And then shaken with 0.04 g of adsorbents at ambient temperature until the equilibrium time was reached.

- **Effect of temperature:**

  To observe the effect of temperature on Phenol and MV adsorption, this study was performed in thermostatic bath (25, 35, 45, 55 °C), initial concentration 5 mg.L^{-1} mixed with 0.04 g of adsorbents at natural pH until the equilibrium time was reached.

The adsorbates removal percentage R (%) can be calculated as C_0 follows:

$$Effeciancy\ Removal\ \% \ = \frac{(C_0 - C_t).V}{W}.100 \ldots\ldots\ldots\ldots\ldots\ldots IV.1$$

Where, C_0 initial adsorbates concentrations, and C_t is the adsorbate concentration (mg.L-1).

The amount of adsorbate adsorbed at time instant and equilibrium conditions (q_t and q_e (mg.g^{-1})) respectively, were calculated by the following equations [9]:

$$q_t = \frac{(C_0 - C_t).V}{W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots IV.2$$

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots IV.3$$

Where qt is the adsorbent capacity, mg.g^{-1}; Ct is the adsorbate concentration, mg. L^{-1}; C0 is the initial concentration of adsorbate, mg·L^{-1}, and W, is the adsorbent mass, g, and V is the solution volume, L. If the adsorption arrives at equilibrium, C_t equals C_e, (Ce is the residual concentrations of adsorbates at equilibrium mg·L^{-1}), while qt equals qe (the equilibrium adsorption capacity) [10].

IV.3.1. Methyl Violet Adsorption

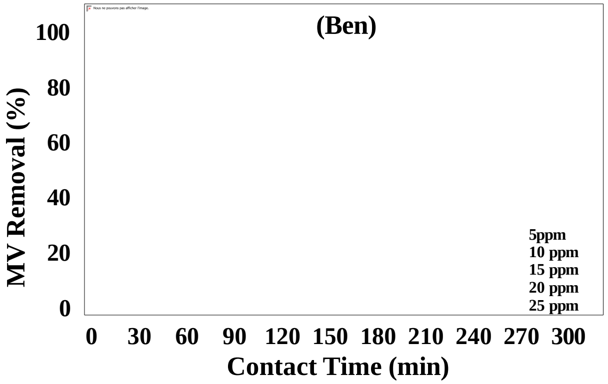
IV.3.1.1. Contact Time and Initial Concentration Effects

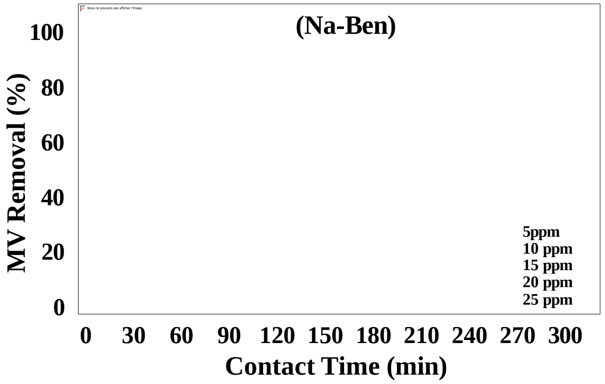
The results of studying the effect of contact time between the tested materials-based adsorbents (Ben, Na-Ben, Hematite-Ben, THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite- CTA-Ben) and MV solutions and the influence of its initial concentrations are presented in Figure IV.9.

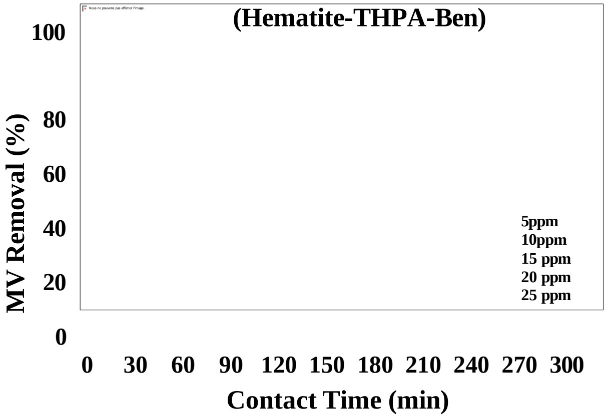
The presented results show that for each adsorbent the adsorption efficiency of MV decreases with the C_0 of MV solution increasing, and the maximum efficiency was determined at C_0= 5 mg.L^{-1}. The decrease in adsorption efficiency by C_0 of MV dye increasing can be due to various factors such as saturation of the adsorption sites of the adsorbents at high concentrations because of the presence of enormous dye molecules in the diluted solution, that causes limiting in the adsorbent SSA, with the increased electrostatic repulsion between the adsorbent surface and dye molecules [7,11].

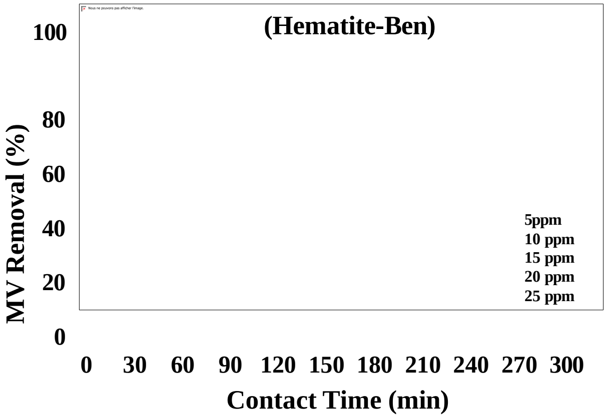
From the plots of MV adsorption onto the studied adsorbents: Ben, Na-Ben, THPA-Ben, CTA- Ben, Hematite-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben, it’s notable that the best color removal is presented at the lowest dye initial concentration (C_0=5 mg.L^{-1}) and the purified bentonite have the lowest adsorption efficiency. Comparing between MV adsorption process onto various bentonites-based adsorbents and from the presented results, it’s seen that by increasing contact time (t) the efficiency of MV dye adsorption process increased until the adsorption reach equilibrium, that is be due to providing sufficient time for the MV dye molecules to be in the adsorption sites of the adsorbent surface. MV adsorption by the tested adsorbents show a rapid MV Dye removal at the first 15 min and, thereafter, the adsorption rate increased gradually and the adsorption reached equilibrium after about 120 min with both Na- Ben and Ben with a percentage removal of: ~39.5% and ~69.7% respectively; however, after 90 min the adsorption of MV reach equilibrium using: THPA-Ben, CTA-Ben, Hematite-Ben by removing ~94%, ~90% and ~78% of the tested quantity of the dye respectively.

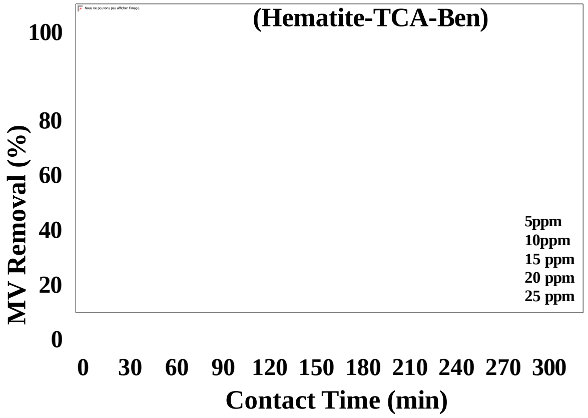
Besides, after 60 min the equilibrium of MV adsorption take place after removing ~98% and~100% of the dye color respectively onto Hematite-THPA-Ben and Hematite-CTA-Ben. The aggregation of the dye molecules with the increase in contact time makes it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. This aggregation negates the influence of contact time as the mesopores get filled up and start offering resistance to diffusion of aggregated dye molecules in the adsorbents [12].

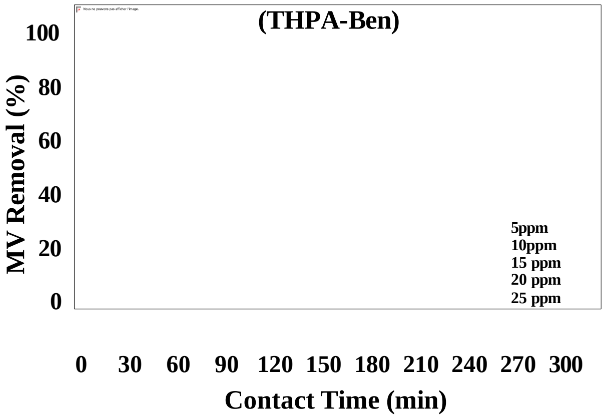

(Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm


(Na-Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm


(Hematite-THPA-Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10ppm
15 ppm
20 ppm
25 ppm


(Hematite-Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm


(Hematite-TCA-Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10ppm
15 ppm
20 ppm
25 ppm


(THPA-Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10ppm
15 ppm
20 ppm
25 ppm

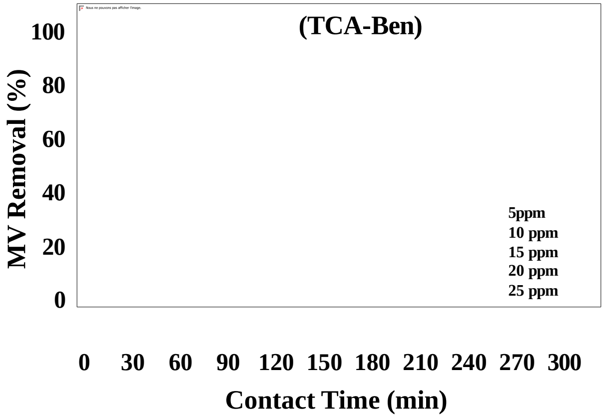

(TCA-Ben)
MV Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm

Figure IV.9: Contact Time and Initial Concentration Effects on Methyl Violet (MV) Adsorption

IV.3.1.2. Adsorbent Dose Effect

The adsorbents dose is one of the important parameters due to its role in determining the absorbent capacity for adsorbing on its surface [13]; adsorption experiments were performed to study the effect of the varied amounts of the used bentonites-based adsorbents at ambient conditions. The dependency of the percentage of the color removal and the adsorbents amounts was shown in Figure IV.10.

From the adsorption process results we conclude that: with increasing the dosage of adsorbent the MV adsorption efficiency increase, and this is due to the increase in the number of adsorption sites available to adsorb the dye molecules at the initial concentration.

It is remarqueble that increasing the adsorbents amounts from 10 to 60 mg, the removal of MV increases from 10, 44, 55, 85, 88, 96 and 97 % to 40, 67, 75, 94, 96, 99 and 100 % for the Ben, Na-B, Hematite-Ben, THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben based-adsorbents respectively, and this can due to the presence of an additional adsorption sites to adsorb the dye molecules that are not occupied. However, a significant increase from 10 to 40 mg but above this amounts the increasing of the adsorbents amounts until 60 mg decrease slightly the capacity of MV removal. This can be explained by the increase in the interaction between them and the adsorbed particles, and the decreases of its surface and increase the thickness of the penetration route and eventually decrease the adsorption density [13,14]. From the previous results we conclude that 40mg is the optimum dose of the adsorbents to use in removing MV, that pillared-intercaled-bentonites have the highest capacity of the dye removing from aqueous solution corresponding to Hematite-TCA-Bentonite with capacity of 100% color's dye removal and 99% for Hematite-THAP-Bentonite.

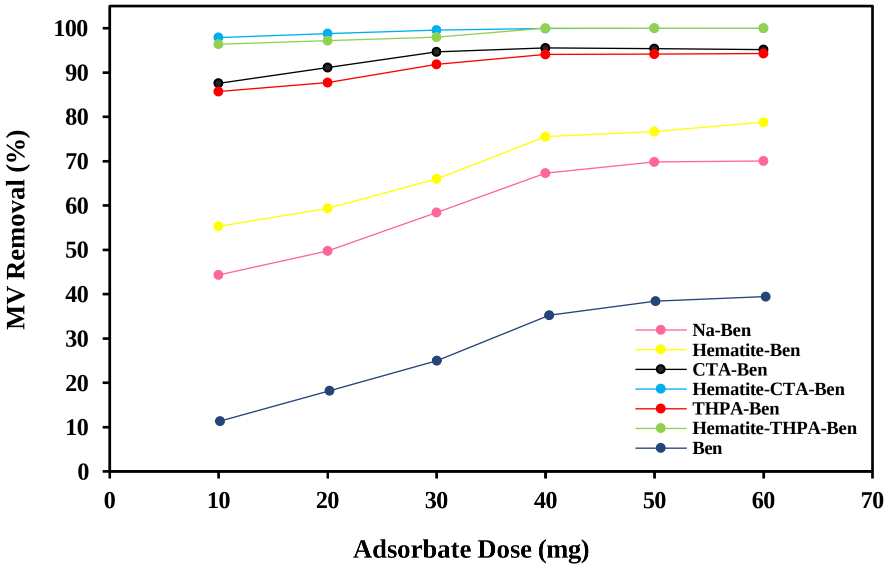


Figure IV.10: Adsorbents Dose Effect on MV Adsorption

IV.3.1.3. pH Media Effect

The pH media provide a key information to understand the interaction between the adsorbent and the adsorbate of the adsorption process which is primarily driven by electrostatic forces. Because of that, some of adsorption experiments were performed at different pH points. The executed pH test was selected from 2 to 9, to analyze the effect of this parameter on the dye removal process. The tests results were organized and presented in Figure IV.11. From the obtained, we remark that the efficiency of MV adsorption onto the studied bentonites (Ben, Na-B, Hematite-Ben, THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA- Ben) is higher at acidic and basic media at the two pH points 2 and 9 and lower at pH values around 5.5 for all the used adsorbents.

With Ben, Na-Ben and Hematite-Ben we note a significant decrease with the increasing of pH from 2 to 5.5, however, at the same pH range we remark a slight decrease of MV adsorption onto THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben. The adsorption capacity decreases is due to the increase of negative surface charge of the adsorbent, which favors the attraction of the cationic dye molecules [15]. Besides, an important increase is noted with Ben, Na-Ben and Hematite-Ben when increasing pH values until 9; besides, the slightly increase for THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben. Although the dependency of pH media and the same evolution as the other adsorbents, the most effective adsorption capacity of MV onto Hematite-CTA-Bentonite is attributed with 100% of color removal percentage at the major pH points and 97% at 5.5 pH point.

MV is basic cationic dye, adsorbed onto the purified and modified bentonites, which develop a positive surface charge in the acidic medium. So the best adsorbed amount was when electric charges are of opposite sign between sorbent and adsorbate [16].

