



Mohamed Khider University of Biskra
Faculty of Exact Sciences and Natural and Life Sciences
Department of Material Sciences

MASTER THESIS

Field of Material Sciences
Sector of Chemistry
Specialty of Materials Chemistry

Ref:

Submitted and Defended by:
MEDJOURI Yamina

27/09/2020

Synthesis and reactivity of new porous materials

Board of Examiners:

Mrs. CHADLI Ilham	MCB	University of M ^{ed} Khider-Biskra	President
Mrs. OUKKAF Amira	MCB	University of M ^{ed} Khider-Biskra	Supervisor
Mrs. MADOUI Nadia	MCB	University of M ^{ed} Khider-Biskra	Chair

Academic Year: 2019-2020



Dedication

Every challenging work needs self efforts as well as guidance of elders especially those who were very close to our hearts

My humble effort i dedicate to my and loving

Father & Mother,

Whose affection, love, encouragement and prays of days and nights make me able to get such a journey and memories ,i love you and may allah protect you for me ;the words could never be enough to express the feeling for you ,

Mom, I would have so much to say to thank you but I know you can feel all the feelings of gratitude and gratitude I have for you, I adore you, you are the best mom in the world.

Dad, I am very proud to be your daughter, it is a huge chance to have you in my life, you have always seen me as a studious student. It is thanks to your advice and words that I had the strength to finish this job.

My Sisters & Brothers,

who i had the laugh and the smile with where they helped me relief my stress and lose my weakness ,

Hala, Anes, Mohammed, Donia

My work sisters and brother,

Thank you for always being by my side and never complined while i could not be with you ,you have been since day one the best co-workers that i can have supporting me and encouraging me my dearest

*Soundess, Zineb, Fatima, Sana, Hadjer, Faisa N
, Asma, Khadija, Halima, Faisa, Nerdjess, Aissa.*

My beloved friends: Youssra, Oumaima , Yasmine.

To class 2020 we did our best it was a taught year but we made it ,see you in the near future.

Yamina



Acknowledgment

I thank Almighty ALLAH who gave me the courage, strength and will to carry out this modest work,

My sincere thanks to my supervisor Mrs . AOUKKAF Amira, for advising, directing and assisting me during the completion of this work,

My thanks go to Mrs .CHADLI Ilham who honor us with her presence as a jury president

My thanks go also to Mrs .MADOUI Nadia who agreed to judge this end of studies thesis .

Without forgetting all the teachers and all the people who contributed to my training and the help they gave me near or far throughout my course.

My huge admirations for the people who have contributed to the realization of this work begin with the persons in charge of the laboratory.

My parents, without all your sacrifices, I won't be here today.

To my friends who I shared this journey with its either happy or sad moments I wish you the luck in the near future.

List of figures

CHAPTER I

Figure I.1. Examples of some colorants with their structures.....	6
Figure I.2. Classification of materials at different scale levels.....	10
Figure I.3. Classification of hybrid materials.....	11
Figure I.4. Selected examples for diverse assembly of building units for hybrid materials	12
Figure I.5. Molecule model of DABCO	14
Figure I.6. Structural formula of oxalic acid	14
Figure I.7. Schematic representation of the Fourier-Transform Infrared Spectroscopy (FT-IR) principles	18
Figure I.8. IR spectroscopy dispositive.....	18
Figure I.9. X-ray diffractometer with Kappa CCD geometry.....	20

CHAPTER II

Figure II.1. Experimental protocol followed for the synthesis.....	30
Figure II.2. Representation of the molecule with the ORTEP program.....	32
Figure II.3. The asymmetric unit of $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$	35
Figure II.4. The elementary cell $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ represented by symmetry operations projected along the axis c.....	36

List of Tables

CHAPTER I

Table I.1. Properties of Methylene blue and its molecule modal	8
Table I.2. Properties of DABCO	14
Table I.3 Properties of anhydrous and dehydrate oxalic acid	15

CHAPTER II

Table II.1. Name and purity of the initialed materials.....	20
Table II.3. Cristalographique data on the cell Fe_2Cl_4 $(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$	29
Table II.2. The experiments carried out at the laboratory level	33

Abbreviation list

nm: nano-meter

mm³: millimeter cube

Å: angstrom

D: dimensions

AD: Alzheimer's disease

MOF: Metal-organic Framework

(d): sub shell

Babco: 1, 2-diazabicyclo (2.2.2) cyclobutane

TEDA: Triethylenediamine

IR: Infrared

FTIR: Fourier Transform Infrared

CCD :(Charge Coupled Device)

IUPAC: The international union of pure and applied chemistry

λ: Lambda (wave length)

μ: Micro

Cif: Crystallographic Information File

Gof: Goodness-of-Fit

MB: Methylene blue

HPM: hybrid porous materials

cm^{-1} : centimeter power⁻¹

Summary

List of figures.....	I
List of Tables.....	II
Abbreviation list.....	III
General introduction.....	01
Bibliographical References.....	03

Chapter I

Hybrid materials study

Introduction.....	05
I. Colorants.....	05
I.1.Generalities.....	05
I.2. Colorants classification	06
II. Water pollution.....	06
II.1. Colorants pollution.....	07
II.1.1. Methylene blue.....	07
II.1.1.1. Utilization.....	08
III. Soft chemistry.....	08
IV. Nanoparticle materials.....	09
V. Hybrid composites materials.....	09
V.1.Composites materials	09
V.2. Hybrid composites.....	09

V.2.1. Classes of hybrid porous material	10
V.3.Organic-inorganic hybrid porous materials.....	11
V.3.1. Metal-Organic Framework (MOFs).....	12
V.3.1.1.Metal-Organic Framework properties	12
VI. Components of organic-inorganic hybrid materials.....	12
VI.1. Transition metal.....	13
VI.2. Amines.....	13
VI.3. Oxalic acid	14
VII. Hybrid porous materials application	15
VIII. Analyzing methods	16
VIII.1.Binocular optical microscope.....	16
VIII.1.1.Observation of samples with a binocular.....	16
VIII.2. Infrared spectroscopy IR.....	16
VIII.2.1. Fourier transform infrared (FTIR).....	17
VIII.2.2.FT-IR Instrumentation.....	17
VIII.3. Single-Crystal X-ray Diffraction.....	19
VIII.3.1 .Principe	19
VIII.3.2.Instruments.....	19
Conclusion	20
Bibliographical References.....	21

Chapter II

Experimental part

Introduction.....	27
I .Departing products.....	27
II .Elaboration.....	29
III. Synthesis.....	29
III .1.Synthesis of $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$	29
III.2.Characterization of $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$	30
III.2.1. X-ray diffraction on the single crystal.....	30
III.2.1.1.Data acquisition.....	30
III.2.1.2.Resolution and refinement of the structure.....	31
III.3. Description of the structure	34
Conclusion.....	35
Bibliographical References.....	36

General Conclusion	38
Abstract	

GENERAL

INTRODUCTION

General introduction

Environmental pollution and its after-effects have become global concerns in recent years. Among all types of pollution, water pollution has been considered as a major threat in recent years; this problem will be even worse in the near future[1].It has caused 1.8 million deaths in 2015, according to a study published in The Lancet. Where every year, unsafe water sickens about 1 billion people [2].

Having access to clean water is a mandatory requirement for the proper development of living beings. So, addressing the removal of contaminants from aquatic systems should be a priority research topic in order to restore ecosystem balance and secure a more sustainable future [3]. In the 90s, Palestinian professor Omar Yaghi developed a fascinating chemical structure known MOF [4], the fascinating structures and striking physical properties of metal–organic frameworks (MOFs) have revealed them as excellent platforms for the removal of harmful species from water [3].

Hybrid porous solids are a new class of porous solids emerged as a new domain of research ca. fifteen years ago and which the MOF classified in. More or less considered at the beginning as a curiosity, it has transformed into a fully qualified field of research with an explosion of papers [5] that's because of the possibility of combining inorganic, organic, and even biological entities and functions in a well-defined host matrix [6].

They result from the reaction between organic and inorganic species in order to build up three-dimensional frameworks whose skeleton contains both organic and inorganic moieties only linked by strong bonds[5],This type of material has always attracted a lot of attention as the presence of pores means that the material possesses an internal surface area of interest for all type of applications [7].These solids can be a huge help in the field of processing pollutants especially liquid pollutants that can be found in factories wastes effluents by adsorption phenomena.

It is in this area of research that our work lies in this master thesis, the aim of which is to prepare new porous materials by means of soft chemistry using organic and inorganic construction entities. Soft chemistry based processes is a chemical pathways at low temperatures and pressures, from molecular, colloidal, or polymeric precursors clearly offer the most favorable paths towards hybrid materials [6].

Our manuscript starts with a general introduction followed with two main parts and ends with a conclusion

- The first part is a bibliographical synthesis which will attempt to make an approach of knowledge on porous materials, their types, focusing the hybrid porous solids its history, how they are effected by while making, their applications also we discuss the different methods of analysis appropriate for the identification of our materials.
- In the second chapter we have exposed the results that we have obtained at the end of numerous synthesis and crystallization tests of our final compound as well as the study of intermolecular and intermolecular hydrogen bonds.

BIBLIOGRAPHICAL REFERENCES

- [1] Samanta, P., Desai, A. V., Let, S., & Ghosh, S. K. (2019). Advanced Porous Materials for Sensing, Capture and Detoxification of Organic Pollutants towards Water Remediation. ACS Sustainable Chemistry & Engineering.
- [2] <https://www.nrdc.org/stories/water-pollution-everything-you-need-know#effects>
- [3] Mon, M., Bruno, R., Ferrando-Soria, J., Armentano, D., & Pardo, E. (2018). Metal–organic framework technologies for water remediation: towards a sustainable ecosystem. Journal of Materials Chemistry A, 6(12) .
- [4] <https://www.magzter.com/article/Science/Innovation-Tech-Today/2019-Innovator-of-the-Year-Omar-Yaghi>
- [5] Gérard Férey.(2007)Hybrid porous solids: past, present, future.
- [6] Hüsing, N., & Hartmann, S. (2009). Inorganic–Organic Hybrid Porous Materials. Hybrid Nanocomposites for Nanotechnology, 131–171.
- [7] Pascal Van Der Voort.;Karen Leus .;Els De Canck .(2019).Introduction to Porous Materials book.Cambridge.John Wiley & Sons Ltd.

CHAPTER I
HYBRID MATERIALS
STUDY

Introduction

The most heard of and talked about word, internationally in the present times, is pollution; [1] it is one of the most serious global challenges [2]; that affects biodiversity, ecosystems, and human health worldwide by contaminating soil and water [3].

Among all types of pollutions, water pollution has been considered as one of the major threat in recent year and this problem will be even worse in near future. In the 21st century, water recycling has become a crucial issue as more regions across the globe are witnessing a water crisis.

Detoxification of wastewater via adsorptive removal or photo catalytic degradation for achieving purified and drinkable water has been determined as environmentally benign, energy economic and cost-effective. In this context, porous materials have gained enormous research consideration for detection of contaminants in effluents and for treatment of wastewater [4].

I. Colorants

Colorants are defined as products capable of coloring a substance in a durable manner. It has groups that give it color: called chromophores and groups that allow it to be attached to the colors [5].

I.1.Generalities

A colorant is a substance that is added or applied in order to change the color of a material or surface [6]. They mainly consist of an assembly of chromophore (-N = N-) and auxochrome (-NH₂, -NHCH₃, -N (CH₃)₂, -HO, -OR) groups to ensure the solubility of the dye in water and conjugated aromatic structures (benzene ring, anthracene, perylene, etc.) [7]

Coloring matters are characterized by their ability to absorb light radiation in the visible spectrum (from 380 to 750 nm). The transformation of white light into light colored by reflection on a body, or by transmission or diffusion, results from the selective absorption of energy by certain groups of atoms called chromophores, the molecule coloring being the chromogen [6].

I.2. Colorants classification

Colorants are classified with respect to chemical structures of colorants and methods application to different substrates (textiles, paper, leather, plastics, etc.)[8].

Textile dyes can be classified according to their chemical composition (Anthraquinone, Azo colorants, diphenylmethane and triphenylmethane, Indigoids, Nitrated and nitrosated, Xanthenes', phthalocyanines) [9] as shown in figure below.