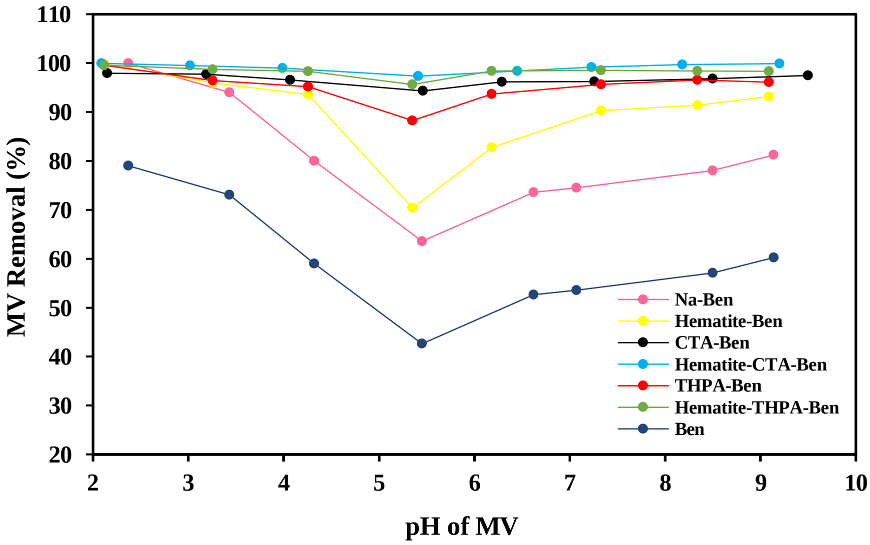


Figure IV.11: pH Effect on MV Adsorption.

IV.3.1.4. Temperature Media Effect

The influence of temperature on the adsorption process was investigated at different T° conditions: 25, 35, 45 and 55 °C, and the results of this study are shown in Figure IV.12.

From the plots, it is notable that, the MV adsorbed amount at equilibrium increases with increasing temperature. It is common that increasing temperature may create a swelling influence inside the adsorbent structure, penetrative the additional big dye molecule [17,18]. The maximum MV removal onto the purified and modified-based Bentonites are found at 55°C with a percentage removal of 97.51, 98.17, 98.18, 99.94, 99.96 and 100% for Ben, Na-B, Hematite-Ben, THPA-Ben, TCA-Ben, Hematite-THPA-Ben and Hematite-TCA-Ben respectively. It is found that the highest color removal is attributed to the use of Hematite- THPA-Ben and Hematite-TCA-Ben as adsorbents to remove MV from aqueous solutions at a temperature of 55°C.

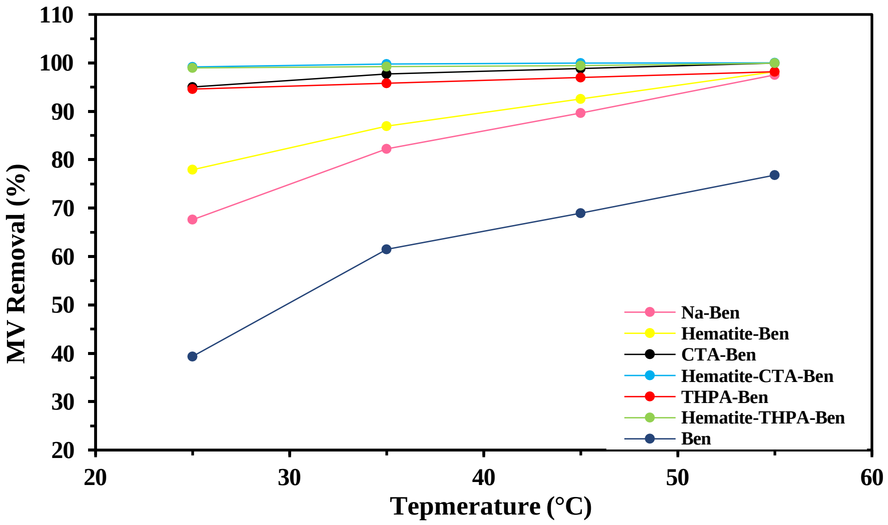


Figure IV.12: Temperature Effect on MV Adsorption.

IV.3.2. Phenol Adsorption

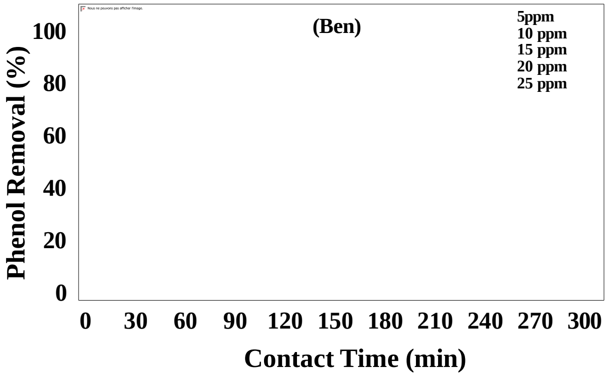
IV.3.2.1. Contact Time and Initial Concentration Effects

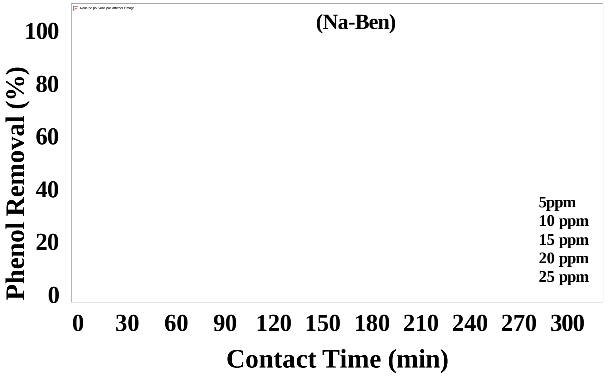
The studies of contacts time and the phenol initial concentrations effects on the adsorption process were performed. Figure IV.13 resume all results that shows that phenol adsorption rate onto the studied adsorbents (unmodified and the modified bentonites).

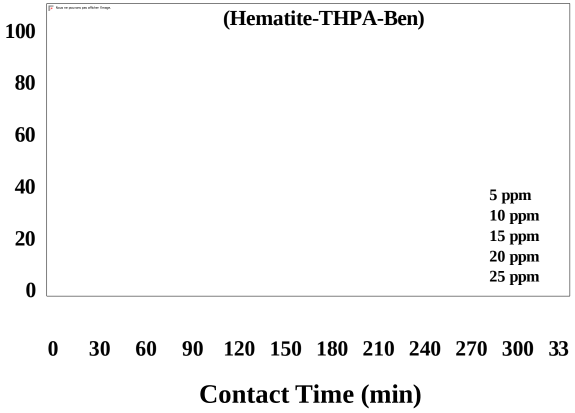
It is remarqueble that a very rapid increase in the efficiency of phenol removal after 30 min of contact, and then it slightly increases until the equilibrium is reached. Where, phenol adsorption reaches equilibrium after 180, 150 min for Ben and Na-Ben respectively; however, for Hematite- Bentonite and the both the THPA-Ben and TCA-Ben the equilibrium was reached after 90 min. Besides, the fastest phenol adsorption process was attributed to its removal onto Hematite-TCA-Ben and Hematite-THPA-Ben where the equilibrium was reached after 30 min. That was because of the abundant adsorption surface sites at the beginning of the adsorption process; and after equilibrium, the vacant sites are less available and hard occupied and that is due to the increasing electrostatic repulsion between the adsorbed phenol molecules of the adsorbate's solution on the surface of the unmodified and modified bentonites used adsorbents [19,20].

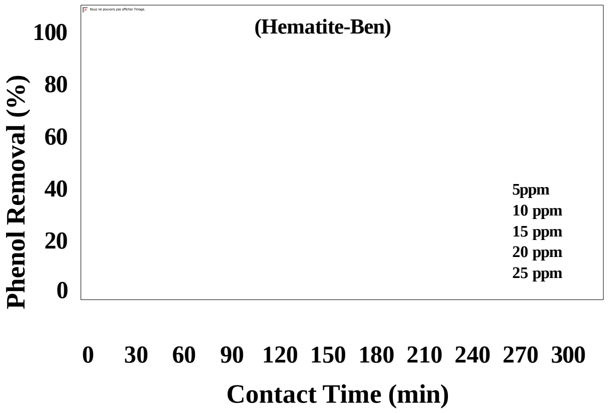
From plots, it's clearly seen that the best efficiency was at C_0= 5 mg. L^{-1}; additively, the increase in initial phenol concentration load to a decrease in the efficiency of phenol adsorption from the aqueous solution and this can be due to various factors, one of them is the limitation in the porous sites of the adsorbents and its specific surface area (SSA) because of the presence of an important amount of the adsorbate molecules at high concentrations, that result an increase in the electrostatic repulsion between the adsorbent surface and the organic molecules [7,11].

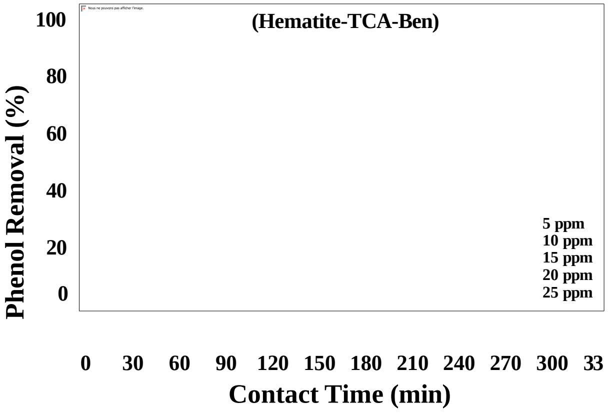
Phenol was totally adsorbed onto the Hematite-THPA-Ben, about ~94.5% of phenol was retinted by Hematite-TCA-Ben. A good efficiency of phenol removal was also notable for THPA-Ben, TCA-Ben and Hematite-Bentonite with ~98%, ~82% and ~78% respectively, comparing with ~67% with Na-Ben and ~36% for the unmodified bentonite Ben [20].

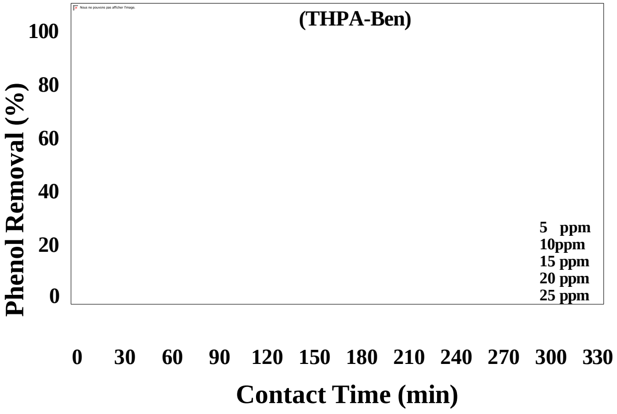

(Ben)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm
Phenol Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)


(Na-Ben)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm
Phenol Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)


(Hematite-THPA-Ben)
5 ppm
10 ppm
15 ppm
20 ppm
25 ppm
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
33
Contact Time (min)


(Hematite-Ben)
5ppm
10 ppm
15 ppm
20 ppm
25 ppm
Phenol Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)


(Hematite-TCA-Ben)
5 ppm
10 ppm
15 ppm
20 ppm
25 ppm
Phenol Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
33
Contact Time (min)


(THPA-Ben)
5 ppm
10ppm
15 ppm
20 ppm
25 ppm
Phenol Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
330
Contact Time (min)

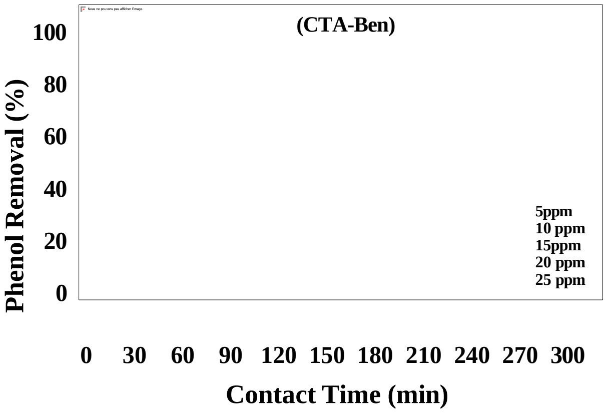

(CTA-Ben)
5ppm
10 ppm
15ppm
20 ppm
25 ppm
Phenol Removal (%)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
270
300
Contact Time (min)

Figure IV.13: Contact Time and Initial Concentration effects on Phenol Adsorption

Phenol Removal (%)

IV.3.2.2. Adsorbent Dose Effect

The adsorbent dose is a crucial parameter, used to evaluate the adsorption process and determine the capacity of retention onto the adsorbent surface [13]. The phenol removal percentage and the amounts of the studied clays based-adsorbents: Ben, Na-Ben, Hematite-Ben, THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben were shown in Figure IV.14. The finding results, show an increase in both the quantity of adsorbents and phenol removal rate as proper in literature [21].

Aldo the increasing in adsorbed amounts with adsorbents doses increase, phenol molecule adsorption still very important onto the modified bentonites. The most of them is for Hematite- THPA-Ben, then Hematite-TCA-Bentonite and THPA-Ben also have a very good phenol retention. Besides, comparing with Ben we conclude that TCA-Ben, the Hematite-Ben and Na- Ben bentonite have a good phenol retention.

With amounts of adsorbents between 10 and 40 mg, the removal of phenol increases significantly, and slightly with increasing the modified bentonites doses from 40 until 60 mg. The quantity of 40 mg is jugged optimum to the phenol adsorption process. The increase of removing phenol and amount of the used adsorbent proportionally is due to increase in the available adsorption sites; however, the adsorbents amount doesn’t have an important influence on the phenol retention with amounts that are higher than 40 mg and this is due the presence of so match adsorption sites that occupied the phenol molecules [13,14].

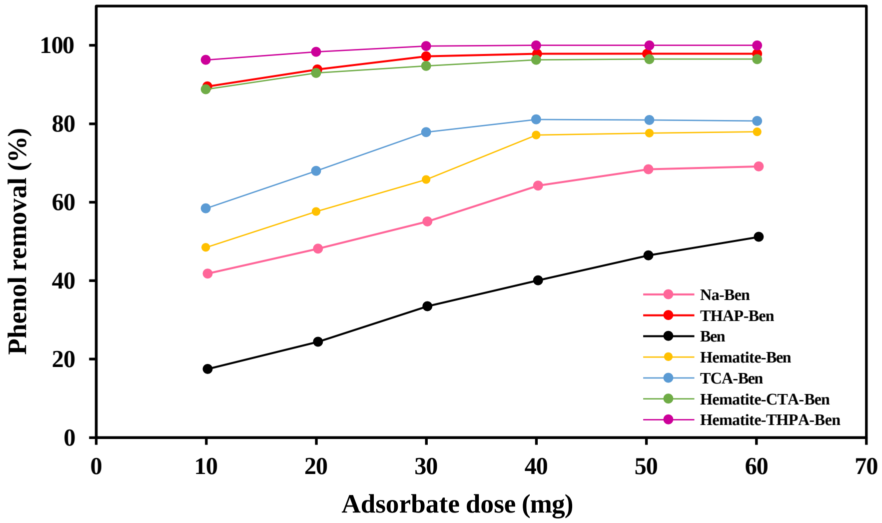


Figure IV.14: Adsorbents Dose Effect on Phenol Adsorption.

IV.3.2.3. pH Media Effect

The surface charge of the adsorbent and the ionization degree of the adsorbate are strongly affected by the pH of the aqueous solutions, hence the uptake of phenol by the adsorbent depends on the solution pH adsorbate [19,22].

The evaluation of pH media effect on phenol adsorption process was performed comparatively on: Ben, Na-Ben, Hematite-Ben, THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite- CTA-Ben, and that in the pH range of 2–9 according to initial phenol solutions (adsorbate). Figure IV.15 presents the resulting experimental results of this study listed bentonites used as adsorbents.

The uptake of phenol by the bentonites-based adsorbents is almost constant for pH points between 2 and 3. Besides, when the pH value exceeds 3 the adsorption of phenol decreases slightly with Hematite-THPA-Ben, THPA-Ben, Hematite-Ben and Na-Ben and decrease with Ben. a significant increase when pH is above 6 pH point [20].

However, the phenol removal increases with Hematite-TCA-Ben, TCA-Ben a Ben for pH values between 3 and 5 and then it decreases only for TCA-Ben a Ben with the increasing of the pH media contrarily with Hematite-TCA-Ben which the adsorb more quantities of phenol in pH media above 6.

At higher pH values, the ionization degree of phenol and the quantity of OH^- ions decrease thereby the diffusion of phenolic ions that are hindered, and the electrostatic repulsion between the negatively charged surface sites of the adsorbent. Bentonite contains metal oxides mainly Al and Si, which are hydrolyzed, in an aqueous solution and so a charge (positive or negative) is created on its surface. This charge is proportional to the pH of the solution which surrounds the oxide particles; so compared to higher pH, phenol removal is greater at lower pH [23].

We resumed that the removal of phenol onto purified and modified bentonite-based adsorbents is very important at lower pH values 2–3, and this proper to literature [1,24,25]. In this work for pH point ~9 was selected as an optimum pH value for the adsorption of phenol onto both THPA-Ben and Hematite-THPA-Ben, pH points 5 for Ben, Na-Ben, and pH point 2 for Hematite-Ben.

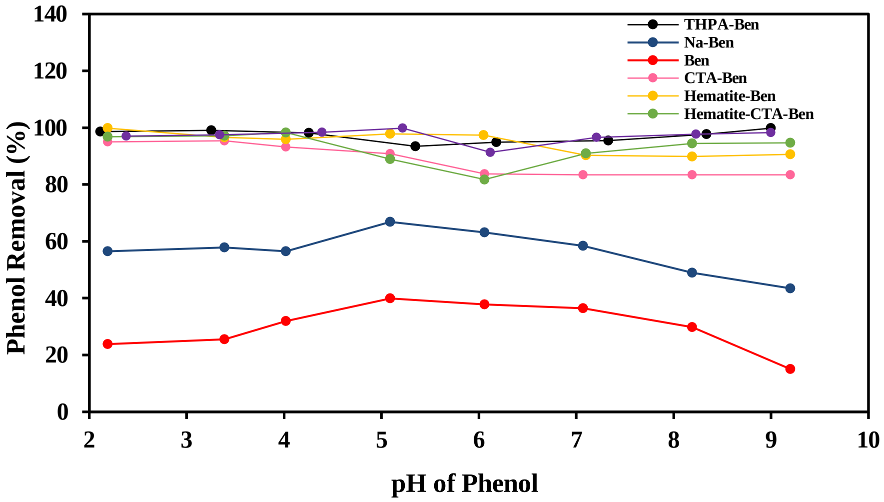


Figure IV.15: pH Effect on Phenol Adsorption

IV.3.2.4. Temperature Media Effect

The studies of temperature effects on the adsorption of phenol onto: Ben, Na-Ben, Hematite- Ben, THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben were performed at different T°: 25, 35, 45, and 55 °C. The adsorption of phenol onto the bentonites-based adsorbents was affected by temperature. The progress of capacity of phenol removal as a function of temperature presented in Figure IV.16. It was notable from the shows results that the most important capacity of phenol removal onto studied adsorbents was at 55°C, and it decreases proportionally with decreasing temperature and that indicates that the sorption of phenol onto the studied adsorbents is endothermic as proper with literature [26].

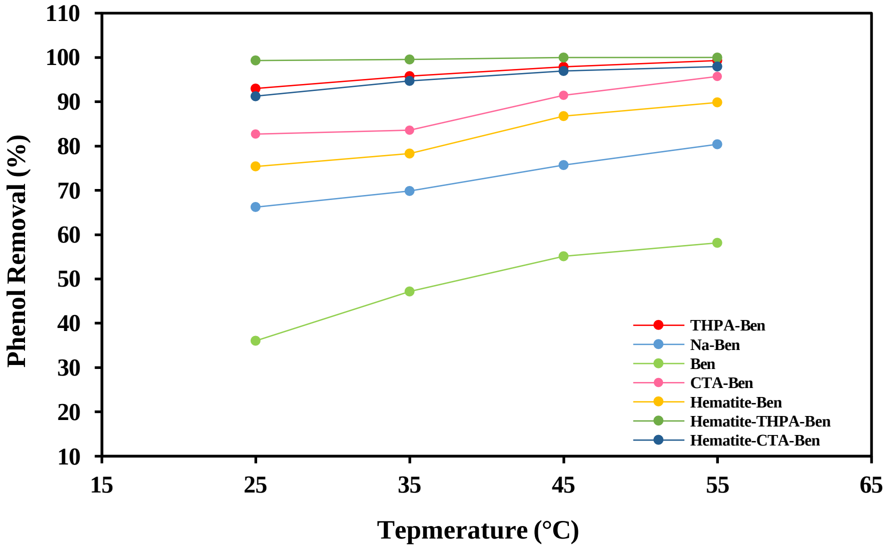


Figure IV.16: Temperature Effect on Phenol Adsorption

IV.4. Comparison Between Different Adsorbents for Phenol and MV Retention

Like zeolite, clays also bentonite have the property that they can expand their layer structure and they may allow big molecules such as surfactants and organics [27].

Besides, phenol can be adsorbed onto bentonite surface through the hydrogen bonding between oxygen atoms of silicate layer and hydroxyl groups of phenol and/or charge transfer complexes [28]. M. Sprynskyy and al. [29] examine the capacity of phenol adsorption onto the raw, 2M NaOH and HDTMA-modified zeolite, their results shows that the HDTMA-modified zeolite is characterized by the its ability for adsorb phenol from aqueous solution. The best efficiency of phenol removal (>90%). Phenol removal increased with time, three stages may be divided in the sorption process: an initial rapid sorption extending over the first 60min; between 60 and 90 min, the stage of slow approach to equilibrium and the equilibrium stage of 8h. Z. Ceylan and al [26], studied the phenol adsorption capacity of cetyltrimethylammonium bromide modified clays (MMT-CTAB) and reported that the highest phenol removal was found also at 4 pH media; her results also show that the increase in temperature at all tested phenol concentrations leads to rise in phenol removal for MMT-CTAB. The initial sorption phenomenon may occur as physical and chemical; This effect may be based on expansion of pore size or creation of some new active sites on the adsorbent surface. In this study, the adsorption efficiency removal of phenol from aqueous solutions onto the synthetized adsorbent different modified bentonites under different conditions was investigated in this work. Where Hematite-THPA-Ben retained successfully and totally phenol from aqueous solution at and this for the lowest initial concentration (C_0=5 mg. L^{-1}). The comparative scientific results of phenol adsorption onto surfactant modified adsorbents given in Table IV.1.

On the other side, we studied the MV adsorption process onto the same materials; E. Altintig and al. (2021) [30], tested the efficiency of the magnetically modified zeolites Fe_3O_4–Z in eliminating MV with >90% efficiency removal after equilibrium time of 150 min. R. Ali and al. (2022) [31], beginning with 50 mg.L^{-1} an amount of 97% of MV eliminated onto the modified Lignin LCF and that after the equilibrium reached after 5 min. in our study, the total amount of MV was eliminated successfully after 60 min onto the Hematite-CTA-Ben and this improve a maximum MV adsorption capacity considered significant comparing with the finding in literature. Our finding and those of literature were comparatively presented in Table IV.2.

Table IV.1: Comparative Scientific Results of Phenol Adsorption

Adsorbents	**Phenol R%**	**$T_{eq\ (min)}$**	**Reference**
Ben	36%	after 180 min	In this study
Na-Ben	~67%	after 120 min	In this study
THPA-Ben	98.2%	after 90 min	In this study
TCA-Ben	~82%	after 90 min	In this study
Hematite-Ben	~78%	after 90 min	In this study
Hematite- THPA-Ben	100%	after 30 min	In this study
Hematite -TCA-Ben	~94.5%	after 30 min	In this study
CTAB-Bentonite	>81.36%	after 90 min	Chun-Yan Cao and al (2013)
MMT-CTAB	71%	after 60 min	Z. Ceylan and al (2018)
HDTMB	~38%	after 120 min	S.H. Lin and al (2001)
CPB	~40%	after 90 min	S.H. Lin and al (2001)
TMAB	~35%	after 120 min	S.H. Lin and al (2001)
BTEAB	~90%	after 90 min	S.H. Lin and al (2001)

Table IV.2: Comparative Scientific Results of MV Dye Adsorption

Adsorbents	**MV R%**	**$T_{eq\ (min)}$**	**Reference**
Ben	~39.5%	after 120 min	In this study
Na-Ben	~69.7%	after 120 min	In this study
THPA-Ben	~94%	after 90 min	In this study
TCA-Ben	~90%	after 90 min	In this study
Hematite-Ben	~78%	after 90 min	In this study
Hematite- THPA-Ben	98%	after 60 min	In this study
Hematite -TCA-Ben	100%	after 60 min	In this study
Fe_3O_4–Z	>90%	after 150 min	E. Altintig and al. (2021)
LCF	97%	after 05 min	R. Ali and al (2022)

IV.5. Conclusion

In this Chapter, we tested the efficiency of organic pollutants adsorption onto the studied adsorbents: the purified Bentonite (Ben) and its different modified forms: sodic bentonite (Na- Ben), pillared-bentonite (Hematite-Ben), intercaled-bentonites (THPA-Ben and CTA-Ben) and the pillared-intercaled-bentonites (Hematite-THPA-Ben and Hematite-CTA-Ben.

To achieve our goal, we first studied the adsorption of the bentonite and modified bentonites to eliminate an organic dye: methyl violet (MV) that cause discomfort or nuisance in the liquid environment; as a second step, the adsorption experiments were performed to test the studied clays-based adsorbents capacity to remove Phenol from aqueous media.

The obtained results confirm that the used bentonites-based adsorbents with their different structures have a significant adsorption capacity to eliminate the two adsorbates: MV and Phenol, this permits us to conclude that the different modifications that bentonite undergone improve its adoption adequacy of the organic compounds. The kinetic of adsorption process is a bit rapid at the pH of the compounds and ambient temperature. however, increasing in temperature increases both adsorption rate and efficiency; without missing the notable effect of pH solutions changes on the adoption process where the most influenceable is the acidic.

Comparing with the natural bentonite, the pillared-intercaled-bentonites with their new structures have the capacity to eliminate totally (100%) the two organics from aqueous media, where Hematite-CTA-Ben and Hematite-THPA-Ben have a high affinity for MV and Phenol respectively. The classification of the adsorption efficiency of the studied adsorbents according to their affinities for both of the two organic compounds is as follows:

- For Phenol:

Ben<Na-Ben<Hematite-Ben<CTA-Ben<THPA-Ben<Hematite-CTA-Ben<Hematite-THPA-Ben;

- For Methyl Violet:

Ben<Na-Ben<Hematite-Ben<THPA-Ben<CTA-Ben<Hematite-THPA-Ben<Hematite-CTA-Ben.

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Chapter V: Adsorption’s Isotherms and Kinetics

V.1. Introduction

The part of our study that was already presented in chapter V proves that all modifications that undergone on the Algerian bentonite, enhance its adsorption properties, making it a promising candidate for environmental remediation.

During adsorption process, contaminants molecules adhere to the surface of adsorbents to enter in the interlayers of the clays-based adsorbents, whereas the others were attached to the clay surface [1]. In this chapter, we will explore the adsorption behavior of the selected organic contaminants (phenol and MV) onto our prepared bentonites-based adsorbents, focusing on the study of the adsorption isotherms and kinetics, and that by investigating the adsorption isotherms, which illustrate the relationship between the concentration of the pollutants and their uptake by the synthetized adsorbents; and the kinetic, which describe the rate of adsorption, this study aims to provide a comprehensive understanding of the efficiency and the dynamics of the modified bentonites as adsorbents for organic pollutants.

V.2. Adsorption Isotherms

The adsorption isotherms are useful for understanding the mechanism of the adsorption process. They expose the particular relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface at a determined surface at a constant temperature [2].

In our study, the Langmuir and Freundlich isotherm models were chosen and applied to describe the adsorption of the selected (MV and phenol) organic compounds experiment onto the purified and modified bentonites (Ben, Na-Ben, Hematite-Ben, TCA-Ben, THPA-Ben, Hematite-TCA-Ben, and Hematite-THPA-Ben,).

The Langmuir model assumes that adsorption takes place at specific homogeneous sites on the surface of the adsorbent and also, when a site is occupied by an adsorbate molecule, no further adsorption can take place at this site.

The linear form of the Langmuir isotherm model can be presented as [3]:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad \text{V. 1}$$

Where: qe (mg. g^{-1}): the amount of the phenol adsorbed per unit mass of adsorbent, Ce (mg. L^{-1}): the equilibrium phenol concentration in the solution, qmax (mg. g^{-1}): the Langmuir constant related to the maximum monolayer adsorption capacity, b (L.mg^{-1}): the constant related the free energy or net enthalpy of adsorption.

The linear plot of Ce/qe versus Ce indicates that adsorption obeys the Langmuir model, and the constants qmax and b are obtained from the slope and intercept of the linear plot, respectively.

The essential features of the Langmuir isotherm model can be expressed in terms of "K_L" a dimensionless constant, separation factor or equilibrium parameter, which is defined by the following equation [3]:

$$K_L = \frac{1}{1+b\,C_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{V.2}$$

Where: Co (mg. L^{-1}): the initial amount of adsorbate, b ($L.mg^{-1}$): the Langmuir constant described above.

The K_L parameter is considered as more reliable indicator of the adsorption. There are four probabilities for the K_L value for:

Favorable adsorption $0<K_L<1$;

Unfavorable adsorption $K_L>1$;

Linear adsorption $K_L=1$;

Irreversible adsorption $K_L=0$.

The Freundlich isotherm model is valid for multilayer adsorption on a heterogeneous ad sorbent surface with sites that have different energies of adsorption which is described by the empirical equation given in Equation V.3 and its linear form presented in Equation V.4 [4,5]:

$$q_e = K_F C_e^{\frac{1}{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{V.3}$$

$$\log q_e = \log K_{F} + \frac{1}{n}\log C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{V.4}$$

Where: the constant K_F is the Freundlich adsorbent capacity (mg. g^{-1} $(L.mg^{-1})^{1/n}$) and n is the reciprocal of reaction order. The values of n depend to the heterogeneity of the adsorbent and for favorable adsorption process the value of n should be less than 10 and higher than unity.