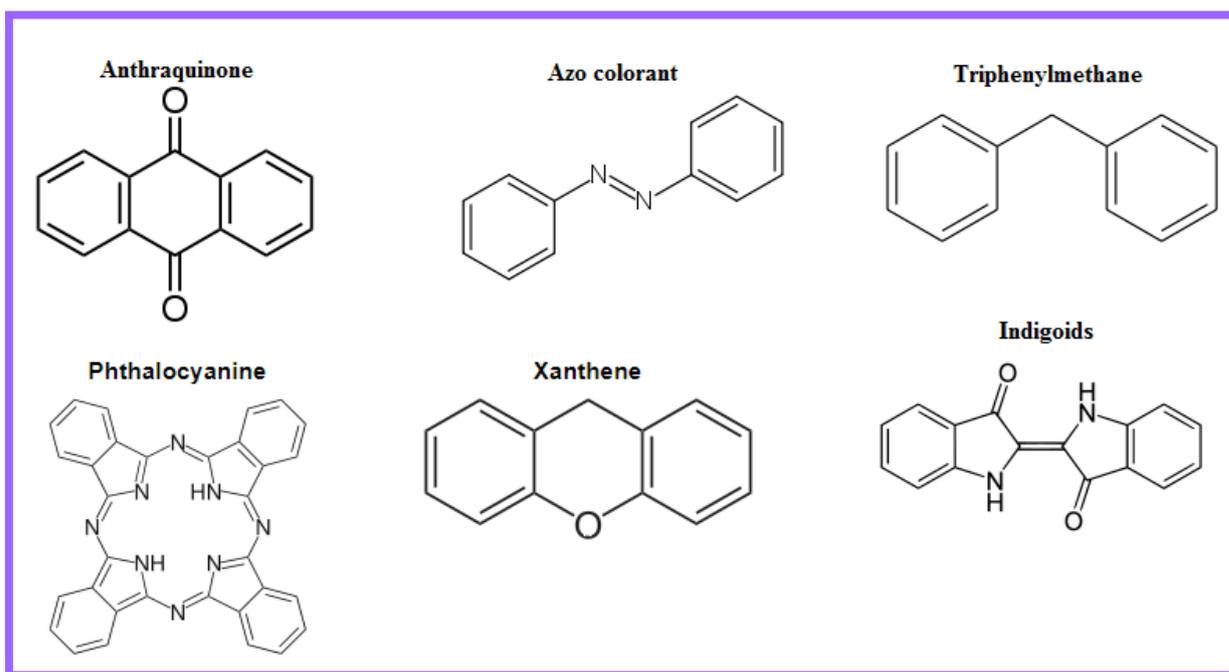


Figure .I.1. Examples of some colorants with their structures.

II. Water pollution

Water pollution occurs when unwanted materials enter in to water, changes the quality of water [10] and harmful to environment and human health [11]. It is reported that 75 to 80% water pollution is caused by the domestic sewage. Waste from the industries like, sugar, textile, electroplating, pesticides, pulp and paper are polluting the water [12].

Water pollution can occur from two sources:

- Point sources of pollution are those which have direct identifiable source. Example includes pipe attached to a factory, oil spill from a tanker, effluents coming out from industries. Point sources of pollution include wastewater effluent (both

municipal and industrial) and storm sewer discharge and affect mostly the area near it.

- Non-point sources of pollution are those which arrive from different sources of origin and number of ways by which contaminants enter into groundwater or surface water and arrive in the environment from different non identifiable sources[13].

II.1. Colorants pollution

It has been estimated that 15% of total colorants produced worldwide are discharged to water bodies which adversely affect aquatic ecosystem. Colorants in water reduces its transparency, thereby declining light penetration in the water, hence influencing photosynthesis which consequently reduces dissolved oxygen which is an alarming situation for both aquatic flora and fauna. Dyes wastewater discharged from huge number of industries like textile, leathers, paint, food, pharmaceutical etc [14].

The discharge of dye effluents in water bodies poses direct and indirect consequences to aquatic ecosystem. The direct effects includes depletion of dissolved oxygen levels, decreased re-oxygenation potential, leaching of dyestuff from soil into groundwater, reduced light penetration into water which hinders photosynthesis (which gives red signal to aquatic flora and fauna) and esthetic issue of water downstream [15, 16].

II.1.1. Methylene blue

Methylene blue was first prepared in 1876, by Heinrich Caro [17]. It is also known as methylthioninium chloride, is a medication and dye [18]. In our study we used methylene blue as a pollutant. It is a model cationic colorant employed by industries such textile industry for a variety of purposes. It is a heterocyclic aromatic chemical compound with a molecular formula $C_{16}H_{18}N_3SCl$.

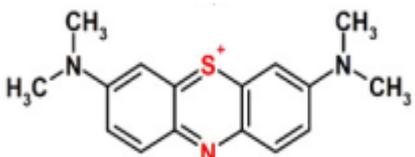
Several methods have been developed for the removal of dye from waste water. Amongst them, adsorption is the method of choice because of its ease of operation and design. Adsorption employs adsorbent- a substance which attaches the substrate or solvent molecule to its surface and several materials have been applied as adsorbent for the treatment of waste water [19, 20].

II.1.1.1. Utilization

Methylene blue (MB), the first synthetic drug, has a 120-year-long history of diverse applications, both in medical treatments and as a staining reagent. In recent years there was a surge of interest in MB as an anti-malarial agent and as a potential treatment of neurodegenerative disorders such as Alzheimer's disease (AD), possibly through its inhibition of the aggregation of tau protein [21].

MB is selected as a model organic compound because it is known to adsorb more easily onto solids and in order to evaluate the behavior of sorbent for the removal of organic pollutants from its aqueous solutions [22].

Table I.1. Properties of Methylene blue and its molecule modal [23, 24]

Product	Properties
	Name : Methylene blue
	Formula : C ₁₆ H ₁₈ ClN ₃ S
	Molar mass : 319.85 g·mol ⁻¹
	Solubility : 40 g·L ⁻¹ à 20 °C
	T°fusion: Decomposes on heating above 190 °C

III. Soft chemistry

Soft chemistry is a type of chemistry that uses reactions at ambient temperature [25, 26]; to synthesize materials [27], the methods of developing inorganic or hybrid nano-materials based on "soft chemistry" ; generate a very strong interest, both in academia and industry.

These synthetic methods involve "polymerization" reactions in the sense wide taking place at room temperature, in aqueous or organic solvent, from molecular or nano-particulate precursors [28].

IV. Nanoparticle materials

A nano-particle or ultrafine particle is usually defined as a particle of matter that is between 1 and 100 nanometers (nm) in diameter [29]. The term is sometimes used for larger particles, up to 500 nm, or fibers and tubes that are less than 100 nm in only two directions [30]. At the lowest range, metal particles smaller than 1 nm are usually called atom clusters instead.