The values of K_F and 1/n are determined from the intercept and slope of linear plot of log qe versus log Ce, respectively.

The results data of this study are in accordance with the classification system for adsorption proposed by Giles.

V.2.1. Methyl Violet "MV" Adsorption Isotherms

The thermodynamic isotherms were performed to compare the adsorption capacity of the studied bentonites-based adsorbents to adsorb MV from aqueous solutions without pH adjustment, with adsorbate initial concentration ranged from 5 to 25 mg. L^{-1} and that at different temperature conditions: 25, 35, 45 and 45°C.

The isotherms are depicted in Figures V.1 and V.2, where the findings were modeled using the Langmuir and Freundlich models. The data gathered is summarized in Table V.1 and Table V.2.

As seen from the data, the adsorption of MV is better modeled 9by Langmuir isotherm than the Freundlich isotherm. The correlation coefficients of Freundlich model (R_F^2) are comparatively higher than the Langmuir model's coefficients (R_L^2) and that for MV adsorption onto Ben, Na- Ben, Hematite-Ben, THPA-Ben, CTA-Ben and both Hematite-THPA-Ben and Hematite-CTA- Ben.

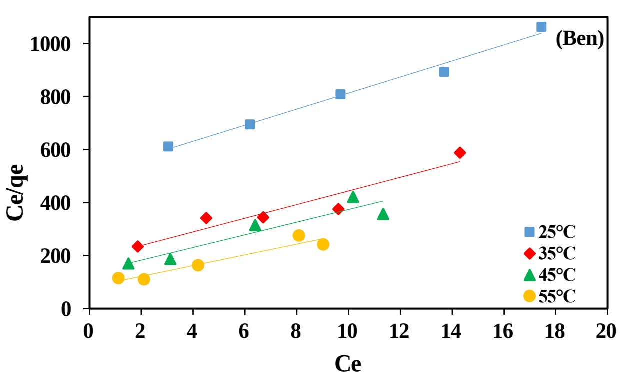
We remark that the phenol adsorption onto: Ben, Na-Ben and Hematite-Ben is better modeled by Freundlich isotherm, while the adsorption pattern of phenol onto CTA-Ben, THPA-Ben, Hematite-CTA-Ben and Hematite-THPA-Ben, is good fitted with both the Langmuir and Freundlich. The results are in accordance with the research's by Rawajfih et al (2006) [6].

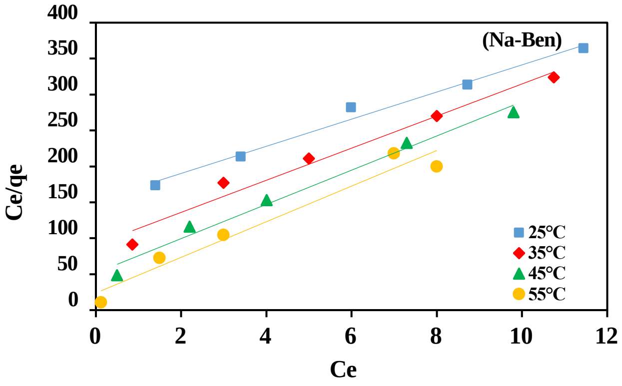
It's seen that K_L values are between 0 and 1 and this indicate that the phenol adsorption is favorable onto the six adsorbents Ben, Na-Ben, Hematite-Ben, THPA-Ben, CTA-Ben and both Hematite-THPA-Ben and Hematite-CTA-Ben.

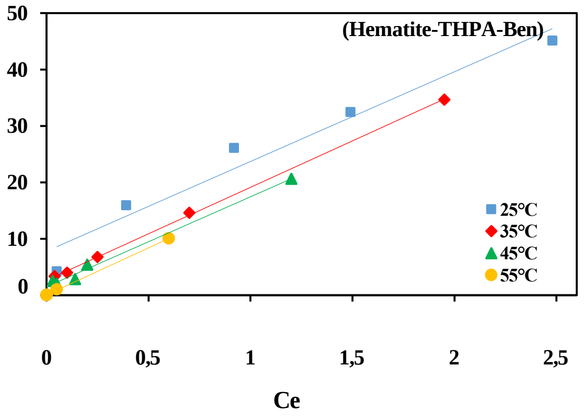
The Langmuir isotherm model, the maximum adsorption capacity of phenol adsorption onto the selected adsorbents increases with the increase in temperature. remarqueble high phenol adsorption capacity for the organo modified bentonite, this indicates that Hematite-CTA-Ben is a promising adsorption material in the environmental remediation.

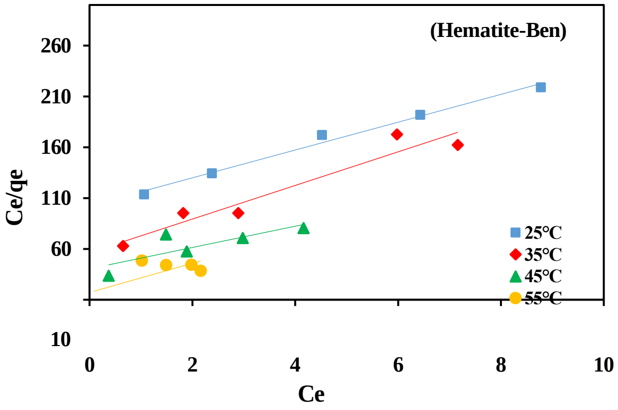
The most adsorption capacity increases in the order:

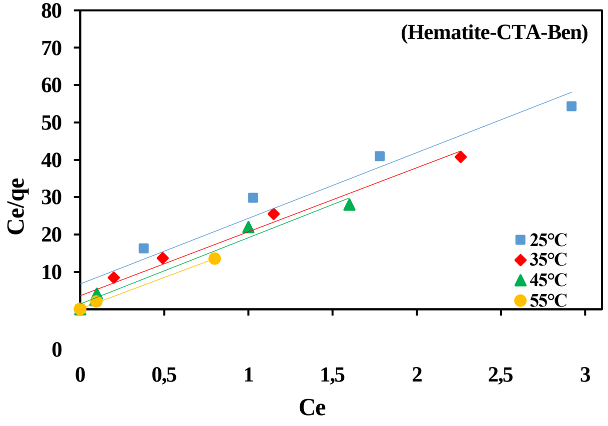
Ben<Na-Ben<Hematite-Ben< THPA-Ben< CTA-Ben < Hematite-THPA-Ben < Hematite-CTA-Ben.

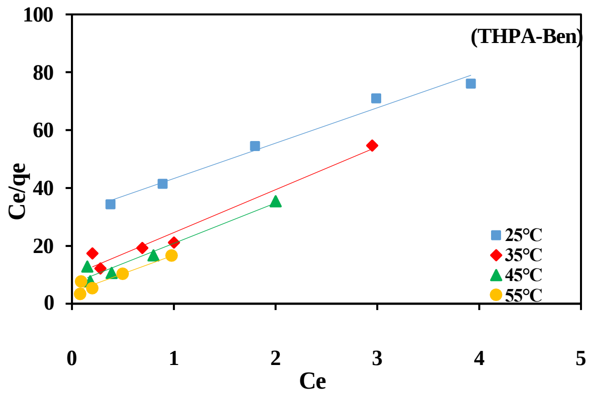

(Ben)
Ce/qe
Ce
0
200
400
600
800
1000
0
2
4
6
8
10
12
14
16
18
20
25°C
35°C
45°C
55°C


(Na-Ben)
Ce/qe
Ce
0
50
100
150
200
250
300
350
400
0
2
4
6
8
10
12
25°C
35°C
45°C
55°C


(Hematite-THPA-Ben)
Ce
0
10
20
30
40
50
0
0,5
1
1,5
2
2,5
25°C
35°C
45°C
55°C


(Hematite-Ben)
Ce/qe
Ce
10
60
110
160
210
260
0
2
4
6
8
10
25°C
35°C
45°C
55°C


(Hematite-CTA-Ben)
Ce/qe
Ce
0
10
20
30
40
50
60
70
80
0
0,5
1
1,5
2
2,5
3
25°C
35°C
45°C
55°C


(THPA-Ben)
Ce/qe
Ce
0
20
40
60
80
100
0
1
2
3
4
5
25°C
35°C
45°C
55°C

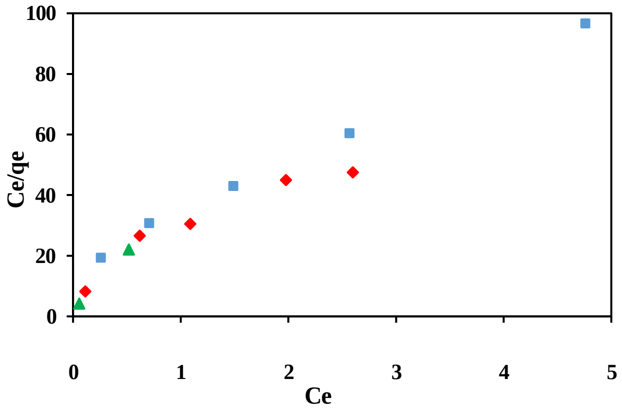
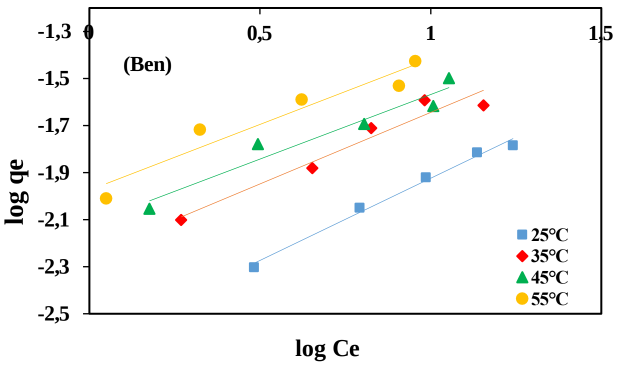
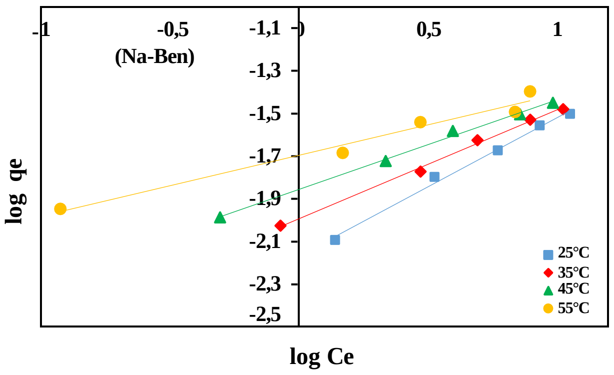
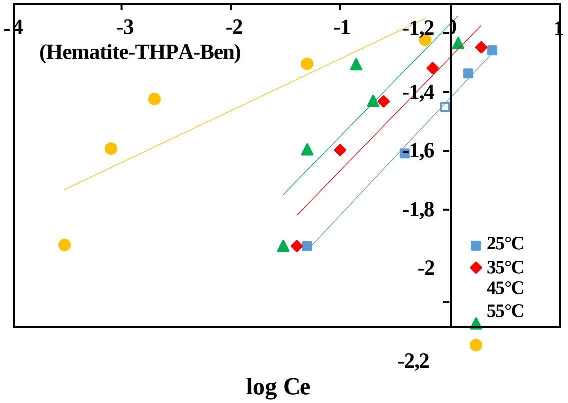

Ce/qe
Ce
0
20
40
60
80
100
0
1
2
3
4
5

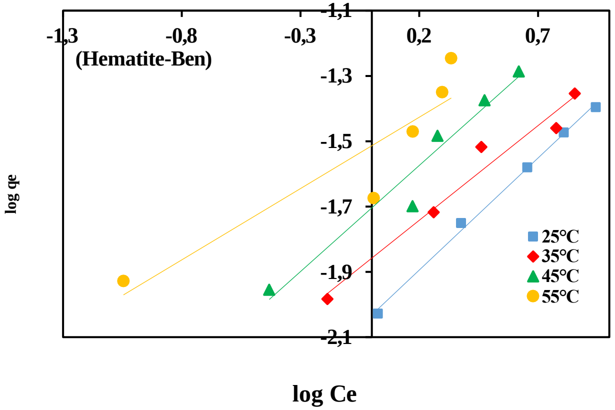
Figure V.1: Langmuir adsorption isotherms of MV adsorption onto purified and modified bentonites (conditions: m= 0.4 g, pH= 5.36)

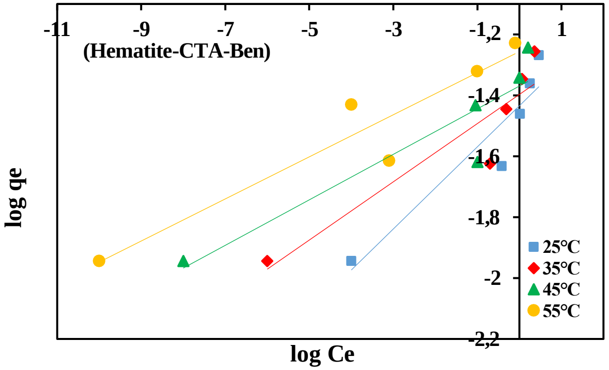
Ce/qe

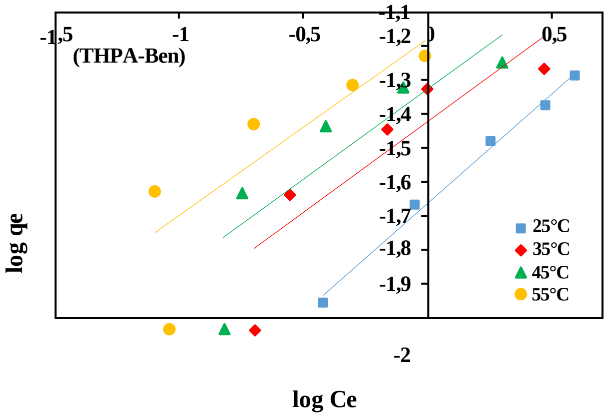

(Ben)
log qe
log Ce
-1,3
-1,5
-1,7
-1,9
-2,1
-2,3
-2,5
0
0,5
1
1,5
25°C
35°C
45°C
55°C


(Na-Ben)
log qe
log Ce
-1
-0,5
0
0,5
1
-1,1
-1,3
-1,5
-1,7
-1,9
-2,1
-2,3
-2,5
25°C
35°C
45°C
55°C


(Hematite-THPA-Ben)
log Ce
-4
-3
-2
-1
0
1
-1,2
-1,4
-1,6
-1,8
-2
-2,2
25°C
35°C
45°C
55°C


(Hematite-Ben)
log qe
log Ce
-1,3
-0,8
-0,3
0,2
0,7
-1,1
-1,3
-1,5
-1,7
-1,9
-2,1
25°C
35°C
45°C
55°C


(Hematite-CTA-Ben)
log qe
log Ce
-11
-9
-7
-5
-3
-1
1
-1,2
-1,4
-1,6
-1,8
-2
-2,2
25°C
35°C
45°C
55°C


(THPA-Ben)
log qe
log Ce
-1,5
-1
-0,5
0
0,5
-1,1
-1,2
-1,3
-1,4
-1,5
-1,6
-1,7
-1,8
-1,9
-2
25°C
35°C
45°C
55°C

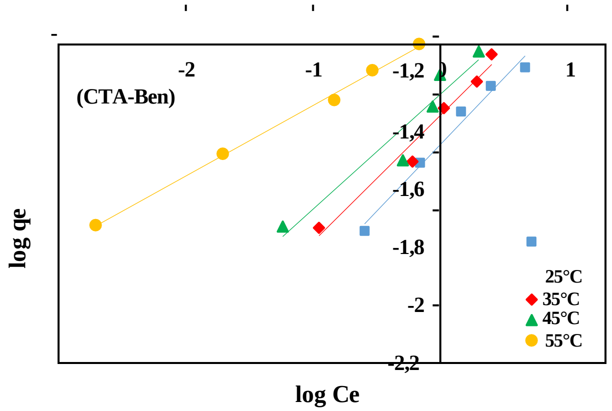

(CTA-Ben)
log qe
log Ce
-2
-1
0
1
-1,2
-1,4
-1,6
-1,8
-2
-2,2
25°C
35°C
45°C
55°C

Figure V.2: Freundlich adsorption isotherms of MV adsorption onto purified and modified bentonites (conditions: m= 0.4 g, pH= 5.36)

log qe

Table V.1: Adsorption Langmuir Isotherm Data of MV Adsorption onto the Studied Materials

		Langmuir			
Adsorbent	**T (°C)**	**Qmax (mg.g^{-1})**	**b (L.mg^{-1})**	**K_L (L.mg^{-1})**	**R_L^2**
Ben	25	70.33	0.0059	0.7699	0.9861
	35	78.39	0.1355	0.5911	0.9058
	45	96.42	0.1769	0.5291	0.8839
	55	99.49	0.2491	0.4438	0.9210
Na-Ben	25	84.53	0.1240	0.6353	0.9856
	35	93.45	0.2446	0.4689	0.9732
	45	100.42	0.4549	0.3198	0.9831
	55	106.40	1.0412	0.1718	0.9551
THPA-Ben	25	140.82	0.3942	0.3457	0.9820
	35	185.067	1.5207	0.1204	0.9670
	45	201.72	2.0250	0.0932	0.9526
	55	246.779	3.0652	0.4379	0.9039
CTA-Ben	25	165.59	0.9782	0.1537	0.9977
	35	198.66	1.2201	0.1271	0.9160
	45	258.69	1.6503	0.0972	0.8559
	55	350.61	2.1617	0.0757	0.9828
Hematite-Ben	25	110.73	0.0133	0.9398	0.9875
	35	142.61	0.2934	0.4152	0.9300
	45	176.95	0.2592	0.4456	0.6662
	55	209.70	0.8392	0.0651	0.5233
Hematite -THPA-Ben	25	220.63	2.0410	0.0926	0.9572
	35	274.61	6.2027	0.0325	0.9995
	45	342.63	10.6019	0.0193	0.9932
	55	381.60	297.2015	0.7020	0.9998
Hematite -CTA-Ben	25	254.57	2.5984	0.0781	0.9433
	35	311.58	4.7327	0.0444	0.9751
	45	380.56	12.4565	0.0173	0.9775
	55	460.59	173.7772	0.0013	0.9991

Table V.2: Adsorption Freundlich Isotherm Data of MV Adsorption onto the Studied Materials

		Freundlich			
Adsorbent	**T (°C)**	**K_F $(g.mg^{-1})(L.mg^{-1})^{1/n}$**	**1/n**	**n**	**R_F^2**
Ben	25	0.002	0.6985	1.4316	0.9891
	35	0.006	0.6078	1.6453	0.9419
	45	0.008	0.5886	1.8228	0.410
	55	0.106	0.5588	1.7895	0.9235
Na-Ben	25	0.007	0.6458	1.5485	0.9934
	35	0.100	0.5089	1.9650	0.9963
	45	0.014	0.4185	2.3895	0.9961
	55	0.020	0.2846	3.5137	0.9721
THPA-Ben	25	0.022	0.6446	1.5514	0.9930
	35	0.038	0.5348	1.8699	0.8337
	45	0.047	0.5311	1.8829	0.8085
	55	0.066	0.5196	1.9246	0.7696
CTA-Ben	25	0.026	0.4595	2.1762	0.9797
	35	0.039	0.4335	2.3068	0.9719
	45	0.039	0.3962	2.5240	0.9182
	55	0.063	0.2434	4.1085	0.9973
Hematite-Ben	25	0.093	0.6862	1.4573	0.9966
	35	0.014	0.5797	1.7253	0.9657
	45	0.020	0.6650	1.5392	0.9503
	55	0.031	0.4369	2.2822	0.8454
Hematite -THPA-Ben	25	0.038	0.3952	2.5304	0.9951
	35	0.052	0.3821	2.6171	0.9000
	45	0.067	0.3786	2.6413	0.7359
	55	0.008	0.1759	5.6851	0.7627
Hematite -CTA-Ben	25	0.037	0.1348	7.4184	0.8812
	35	0.040	0.0956	10.3627	0.8642
	45	0.043	0.0747	13.3869	0.8542
	55	0.055	0.069	16.6660	0.8983

V.2.2. Phenol Adsorption Isotherms

The study involved thermodynamic isotherms to assess the ability of the bentonite-based adsorbents to adsorb phenol from aqueous solutions without adjusting the pH, with initial phenol concentrations ranging from 5 to 25 mg L-1 across different temperature settings: 25, 35, 45, and 55°C. The isotherms are illustrated in Figures V.3 and V.4, with the results being modeled according to the Langmuir and Freundlich models, and the extracted data is systematically arranged in Table V.3 and Table V.4.

The data indicates that the adsorption of phenol is more accurately represented by the Langmuir isotherm compared to the Freundlich isotherm.

The results show that the correlation coefficients for the Freundlich model (R_F^2) are generally higher for the Langmuir model (R_L^2) across various adsorbents including Ben, Na-Ben and Hematite-Ben, this suggests that phenol adsorption on Ben, Na-Ben and Hematite-Ben aligns more closely with the Freundlich isotherm. however, close values of R_F^2 and R_L^2 are noted for the other adsorbents: THPA-Ben, CTA-Ben, Hematite-THPA-Ben and Hematite-CTA-Ben exhibit a good fit for Langmuir isotherms. These findings corroborate the studies conducted by Y. Xu et al (2018) [7] and H. Alidra et al (2023) [8].

Close values comparing The K_L values, which range from 0 to 1, indicate that phenol adsorption is favorable on all studied adsorbents.

According to the Langmuir isotherm model, the maximum adsorption capacity for phenol increases with temperature. The notably high phenol adsorption capacity of the modified bentonite suggests that Hematite-THPA-Ben is a viable material for environmental remediation.

The adsorption capacity ranks as follows:

Ben< Na-Ben<Hematite-Ben< CTA-Ben < THPA-Ben < Hematite-CTA-Ben < Hematite-THPA-Ben.

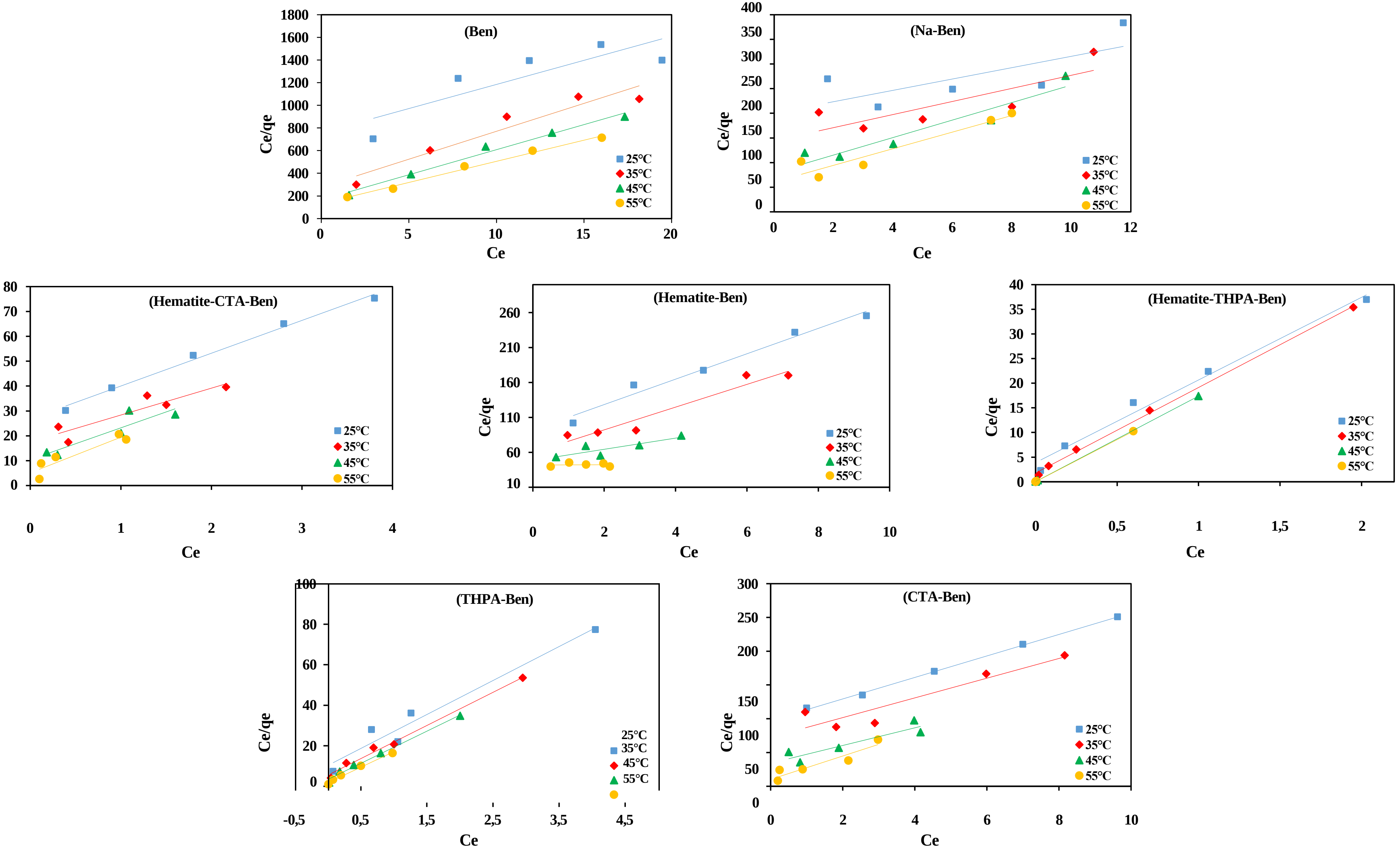
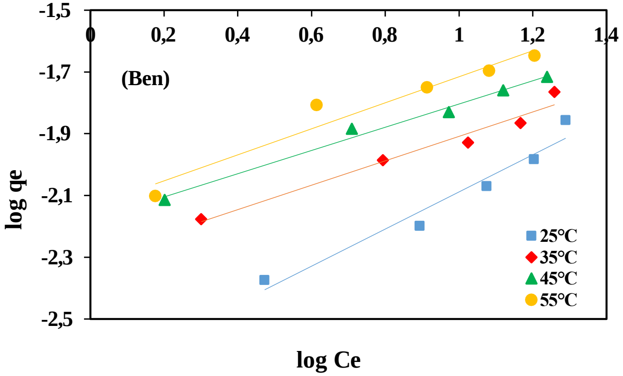
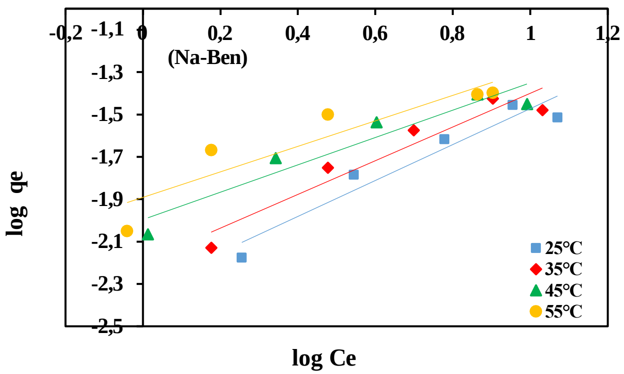
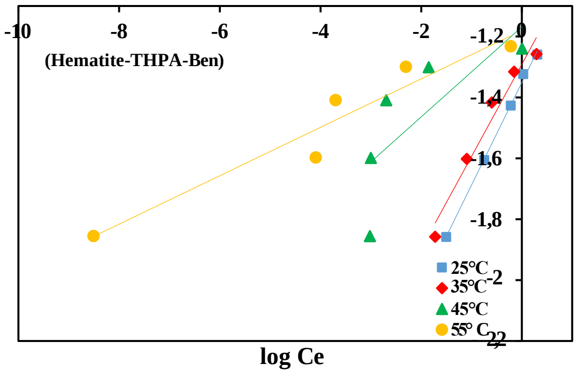

(Ben)
Ce/qe
Ce
0
200
400
600
800
1000
1200
1400
1600
1800
0
5
10
15
20
25°C
35°C
45°C
55°C
(Na-Ben)
Ce/qe
Ce
0
50
100
150
200
250
300
350
400
0
2
4
6
8
10
12
25°C
35°C
45°C
55°C
(Hematite-CTA-Ben)
Ce/qe
Ce
0
10
20
30
40
50
60
70
80
0
1
2
3
4
25°C
35°C
45°C
55°C
(Hematite-Ben)
Ce/qe
Ce
10
60
110
160
210
260
0
2
4
6
8
10
25°C
35°C
45°C
55°C
(Hematite-THPA-Ben)
Ce/qe
Ce
0
5
10
15
20
25
30
35
40
0
0,5
1
1,5
2
25°C
35°C
45°C
55°C
(THPA-Ben)
Ce/qe
Ce
0
20
40
60
80
100
-0,5
0,5
1,5
2,5
3,5
4,5
25°C
35°C
45°C
55°C
(CTA-Ben)
Ce/qe
Ce
0
50
100
150
200
250
300
0
2
4
6
8
10
25°C
35°C
45°C
55°C

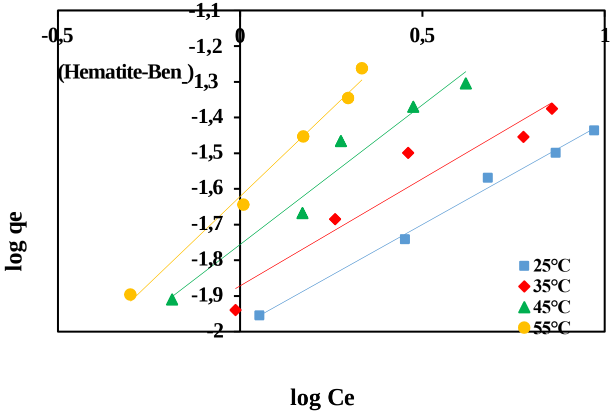
Figure V.3: Langmuir Isotherms of phenol adsorption onto purified and modified bentonites, (conditions: m= 0.4 g, pH= 5.7)