They are usually distinguished from micro particles (1-1000 μm), "fine particles" (sized between 100 and 2500 nm), and "coarse particles" (ranging from 2500 to 10,000 nm), because their smaller size drives very different physical or chemical properties, like colloidal properties and optical or electric properties [31].

V. Hybrid composites materials

V.1. Composites materials

Composites are formed by combining individual materials referred to as constituent materials. These constituent materials include matrix (organic or inorganic) and reinforcement (fibers). Matrix (organic or inorganic) and reinforcement (fibers). The matrix material helps support the reinforcement materials by surrounding them, maintaining their positions and in return reinforcement materials impart mechanical and physical properties to enhance the matrix properties [32].

Composite materials are not a new concept. Since ancient times, materials have been combined to produce a new material with performance and efficiency unattainable by the individual materials. Many materials could actually be considered as composites.

V.2. Hybrid composites

Hybrid composites combine different kinds of materials at the submicron level. The word "hybrid" means the hybridization of a macroscopic mixture at the metallographic scale. Various definitions of hybrid composites have been proposed [33].

Hybrid materials are described as materials involving two or more kinds of chemical bonds created by "hybridizing" two or more monolithic materials [34].

They are typically either homogeneous systems derived from monomers or miscible organic and inorganic components, or heterogeneous systems (nano composites) in which at least one of the components domains has dimensions ranging from some Å to several nanometers [35, 36].

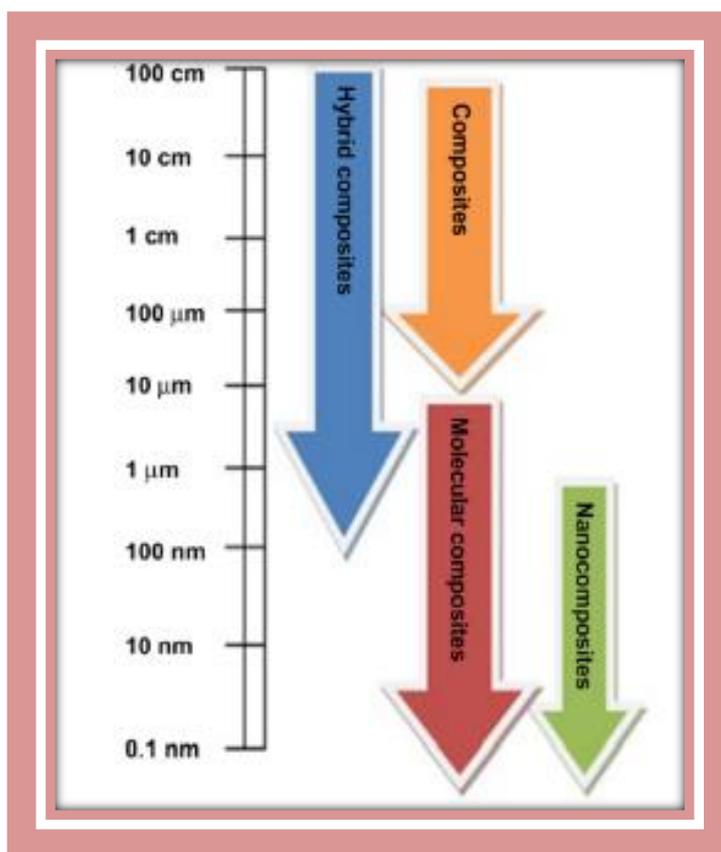


Figure I.2. Classification of materials at different scale levels [37].

V.2.1. Classes of hybrid porous material

Hybrid materials have been classified in many ways based on different concepts where Kicelbick has categorized the hybrid materials according to the strength of the interactions of the organic and inorganic building blocks in two classes: Class I (weak interactions) and Class II (strong interactions) hybrids.

- ✚ **Class I** hybrids may be built up by a combination of inorganic clusters with organic polymers (e.g. Zeolite/Low-density polyethylene hybrid) or interpenetration of inorganic and organic networks (e.g. Ring-opening metathesis of a polymer with a silica network)).

- ✚ **Class II** hybrids may be formed when inorganic clusters are covalently bonded to organic polymers (e.g. Metal oxide cluster reinforced Poly (methyl methacrylate)) (PMMA) or dual inorganic and organic networks connected by covalent bonds (e.g. Hybrid scaffolds of chitosan/silica) [38].

Hybrid materials can also be functionally classified and categorized into three types as structurally hybridized materials (composites), materials hybridized in chemical-bond, and functionally hybridized materials as it is classified according to Figure I.3.

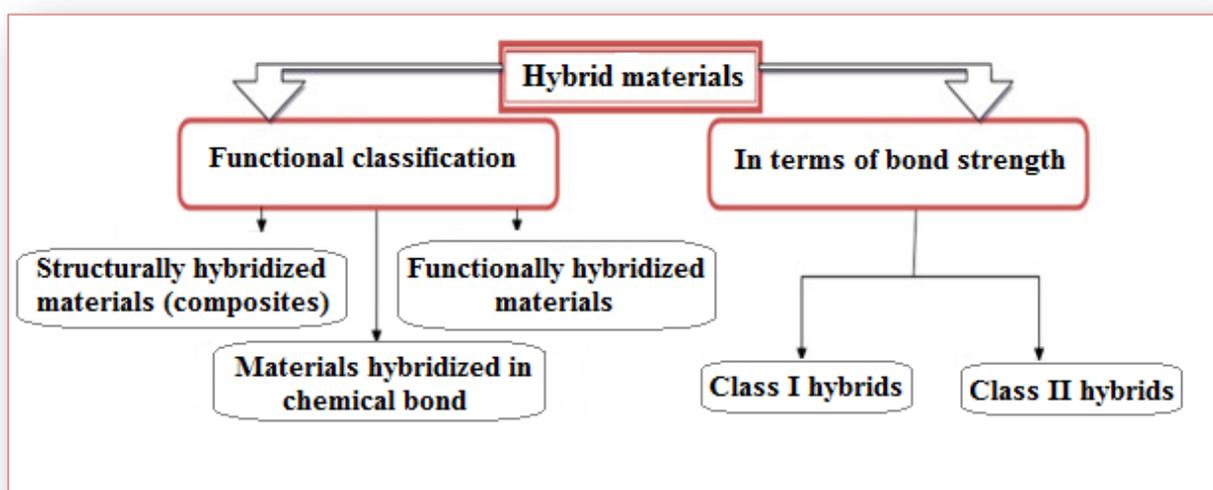


Figure I.3. Classification of hybrid materials [39].