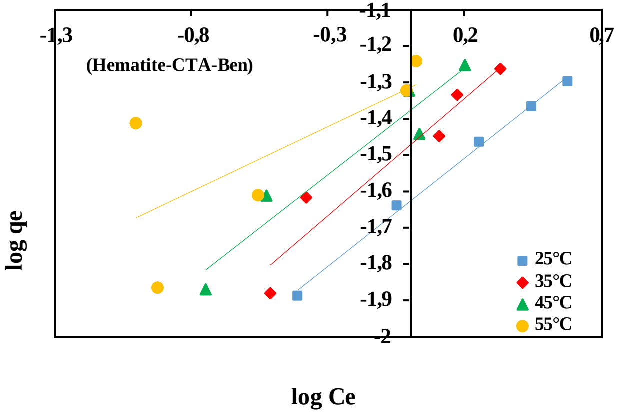
Ce/qe

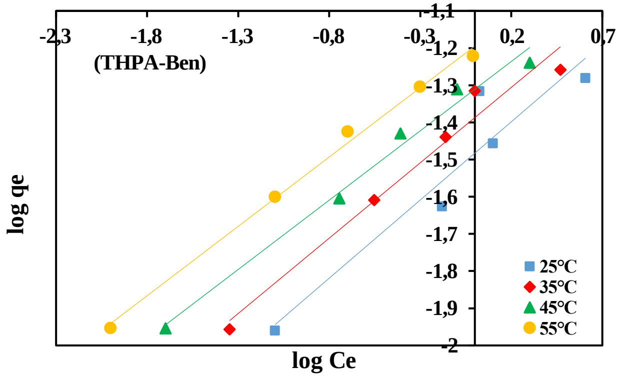

(Ben)
log qe
log Ce
0
0,2
0,4
0,6
0,8
1
1,2
1,4
-1,5
-1,7
-1,9
-2,1
-2,3
-2,5
■ 25°C
◆ 35°C
▲ 45°C
● 55°C


(Na-Ben)
log qe
log Ce
-0,2
0
0,2
0,4
0,6
0,8
1
1,2
-1,1
-1,3
-1,5
-1,7
-1,9
-2,1
-2,3
-2,5
■ 25°C
◆ 35°C
▲ 45°C
● 55°C


(Hematite-THPA-Ben)
log Ce
-10
-8
-6
-4
-2
0
-1,2
-1,4
-1,6
-1,8
-2
-2,2
■ 25°C
◆ 35°C
▲ 45°C
● 55° C


(Hematite-Ben)
log qe
log Ce
-0,5
0
0,5
1
-1,1
-1,2
-1,3
-1,4
-1,5
-1,6
-1,7
-1,8
-1,9
-2
■ 25°C
◆ 35°C
▲ 45°C
● 55°C


(Hematite-CTA-Ben)
log qe
log Ce
-1,3
-0,8
-0,3
0,2
0,7
-1,1
-1,2
-1,3
-1,4
-1,5
-1,6
-1,7
-1,8
-1,9
-2
■ 25°C
◆ 35°C
▲ 45°C
● 55°C


(THPA-Ben)
log qe
log Ce
-2,3
-1,8
-1,3
-0,8
-0,3
0,2
0,7
-1,1
-1,2
-1,3
-1,4
-1,5
-1,6
-1,7
-1,8
-1,9
-2
■ 25°C
◆ 35°C
▲ 45°C
● 55°C

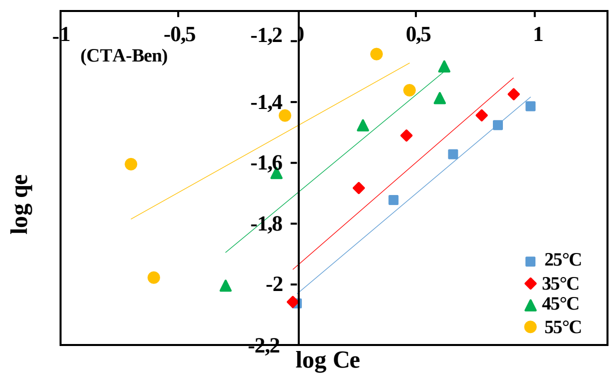

(CTA-Ben)
log qe
log Ce
-1
-0,5
0
0,5
1
-1,2
-1,4
-1,6
-1,8
-2
-2,2
■ 25°C
◆ 35°C
▲ 45°C
● 55°C

Figure V.4: Freundlich Isotherms of Phenol Adsorption onto Purified and Modified Bentonites,

log qe

Table V.3: Adsorption Freundlich Isotherm Data of Phenol Adsorption onto the Studied Materials

Langmuir					
Adsorbent	**T (°C)**	**Q_{max} (mg. g^{-1})**	**b (L.mg^{-1})**	**K_L (L.mg^{-1})**	**R_L^2**
Ben	25	59.60	0.0221	0.9004	0.7254
	35	61.12	0.0589	0.7725	0.9208
	45	62.39	0.0959	0.6759	0.9843
	55	65.01	0.1161	0.6327	0.9417
Na-Ben	25	67.82	0.0574	0.7770	0.5157
	35	75.33	0.0920	0.6849	0.6656
	45	79.43	0.2225	0.4734	0.9048
	55	80.33	0.2776	0.4187	0.9091
THPA-Ben	25	89.06	1.6301	0.1093	0.9963
	35	93.15	2.9794	0.0629	0.9912
	45	95.95	4.7197	0.0406	0.9911
	55	120.11	8.9137	0.0219	0.9951
CTA-Ben	25	63.22	0.2003	0.5282	0.9987
	35	69.45	0.2014	0.5269	0.8703
	45	86.32	0.3814	0.3703	0.8380
	55	111.11	8.9137	0.0219	0.8746
Hematite-Ben	25	69.55	0.1963	0.4781	0.9758
	35	77.62	0.2729	0.3973	0.9343
	45	80.25	0.1655	0.5207	0.7566
	55	104.48	0.0053	0.9712	0.0037
Hematite -THPA-Ben	25	125.59	0.4307	0.2942	0.9857
	35	162.58	9.7265	0.0182	0.9986
	45	190.57	544.2354	3.2977	1.0000
	55	210.58	38156.2881	4.70518	1.0000
Hematite -CTA-Ben	25	96.01	0.4919	0.2674	0.9916
	35	110.00	0.6167	0.2255	0.8370
	45	144.78	1.2277	0.1276	0.8266
	55	170	2.8077	0.0601	0.8588

Table V.4: Adsorption Freundlich Isotherm Data of Phenol Adsorption onto the Studied Materials

		Freundlich			
Adsorbent	**T (°C)**	**K_F $(g.mg^{-1})(L.mg^{-1})^{1/n}$**	**1/n**	**n**	**R_F^2**
Ben	25	0.020	0.6011	1.6636	0.9528
	35	0.049	0.3953	2.5297	0.9665
	45	0.066	0.3761	2.6589	0.9870
	55	0.073	0.4213	2.3736	0.9935
Na-Ben	25	0.088	0.8488	1.1781	0.9223
	35	0.096	0.7960	1.2563	0.9151
	45	1.015	0.6458	1.5485	0.9104
	55	1.588	0.6021	1.6608	0.9438
THPA-Ben	25	4.298	0.4207	2.3770	0.9956
	35	8.109	0.4055	2.4661	0.9692
	45	9.809	0.3731	2.6802	0.9962
	55	16.39	0.3731	2.6802	0.9970
CTA-Ben	25	0.010	0.6585	1.5186	0.8896
	35	0.012	0.6785	1.4738	0.8820
	45	0.020	0.6467	1.5463	0.8896
	55	0.003	0.0438	2.2844	0.6702
Hematite-Ben	25	0.010	0.5712	1.7507	0.9939
	35	0.013	0.6000	1.6666	0.9195
	45	0.017	0.7823	1.2782	0.9638
	55	0.024	0.9772	1.0233	0.9900
Hematite -THPA-Ben	25	0.044	0.3371	2.9665	0.9978
	35	0.063	0.3028	3.3025	0.9613
	45	0.068	0.1478	6.7659	0.5671
	55	0.066	0.0795	12.5786	0.9297
Hematite -CTA-Ben	25	0.024	0.5956	1.6790	0.9961
	35	0.034	0.6459	1.5482	0.9227
	45	0.418	0.5866	1.7047	0.9236
	55	0.049	0.3572	2.7941	0.4820

V.3. Modelling Adsorption Kinetics

To identify the dynamic mechanism and the kinetic of adsorption of the studied organic compounds selected as water contaminants and pollutants MV and phenol onto the purified and modified bentonites using as adsorbents in this study, we applied the two kinetic models pseudo-first-order and pseudo-second-order [9].

The kinetic of adsorption can be evaluated through the kinetic parameters and constants. The use the specified from the first-order rate expression given by Lagergren expressed as Equation V.5 to sort out the kinetic constant K_1 that is obtained from the slopes of the linear plots of ln (q_e - q_t) versus t [10,11]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{ ....V. 5}$$

k_1: the kinetic equilibrium rate constant of the pseudo-first order in min^{-1},

q_e: the amount of the adsorbate molecules adsorbed per unit mass of adsorbent at equilibrium in mg. g^{-1};

q_t: the mass of adsorbed solute per unit mass of adsorbent at time t in mg. g^{-1}.

The pseudo-second-order model is depended on the supposition of chemisorption of the adsorbate on the adsorbents. This model can be expressed as Equation V.6 [11]:

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{t}{qe} \quad \text{... .... V. 6}$$

Where k_2 in (g. mg^{-1}.min^{-1}) is the equilibrium rate constant for the pseudo second-order adsorption and qe can be obtained from the plot of t/qt against t.

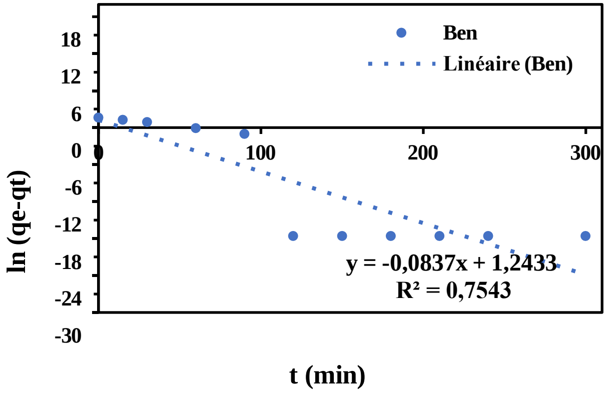
V.3.1. MV Adsorption Kinetics

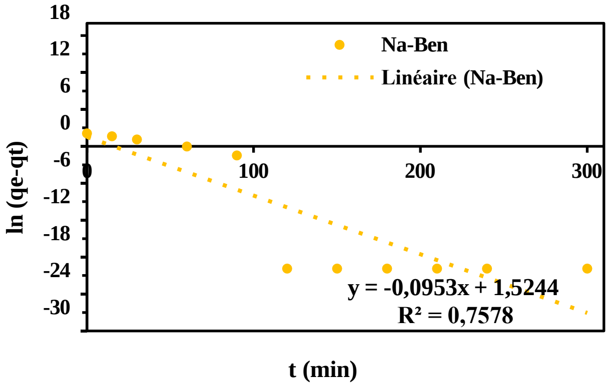
The modeling the adsorption process of MV onto all of the studied adsorbents: Ben, Na-Ben, Hematite-Ben, TCA-Ben, THPA-Ben, Hematite-TCA-Ben and Hematite-THPA-Ben was realized by applying the two kinetics models.

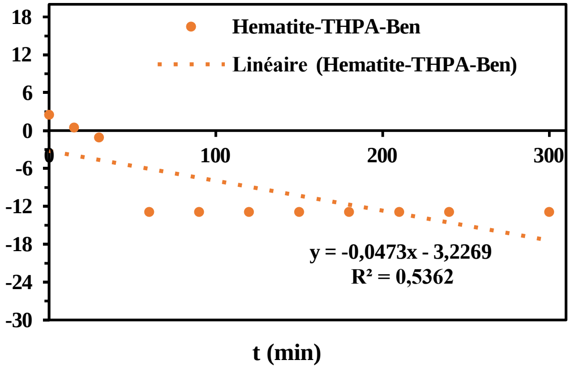
The fitted results are resumed in Figures V.5 and V.6 for both pseudo-first order and pseudo- second-order respectively the data are resumed in Table V.5. The comparison between the finding results, put the attention on the correlation coefficients for the first-order and second- order kinetic models, where we remarqued that the second-order model is the best fitted model for experimental kinetic data, this because of the value of the calculated qe that approve very well with the experimental data and R^2 for all adsorbents is ranged between 0.9891 and 1.000. These results also indicated the applicability of this kinetic equation and the second-order nature of the adsorption process of MV on clays.

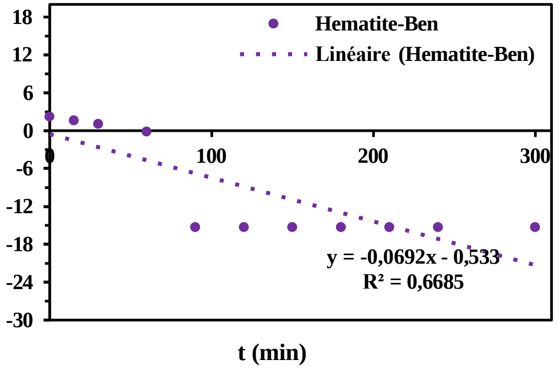
The two kinetic models pseudo-first order and pseudo-second-order were applied on the adsorption process of MV onto the seven adsorbents: Ben, Na-Ben, Hematite-Ben, TCA-Ben, THPA-Ben, Hematite-TCA-Ben and Hematite-THPA- Ben. These results also indicated the applicability of this kinetic equation and the second-order nature of the adsorption process of phenol on clays.

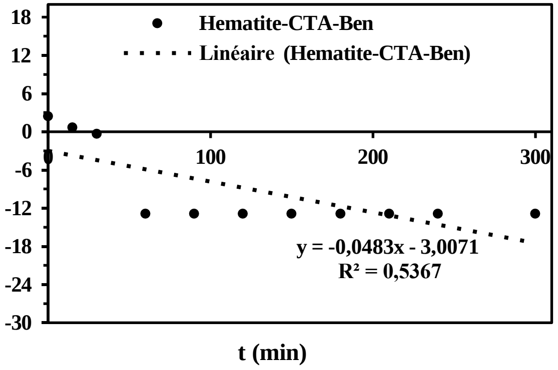
From the obtained tabulated parameters for MV adsorption onto the analyzed bentonites after fitting the pseudo-first and pseudo-second orders kinetic models, we understand that The Hematite-CTA-Ben, presents the highest correlation coefficients which indicated that the pseudo-second order ($R^2 > 1.000$) models described the MV adsorption kinetic well as proper with literature [3].

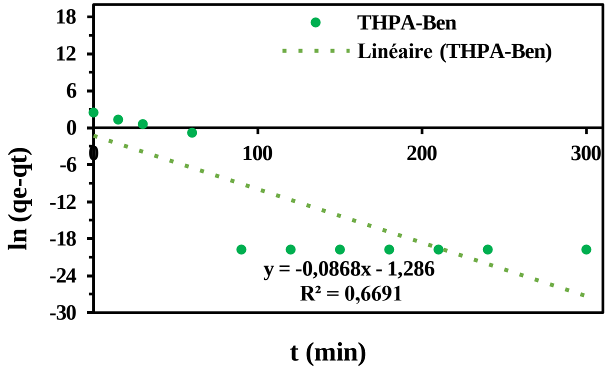

Ben
Linéaire (Ben)
y = -0,0837x + 1,2433
R² = 0,7543
ln (qe-qt)
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300


Na-Ben
Linéaire (Na-Ben)
y = -0,0953x + 1,5244
R² = 0,7578
ln (qe-qt)
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300


Hematite-THPA-Ben
Linéaire (Hematite-THPA-Ben)
y = -0,0473x - 3,2269
R² = 0,5362
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300


Hematite-Ben
Linéaire (Hematite-Ben)
y = -0,0692x - 0,533
R² = 0,6685
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300


Hematite-CTA-Ben
Linéaire (Hematite-CTA-Ben)
y = -0,0483x - 3,0071
R² = 0,5367
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300


THPA-Ben
Linéaire (THPA-Ben)
y = -0,0868x - 1,286
R² = 0,6691
ln (qe-qt)
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300

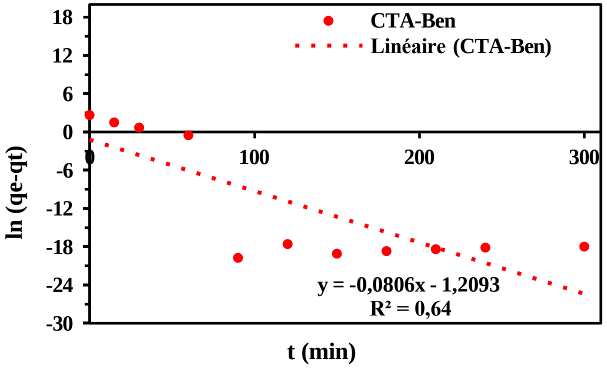
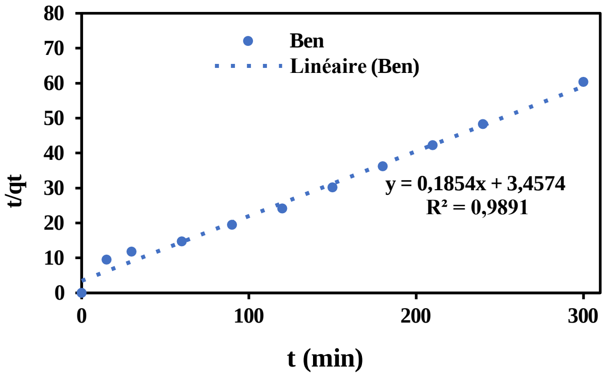
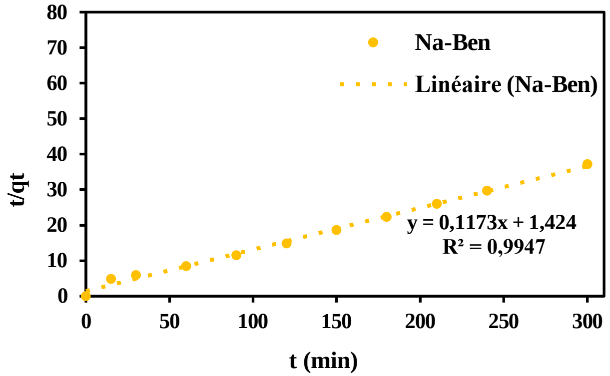
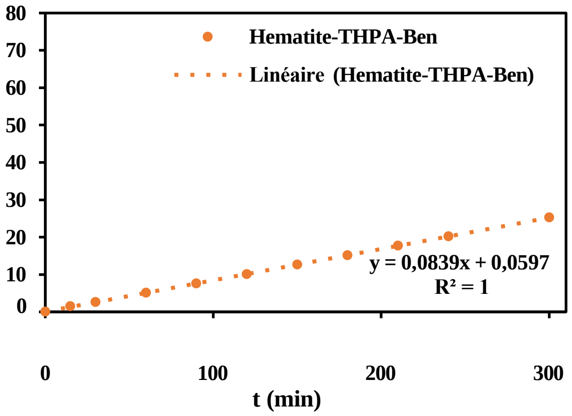
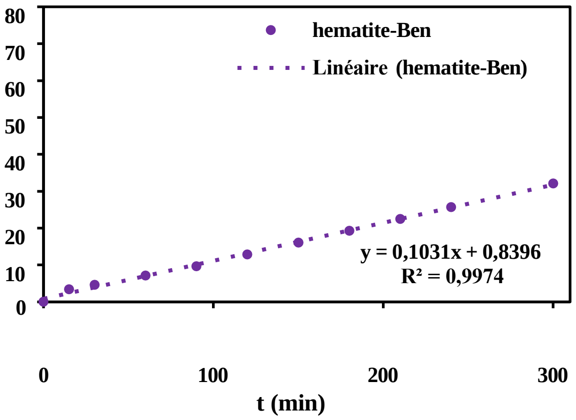

CTA-Ben
Linéaire (CTA-Ben)
y = -0,0806x - 1,2093
R² = 0,64
ln (qe-qt)
t (min)
18
12
6
0
-6
-12
-18
-24
-30
0
100
200
300

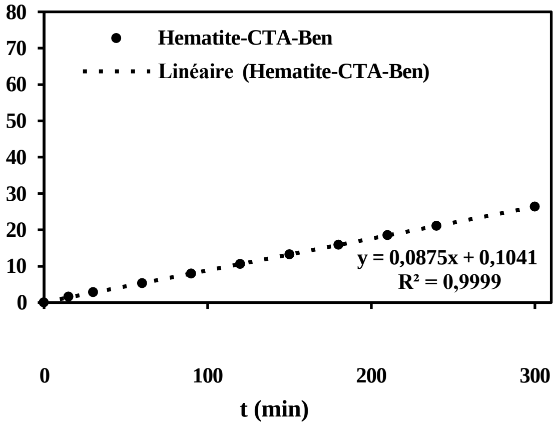
Figure V.5: Kinetic Pseudo -first-order model of the MV removal onto purified and modified bentonites

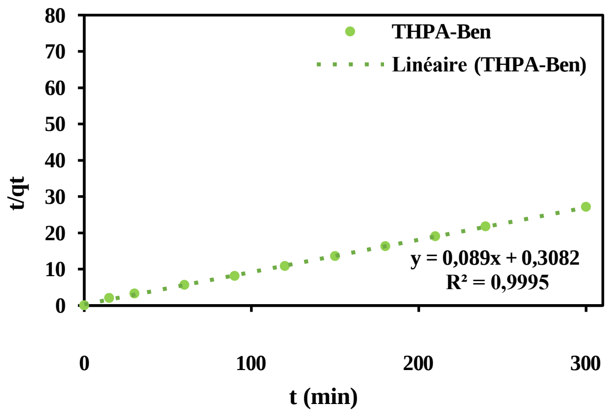

Ben
Linéaire (Ben)
y = 0,1854x + 3,4574
R² = 0,9891
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


Na-Ben
Linéaire (Na-Ben)
y = 0,1173x + 1,424
R² = 0,9947
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
50
100
150
200
250
300


Hematite-THPA-Ben
Linéaire (Hematite-THPA-Ben)
y = 0,0839x + 0,0597
R² = 1
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


hematite-Ben
Linéaire (hematite-Ben)
y = 0,1031x + 0,8396
R² = 0,9974
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


Hematite-CTA-Ben
Linéaire (Hematite-CTA-Ben)
y = 0,0875x + 0,1041
R² = 0,9999
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


THPA-Ben
Linéaire (THPA-Ben)
y = 0,089x + 0,3082
R² = 0,9995
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300

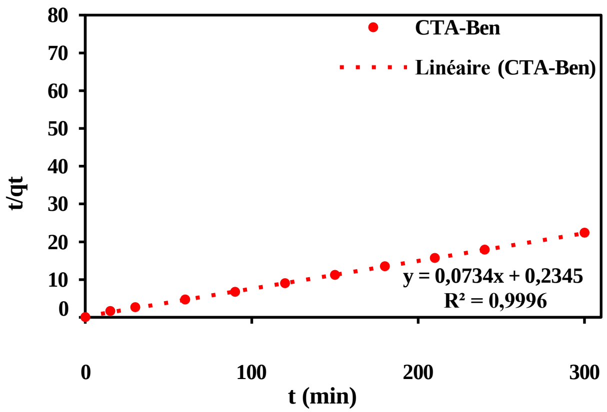

CTA-Ben
Linéaire (CTA-Ben)
y = 0,0734x + 0,2345
R² = 0,9996
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300

Figure V.6: Kinetic Pseudo-second-order model of the MV removal onto purified and modified bentonite

Table V.5: Kinetics Models Constants and Parameters of MV Asorption

			Pseudo-first-order		*Pseudo-second-order*	
Adsorbents	**C_0 (mg. L^{-1})**	**$q_{e\ exp}$ (mg. g^{-1})**	**K_1 (min^{-1})**	**R_1^2**	**K_2 (g. $mg^{-1}min^{-1}$)**	**R_2^2**
Ben	5.03	4.975	0.0837	0.7543	5.3937	0.9891
Na-Ben	4.63	8.075	0.0953	0.7578	8.5251	0,9947
THPA-Ben	4.802	1.055	0.0680	0.6691	11.2359	0,9995
CTA-Ben	5.627	1.417	0.0806	0.6400	13.6239	0.9996
Hematite-Ben	4.80	9.355	0.0692	0.6685	9.6993	0.9974
Hematite-HPTA-Ben	4.802	11.880	0.0473	0.5362	11.9189	1.0000
Hematite-CTA-Ben	4.546	13.765	0.0830	0.5367	11.4258	0.9999

V.3.2 Phenol Adsorption Kinetics

The two kinetic models pseudo-first order and pseudo-second-order were applied on the adsorption process of phenol onto the seven adsorbents: Ben, Na-Ben, Hematite-Ben, TCA- Ben, THPA-Ben, Hematite-TCA-Ben and Hematite-THPA-Ben.

The data are presented in Figures V.7 and V.8 and the kinetic constants and parameters are resumed in Table V.6.

From the compared results of the correlation coefficients for the first-order kinetic and second- order kinetic models its clearly seen that the second order model is the best fitted model for experimental kinetic data, and this for the reason that the calculated values qe approve very well with the experimental data and the R^2 for all adsorbents is ranged between 0.9737 and 0.9999.

These results also indicated the applicability of this kinetic equation and the second-order nature of the adsorption process of phenol on clays.

From the model parameters obtained for phenol adsorption onto the analyzed bentonites after fitting the pseudo-first and pseudo-second orders kinetic models.

The Hematite-TCA-Ben, presents the highest correlation coefficients which indicated that the pseudo-second order (R^2 > 0.9999) models described the Phenol adsorption kinetic well as proper with literature [3].

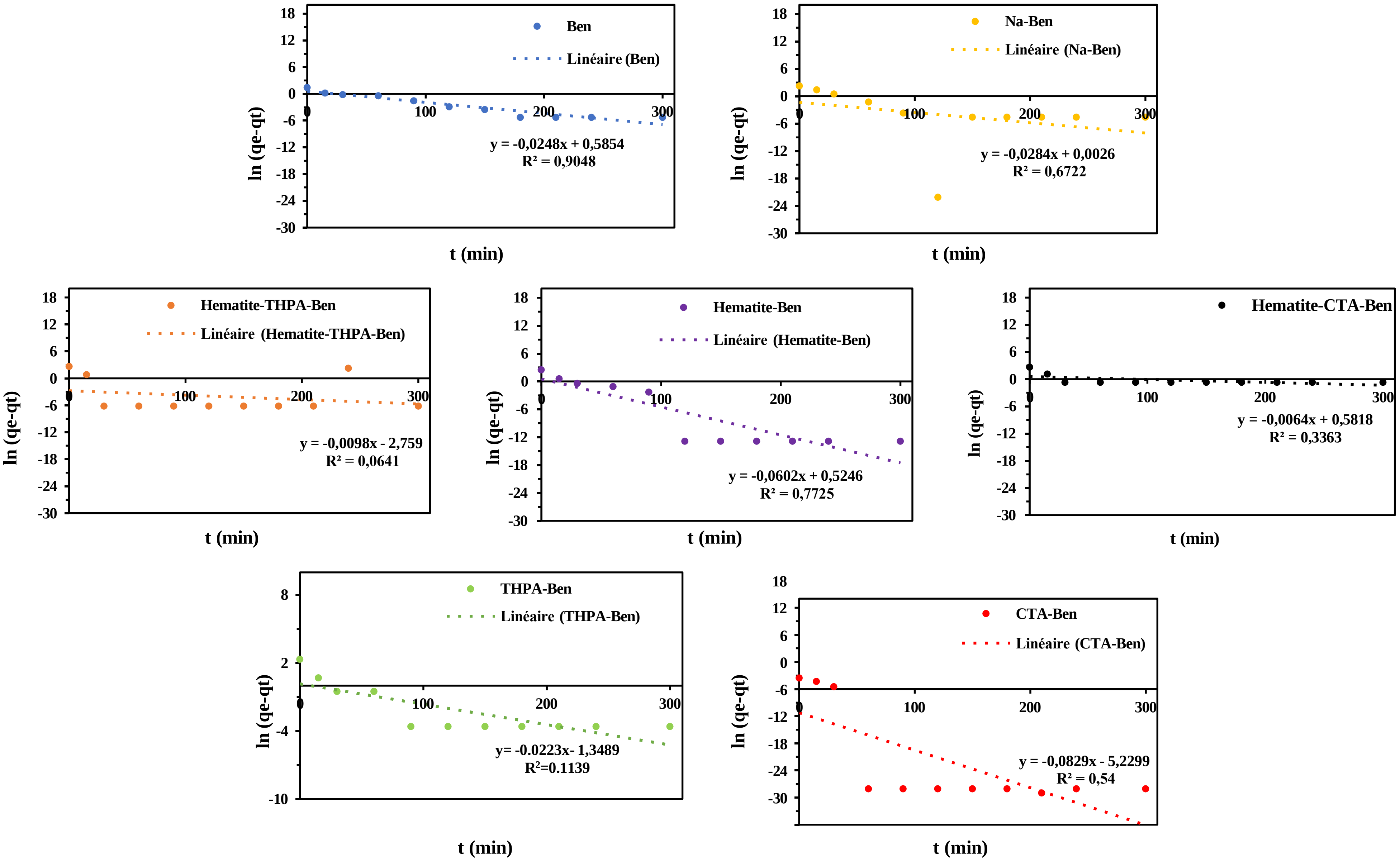
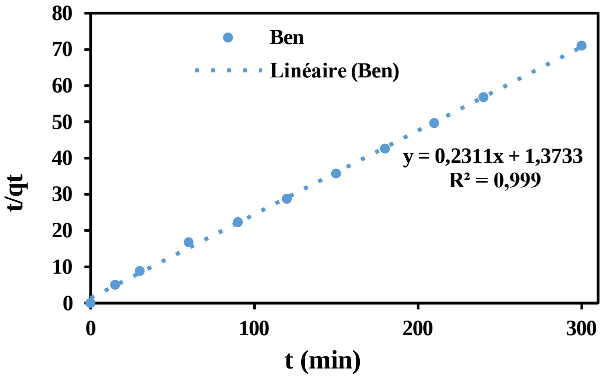
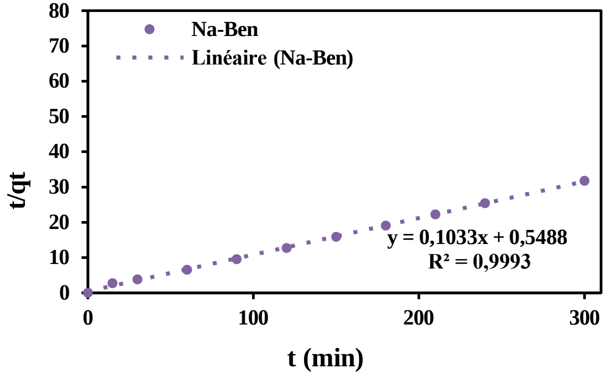
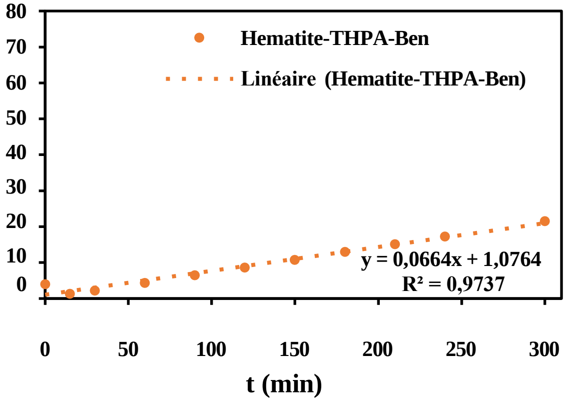
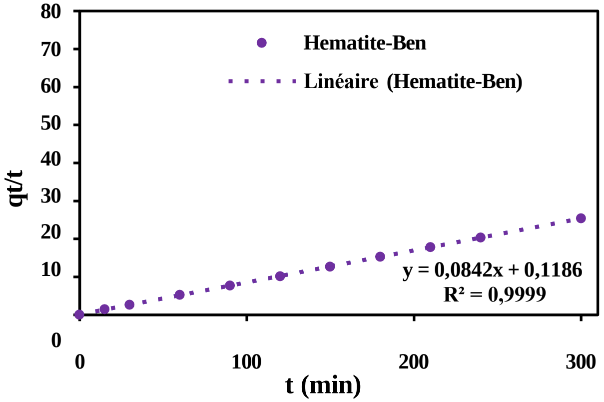