V.3.Organic-inorganic hybrid porous materials

Hybrid organic-inorganic materials in general represent the natural interface between two worlds of chemistry each one with a very significant contributions to the field of materials science, and with characteristic properties that result in distinct advantages and limitations [40]. They are not just physical mixtures of inorganic and organic moieties.

They can be defined as nano-composites with organic and inorganic components that are intimately mixed on a molecular level such as (MOF, 0D coordination clusters, 1Dcoordination of polymers, 2Dcoordination of polymers...) (Figure I.4).

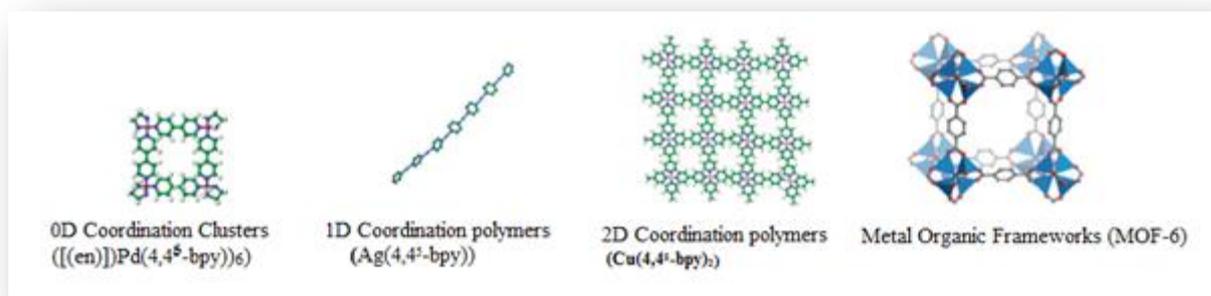


Figure I.4. Selected examples for diverse assembly of building units for hybrid materials [41].

V.3.1. Metal-Organic Framework (MOFs)

Metal-organic frameworks, commonly denoted as MOFs, are a hybrid porous material composed of both organic and inorganic groups. They are usually made from a metal ion and an organic ligand, the structure of a MOF is crystalline and three-dimensional in nature and utilizes a combination of rigid inorganic groups (often metal ions or metallic clusters) and flexible organic linker ligands. The utilization of both rigid and flexible groups enables MOFs to possess long-range tunable pores that can accommodate a wide range of molecules and can be tuned to be selective in which types of molecules they allow into their pores [42, 43]; because of these pores they emerged as one of the suitable candidates for the remediation of the environmental pollution [44].

V.3.1.1. Metal-Organic Framework properties

Metal organic frameworks (MOFs) have unique properties that make them excellent candidates for many high-tech applications. They have high porosity and surface area, good stability in various environments and are inexpensive to prepare. However, one major drawback is their electric resistance, which makes them incompatible for use in electrical devices [45]. This type of compounds possess a greater surface area with an advantage of changing pore sizes, diversified and beautiful structure which withdrew an intense interest in this field [46].

VI. Components of organic-inorganic hybrid materials

In order to form an organic-inorganic hybrid material; we need to create the combination of inorganic, organic, entities and functions in a well-defined host matrix [47].

It consists of the 1st part the organic part that is represented by amines, acids; the 2nd part is the inorganic part which is the metal or précised the metal cation.

VI.1. Transition metal

According to IUPAC a transition metal is "an element whose atom has a partially filled(d) sub-shell, or which can give rise to cations with an incomplete(d)sub-shell"[48]. It is described as any element in the d-block of the periodic table, which includes groups 3 to 12 on the periodic table. In actual practice, the f-block lanthanide and actinide series are also considered transition metals and are called "inner transition metals"[49,50]. They have high tensile strength and good conductors of heat and electricity [51].

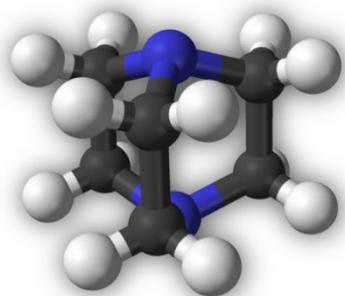
There are a number of properties shared by the transition elements that are not found in other elements, which results from the partially filled d shell. These include

- The formation of compounds whose color is due to d–d electronic transitions
- The formation of compounds in many oxidation states, due to the relatively low energy gap between different possible oxidation states [52].
- The formation of many paramagnetic compounds due to the presence of unpaired *d* electrons. A few compounds of main group elements are also paramagnetic (e.g. nitric oxide, oxygen)

Most transition metals can be bound to a variety of ligands , allowing for a wide variety of transition metal complexes [53].

VI.2. Amines

Are compounds and functional groups; that contain a basic nitrogen atom with alone pair. Amines are formally derivatives of ammonia, where in one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group [54].In our study we focus on 1, 4-Diazabicyclo [2.2.2.]Octane (DABCO) also known as triethylenediamine is a bicyclic compound with molecular formula $N_2C_6H_{12}$ (figure I.5). It is a tertiary amine having high nucleophilic character and act as Lewis base in variety of reactions leading to important organic scaffolds [55].

Table I.2. Properties of DABCO [56].**Figure I.5.** Molecule model of DABCO [57].

Properties	
Chemical formula	$C_6H_{12}N_2$
Molar mass	$112.176 \text{ g}\cdot\text{mol}^{-1}$
Melting point	156 to 160°C (429 to 433 K)
Boiling point	174°C (345°F; 447 K)
Solubility in water	Soluble, hygroscopic

VI.3. Oxalic acid

Anhydrous oxalic acid occurs as translucent, colorless, hygroscopic crystals, partially soluble in certain solvents such as ethanol .Oxalic acid dehydrate is generally found in commerce, also comes in the form of translucent crystals, colorless, partially soluble in water and some solvents such as ethanol and diethyl ether .When heated, oxalic acid decomposes, above 160°C, into formic acid, carbon monoxide and dioxide and water.

Aqueous solutions of oxalic acid are sensitive to the action of air and light, with formation of carbon dioxide, under the influence of ultraviolet light, oxalic acid, anhydrous or in solution, are broken down into formic acid and carbon dioxide. Oxalic acid can react dangerously with strong oxidants [58, 59].

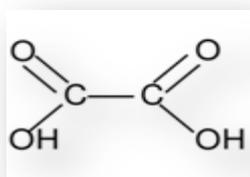
**Figure I.6.** Structural formula of oxalic acid [60].