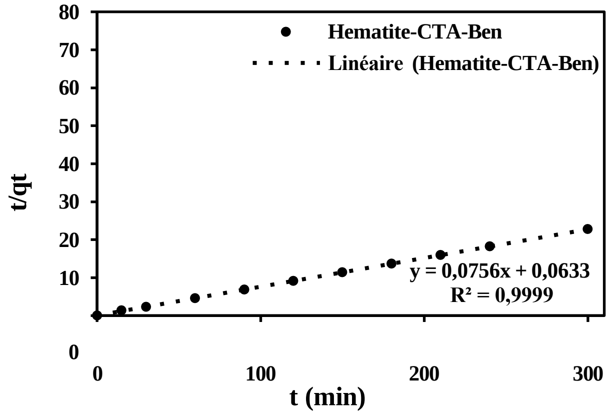
Figure V.7: Kinetic Pseudo-First-Order Model of Phenol Adsorption onto Modified Bentonites

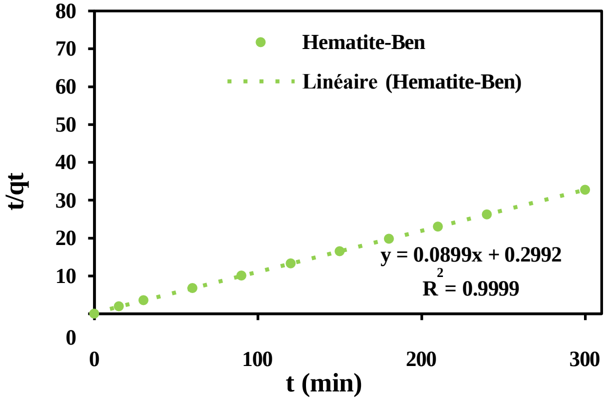

Ben
Linéaire (Ben)
y = 0,2311x + 1,3733
R² = 0,999
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


Na-Ben
Linéaire (Na-Ben)
y = 0,1033x + 0,5488
R² = 0,9993
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


Hematite-THPA-Ben
Linéaire (Hematite-THPA-Ben)
y = 0,0664x + 1,0764
R² = 0,9737
t (min)
0
10
20
30
40
50
60
70
80
0
50
100
150
200
250
300


Hematite-Ben
Linéaire (Hematite-Ben)
y = 0,0842x + 0,1186
R² = 0,9999
qt/t
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


Hematite-CTA-Ben
Linéaire (Hematite-CTA-Ben)
y = 0,0756x + 0,0633
R² = 0,9999
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300


Hematite-Ben
Linéaire (Hematite-Ben)
y = 0.0899x + 0.2992
R² = 0.9999
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
100
200
300

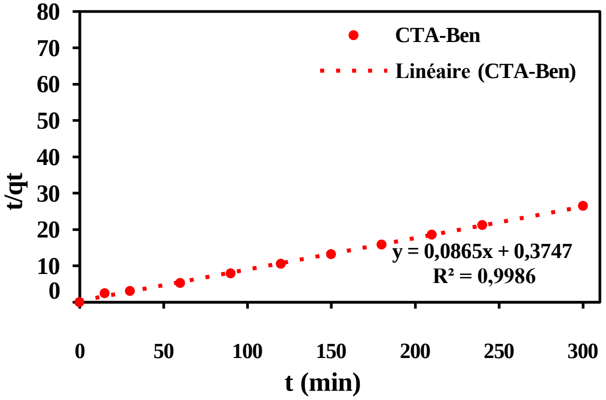

CTA-Ben
Linéaire (CTA-Ben)
y = 0,0865x + 0,3747
R² = 0,9986
t/qt
t (min)
0
10
20
30
40
50
60
70
80
0
50
100
150
200
250
300

Figure V.8: Kinetic pseudo-second-order model for phenol adsorption purified and modified bentonites

t/qt

Table V.6: Kinetics Models Data of the Phenol Adsorption

			Pseudo-first-order		*Pseudo-second-order*	
Adsorbents	**C_0 (mg. L^{-1})**	**$q_{e\ exp}$ (mg. g^{-1})**	**K_1 (min^{-1})**	**R_1^2**	**K_2 (g. $mg^{-1}min^{-1}$)**	**R_2^2**
Ben	4.66	0.7	0.0248	0.9048	0.2311	0.999
Na-Ben	5.57	0.81	0.0284	0.6722	0.1033	0.9993
THPA-Ben	4.46	1.19	0.0223	0.1139	0.0899	0.9999
CTA-Ben	5.57	1.03	0.0829	0.54	0.0865	0.9986
Hematite-Ben	5.57	10.80	0.060	0.7725	0.0842	0.9999
Hematite-HPTA-Ben	4.46	13.97	0.0098	0.641	0.0664	0.9737
Hematite-CTA-Ben	5.57	11.92	0.0064	0.3363	0.0756	0.9999

V.4. Conclusion

In this chapter, we present the isotherm and kinetics models of adsorption for both of methyl violet (MV) and phenol onto the studied adsorbents Ben, Na-Ben, Hematite-Ben, TCA-Ben, THPA-Ben, Hematite-TCA-Ben and Hematite-THPA-Ben.

At the end of this study, we conclude that:

- The maximum adsorption capacity of both MV and phenol adsorption onto the selected adsorbents increases with the increase in temperature;
- A remarqueble high MV and phenol adsorption capacity for the modified bentonites, according to Langmuir isotherm model indicates that respectively Hematite-CTA-Ben and Hematite-THPA-Ben are a promising adsorption material in the environmental remediation;
- The MV dye adsorption capacity increases in the order:

Ben<Na-Ben<Hematite-Ben<THPA-Ben< CTA-Ben < Hematite-THPA-Ben <Hematite-CTA-Ben.

- The Phenol adsorption capacity increases in the order:

Ben**<**Na-Ben<Hematite-Ben< CTA-Ben<THPA-Ben < Hematite-CTA-Ben < Hematite-THPA-Ben;

- The Hematite-CTA-Ben, presents the highest correlation coefficients which indicated for the pseudo-second order ($R^2 > 1.000$) models that well described MV adsorption process;
- The Hematite-HPTA-Ben, presents the highest correlation coefficients which indicated for the pseudo-second order ($R^2 > 0.9999$) models that well described Phenol adsorption process.

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General Conclusion

General Conclusion

This doctoral research, categorized under environmental engineering, is dedicated to the decontamination of water that that are harmful to humans, the environment, and ecosystems. Our research is directed towards on the development of novel materials intended for the effective elimination of two toxic organic pollutants: phenol and methyl violet “MV2B” dye.

The main focus of this study is the synthetize of low-cost, environmentally sustainable materials through the application of simple and safe techniques using green materials and products. In this work, composite materials based on Algerian Bentonite of M'Zila’s deposit were synthesized and subsequently characterized and analyzed for their use as adsorbents to eliminate organic pollutants from aqueous solutions. The methodology for their preparation described in chapter III of this manuscript is applied only by us.

The synthesis process involves a series of operations designed to maximize the adsorption efficiency for the extraction of hazardous substances from polluted aqueous environments. This approach is based on sequential four-step process: the purification of raw bentonite, Na^+ cation exchange, intercalation of CTAC and THPAB into the sodic-exchanged bentonite and then the most essential step consisted on pillaring the Hematite α-Fe_2O_3 nanoparticles. This research study involved the successful preparation of the composites (Inorgano-Organo-Bentonite) Hematite-CTA-Bentonite and Hematite-THPA-Bentonite, the central to this study, and that was carried out after the utilization of intermediate materials: the Organo-Bentonite’s witch are THPA-Bentonite, CTA-Bentonite, without missing the Na-Bentonite.

The characterization of the obtained materials, was performed by the application of several methods destined for the characterization of physicochemical properties the prepared materials. The X-ray diffraction (XRD) and Energy-dispersive spectroscopy (EDS) analyses, Scanning electron microscopy (SEM) and Brunauer Emmett Teller (BET) results indicate the favorable properties of the synthesized materials. The findings the mineralogical and structural investigations of this part of our work allowed us to confirm:

- The intercalation of the surfactants molecules into the surface of the Algerian bentonite and this was proven by elementary analysis that confirm presence of C and N in the composition of: the organo-modified bentonite CTA-Bentonite and THPA-Bentonite;
- The incorporation of inorgano elements related to the presence of Hematite nanoparticles in the structure of the composite’s materials;

- The efficient modification of the Algerian Bentonite, and the incorporation of the modifier's molecules (CTA^+, $THPA^+$, and α-Fe_2O_3) within the interlayer space of Algerian bentonite, was confirmed with the developed mesopore in the morphology of the clay ;
- The Thermogravimetric Analysis TGA, demonstrates a high stability of the modified bentonite.

The studied materials were tested, and the capacity of removal of phenol and MV from aqueous media was investigated comparatively between the six modified-bentonite based adsorbent and the natural Algerian bentonite. from the finding we conclude that:

- As basic materials, both natural and sodic bentonites have the capacity to remove the two organic compounds (phenol and MV);
- The organo modification of improve the adsorption properties of the new intermediate material THPA-Bentonite with a good affinity against phenol. Where the material eliminated 98% of phenol from aqueous solution;
- The environmentally sustainable composite "Hematite-CTA-Ben" demonstrates its strong affinity for the dangerous methyl violet (MV) dye;
- The new composite: Hematite-CTA-Ben have a big attraction to Phenol, and that favorize an important adsorption of this organic from aqueous media;
- The novel composites (Hematite-CTA-Bentonite and Hematite-THPA-Bentonite), with their new structures have are an environmental solutions to eliminate totally (100%) the two organics from aqueous media;
- Some parameters, such as: adsorbent amount, initial concentrations, pH of the compound's solutions and temperature; have a significant influence on the adsorption process of the tow organic water contaminants. Increasing the adsorbent amount increase the pollutant removal contrarily increasing the initial concentrations decrease the adsorption capacity of the two organic compounds. however, increasing in temperature increases the adsorption of phenol and MV onto the studied adsorbents. A notable effect of pH solutions changes on the adoption process where the most influenceable is the extreme (acidic and basic) pH medium.

From the precedent finding we can resume that bentonites-based adsorbents with their different structures have a significant adsorption capacity to eliminate the two adsorbates: MV and Phenol, this permits us to conclude that the different modifications that bentonite undergone improve its adoption adequacy of the organic compounds.

Regarding the factors that influence the adsorption of the two organic compounds. These factors encompass the type and quantity of adsorbent materials, including purified Bentonite, Hematite-Bentonite, Organo-Bentonites, and Hematite-Organo-Bentonites.

The research also explored the roles of exchangeable cations (Na^+, $THPA^+$, CTA^+), the pH of the adsorption medium, and temperature. Additionally, we were able to ascertain the likely adsorption processes for both phenol and methyl violet (MV) onto Modified-Bentonite supports. Importantly, our results indicate that organic compounds can be effectively adsorbed onto purified natural Bentonite without further modifications, and the addition of organic molecules enhances the adsorption of the target adsorbates onto the synthesized materials. This leads us to conclude that the various clear-cut, cost-effective and safety modifications techniques applied on the Algerian bentonite enhance its effectiveness in adsorbing organic matters from aqueous media.

At the end of this study of our investigation, we have concluded that the techniques used to alter M'Zila bentonite are distinguished by their simplicity, safety and economic viability, with the selected materials being both inexpensive and less detrimental to human health and the environment.

Perspectives

Perspectives

This part outlines the broader implications of the findings and identifies potential avenues for further investigation, notably:

- Thermodynamic study of both Phenol and MV Dye adsorption, to better understand the process;
- Adsorbent’s regeneration, to control the pollution and avoid transfer of pollutants from aqueous phase to solid phase;
- Testing the prepared materials in heavy metals adsorption onto the synthetized materials, to give value to the new materials;
- Feasibility study of the project while adopting the results of this work, to refine the market of the industrial sector with new economical effectives solutions.