Table I.3 Properties of anhydrous and dehydrate oxalic acid [61].

Properties	
Chemical formula	$C_2H_2O_4$
Molar mass	90.034 $g \cdot mol^{-1}$ (anhydrous) 126.065 $g \cdot mol^{-1}$ (dehydrate)
Density	1.90 $g \cdot cm^{-3}$ (anhydrous, at 17°C) 1.653 $g \cdot cm^{-3}$ (dehydrate)
Melting point	189to191°C 101.5°C dehydrate
Solubility in water	In water : 90-100 g/L (20°C)

VII. Hybrid porous materials application

Hybrid inorganic–organic porous materials find applications in various fields, depending on their chemical composition, structure and porosity, surface area and pores size distributions. Catalysis plays a vital role in life today, such as in cleaning and production of energy and fuels, fine chemicals, pharmaceuticals, and commodity chemicals.

Or storage and adsorption of molecules Gas, storage is of major importance especially with respect to the uptake of fuel gases such as methane or hydrogen, which are highly attractive candidates as replacements for fossil fuels.

As a membranes and monolithic chromatography columns, Hybrid inorganic–organic membranes offer consistent and unique opportunities to combine the specific transport properties of organic and inorganic materials in order to produce highly perm selective membranes [62].

MOFs and porous organic materials have emerged as one of the suitable candidates for the remediation of the environmental pollution.

Among the features possessed by artificially porous solids, the ability to modulate and achieve specific electronic traits leads to this class of materials being able to function as host matrices for read-out of targeted/specific guest molecules [63].

VIII. Analyzing methods

VIII.1. Binocular optical microscope

Microscopy is the technical field of using microscopes to view samples and objects that cannot be seen with the unaided eye (objects that are not within the resolution range of the normal eye). There are three well-known branches of microscopy: optical, electron, and scanning probe microscopy.

The optical microscope, also referred to as a light microscope, is a type of microscope that commonly uses visible light and a system of lenses to generate magnified images of small objects. Basic optical microscopes can be very simple, although many complex designs aim to improve resolution and sample contrast.

The object is placed on a stage and may be directly viewed through two eyepieces on the microscope [64].

VIII.1.1. Observation of samples with a binocular

Once the products are synthesized, washed and dried, will be systematically observed with an optical microscope which allows a preliminary determination on the poly-phasic or homogeneous nature of the samples and the presence or not of single crystals which can be characterized by the use of the X-ray diffraction method by the single crystal. Viewing the samples with a binocular gives a first impression on the nature and quality of the products [65].

VIII.2. Infrared spectroscopy IR

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material; because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum [66].

VIII.2.1. Fourier transform infrared (FTIR)

Fourier Transform Infrared Spectroscopy (or FTIR: Fourier Transformed Infra Red spectroscopy) is based on the absorption of infrared radiation by the material analyzed. It allows, via the detection of the characteristic vibrations of chemical bonds, to analyze the chemical functions present in the material. When the wavelength (energy) provided by the light beam is close to the vibration energy of the molecule, the latter will absorb the radiation and there will be a decrease in the reflected or transmitted intensity. The infrared range between 4000 cm^{-1} and 400 cm^{-1} ($2.5 - 25\text{ }\mu\text{m}$) corresponds to the vibrational energy range of molecules [67].

VIII.2.2. FT-IR Instrumentation

It was in the 1960s when Fourier transform (FT) instruments came to the scene. The iconic part in it was the presence of interferometers. The output of the FT-IR instrument is then called an interferogram. FT-IR instruments, though were intended to extend the use of IR, had limited applications and were used only for advanced research. This was mainly because of the expensive component electronics and the need for supercomputers to record the generated data. However, after the microelectronic revolution, the capabilities and availability of these instruments have been greatly improved [68].

The FTIR spectrometer consists of an infrared source, a sample chamber with a provision for holding the sample, a monochromator, a detector and a recorder, which are integrated with a computer. Interferometric multiplex instruments make use of the Fourier transform. At present, all commercially available infrared spectrophotometers employ reflection gratings rather than prisms as dispersing elements [69].

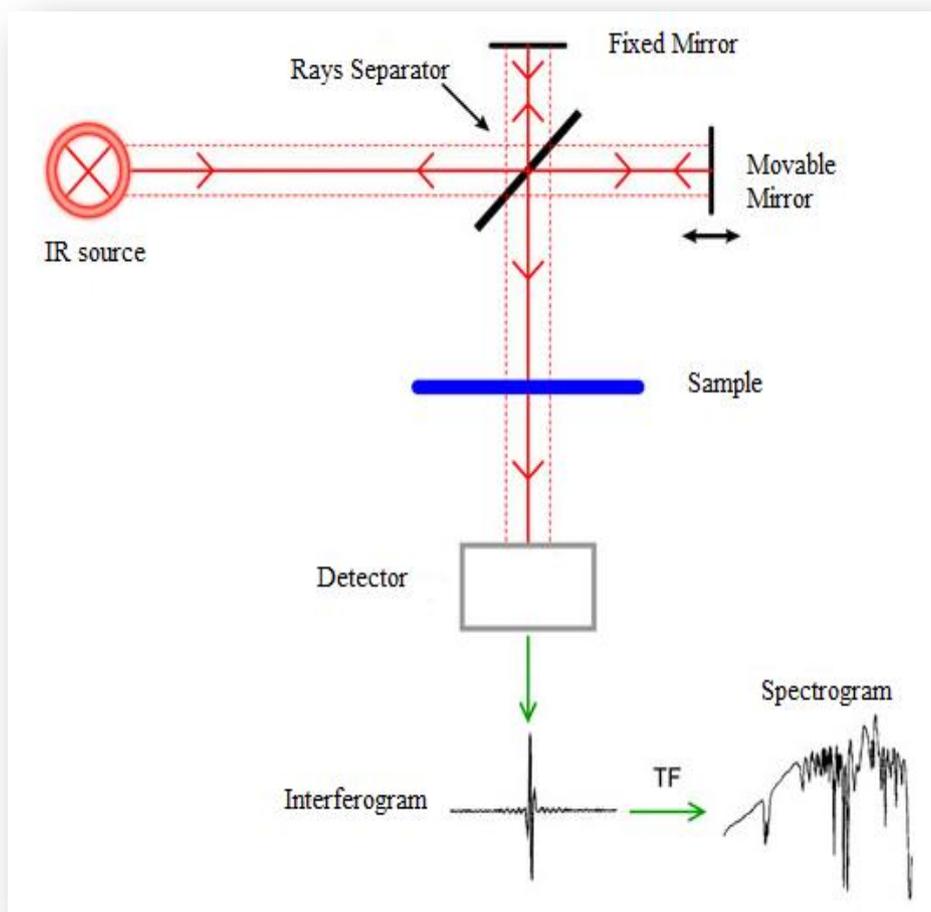


Figure I.7. Schematic representation of the Fourier-Transform Infrared Spectroscopy (FT-IR) principle [70].

In our project, we used the FTIR spectrophotometer 8400S type SHIMADZU that the wavelength range is among 400 to 4000cm^{-1} .



Figure I.8. IR spectroscopy dispositive.

VIII.3. Single-crystal X-ray Diffraction

VIII.3.1 .Principe

X-ray diffraction by crystals is a privileged tool of determination of the three-dimensional structure of molecules. Indeed, X-rays interact with the electronic cloud of crystal atoms. The crystal being a medium periodic three-dimensional, these scattered waves interfere and cause the phenomenon of diffraction [71-72].

The measurement of these diffracted intensities then gives access to the components of Fourier of the electron density of the molecule. A structural determination therefore consists to locate, after a certain number of calculation steps, the electron density maxima, that we assimilate to atomic positions. The intensities are measured by single crystal diffractometers [73] fitted with electronic detectors (proportional or scintillation counters).

VIII.3.2.Instruments

we used for crystallographic study and structural determination, using diffraction data acquired with a four-circle Kappa CCD (Charge Coupled Device) two-dimensional detector diffractometer from Bruker (Figure I.9).

This Kappa geometry device is characterized by the following four elements:

- ✓ A source of X-rays
- ✓ A graphite blade monochromator
- ✓ A goniometer allowing the rotation of the crystal around the three axes and the positioning of the reticular planes in diffraction position in the horizontal plane (detector plane).
- ✓ A two-dimensional CCD-type detector, whose high sensitivity makes it possible to measure the diffraction of small crystals ($5 \cdot 10^{-3} \text{ mm}^3$) or with low power diffracting [74].

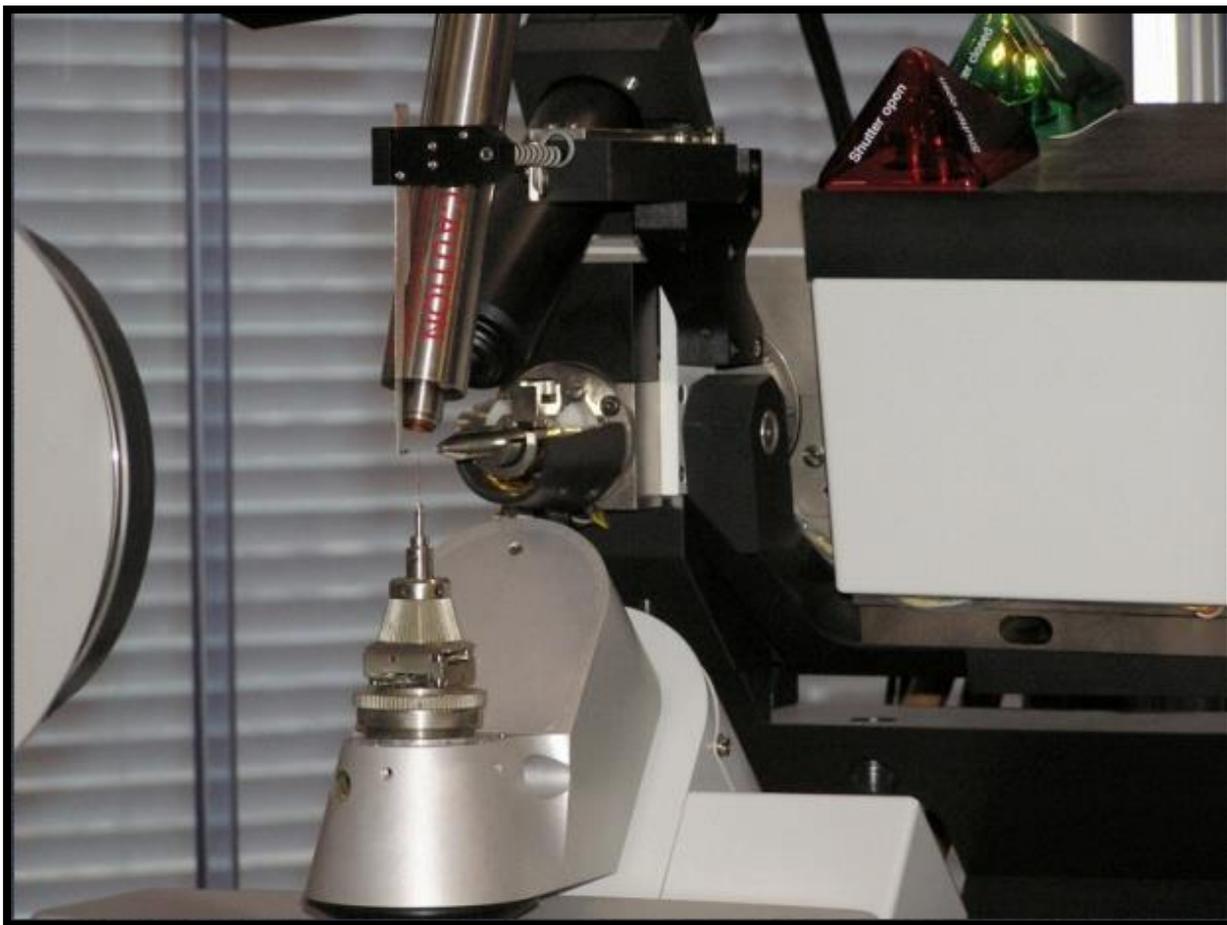


Figure I.9. X-ray diffractometer with Kappa CCD geometry.

Conclusion

The pressing need to sequester environmental pollutants has called for development of novel materials or methods. In particular, the growing accumulation of organic pollutants in different water streams, which cause adverse ecological impacts, has caused a global concern.

Porous solids having high surface areas, functioning as sorbents, have emerged as frontrunners in this regard. MOF's porous organic have improved over conventional porous compounds owing to feasible accessibility to tuning pore size, shape and functionalities. In particular, the emergence of water stable MOF's has actuated research toward practical applications, as there is greater understanding of the strategies that lead to formation of stable compounds [75]; where we to focus on the comprehend of hybrid porous materials; as we explained there deferent's classes and with the understanding of MOF's and some its properties and passing through the IR-FT and XRD characterization methods to get a full picture of their structure.

BIBLIOGRAPHICAL REFERENCES

- [1] Shafi, S.M. Environnemental Pollution.
- [2] Pandey, V. C.; Singh, V. (2019). Exploring the Potential and Opportunities of Current Tools for Removal of Hazardous Materials from Environments. *Phytomanagement of Polluted Sites*, 501–516.
- [3] Hesthaven, J.S.; Rachid, B.; Azooz, M.M.; Hossain, M.A.; Parvaiz, A. (2016). Genetic Strategies for Advancing Phytoremediation Potential in Plants: A Recent Update, Chapter 17 pp 431-454 in: *Plant Metal Interaction Emerging Remediation Techniques*, Edited by Parvaiz Ahmad, 1st Edition
- [4] Samanta, P.; Desai, A. V.; Let, S.; & Ghosh, S. K. (2019). Advanced Porous Materials for Sensing, Capture and Detoxification of Organic Pollutants towards Water Remediation. *ACS Sustainable Chemistry & Engineering*.
- [5] Lamri, N. (2010). Elimination du colorant orange II en solution aqueuse, par voie photochimique et par adsorption. Thèse de magister en chimie. Université Mentouri de Constantine faculté des sciences exactes Département de chimie. Algérie.
- [6] Capon, M. ; Courilleu, V ; Valtte, C. (1999). Chimie des couleurs et des odeurs, culture et technique.
- [7] Amrin, A. R. Photocatalytic oxidation of Congo red dye by using $\text{CO}_2\text{O}_3\text{-Cr}_2\text{O}_3$ as a Photo catalyst. 2016, 2 (2), 66-74.
- [8] Breuer, H. (2000). « Atlas de la chimie », Librairie Générale Française.
- [9] Khelloul, N. (2011). Dégradation d'un mélange de colorants par plasma glidarc. Etude de l'influence de différentes substances. Université Abdelhamid ibn badis Mostaganem faculté des sciences et de la technologie.
- [10] Alrumman, S.A.; El-kott, A.F.; Kehsk, M.A. Water pollution: Source and treatment. *American journal of Environmental Engineering*. 2016;6(3):88-98.
- [11] Briggs, D. Environmental pollution and the global burden of disease. *British medical bulletin*. 2003; 68:1-24.
- [12] Kamble, S.M. (2014). Water pollution and public health issues in Kolhapur city in Maharashtra. *International journal of scientific and research publications*; 4(1):1-6.
- [13] Singh, M.R.; Gupta, A. Water pollution-sources, effects and control Centre for Biodiversity, Department of Botany Nagaland University, 2019.
- [14] Hussain, S.; Khan, N.; Gul, S.; Khan, S.; Khan, H. Contamination of Water Resources by Food Dyes and Its Removal Technologies.
- [15] Lachheba, H.; Puzenata, E.; Houasb, A.; Ksibib, M.; Elalouib, E.; Guillarda, C.; Herrmanna, J.M. Photo catalytic degradation of various types of dyes (alizarin

S, Crocein Orange G, methyl red, Congo red, methylene blue) in water by UV-irradiated titania. 2002 ; 39 :75-90.

[16] De Oliveira, G. ; Leme, D.M. ; de Lapuente, J. ; Brito, L.B. ; Porredón, C. ; de Rodrigues, L.B, et al. A test battery for assessing the ecotoxic effects of textile dyes. *Chemico-Biological Interactions*. 2018; 291:171-179.

[17] Iqbal, A.; Farrukh, A. (2008). *New Strategies Combating Bacterial Infection*. John Wiley & Sons. P.91.

[18]"MethyleneBlue".TheAmerican Society of Health-System Pharmacists. Archived from 2017.

[19] Oliveira, L. S.; Franca, A. S.; Alves, M. T.; Rocha, S. D. J. Harz. *Mater* 133 (2008) 507-512.

[20] Umoren, S. A.; Etim, U. J. Adsorption of Methylene blue from industrial effluent using poly (vinyl alcohol), University of Uyo, Uyo, Nigeria. (2012).

[21] Schirmer, R. H.; Adler, H.; Pickhardt, M.; & Mandelkow, E. (2011). "Lest we forget you — methylene blue" *Neurobiology of Aging*, 32 (12).

[22] Hamed, M. M., Ahmed, I. M., & Metwally, S. S. Adsorptive removal of methylene blue as organic pollutant by marble dust as eco-friendly sorbent. *Journal of Industrial and Engineering Chemistry*. (2014).

[23] Guttman, P.; Ehrlich, P. (1891). U"ber die Wirkung des Methylenblau bei Malaria. *Berlin. Klin. Woch.* 28, 953–956.

[24] « 3,7-Bis (dimethylamino)-phenoazathionium chloride » dans la base de données de produits chimiques GESTIS de la IFA (organisme allemand responsable de la sécurité et de la santé au travail). (2018).

[25] Sanchez, C.; Rozes, L.; Ribot, F.; Laberty-Robert, C.; Grosso, D.; Sassoie, C.; Boissiere, C.; Nicole, L. (2010). "Chimie douce": A land of opportunities for the designed construction of functional inorganic and hybrid organic-inorganic nanomaterials", *Comptes Rendus Chimie*.

[26] Gopalakrishnan, J. (1995). "Chimie Douce Approaches to the Synthesis of Metastable Oxide Materials", *Chemistry of Materials*.

[27] Brec, R.; Rouxel, J.; Tournoux, M. (1994), *Soft chemistry routes to new materials: chimie douce: proceedings of the international symposium held in Nantes, France, September 6–10, 1993*, Aedermannsdorf, Switzerland: Trans Tech Pubs.

[28] Sanchez, C. *Chimie des matériaux hybrides cours : chimie des matériaux hybrides*.

- [29] U.S. Environmental Protection Agency: "Module 3: Characteristics of Particles Particle Size Categories" .EPA.
- [30] Vert, M.; Doi, Y.; Hellwich, K. H.; Hess, M.; Hodge, P.; Kubisa, P.; Rinaudo, M.; Schué, F.O.(2012)."Terminology for biorelated polymers and applications(IUPAC Recommendations 2012)". Pure and Applied Chemistry. 84 (2): 377 410.
- [31]Chae, S.Y.; Park, M. K.; Lee, S.K.; Kim, T.Y.; Kim, S.K.; Lee, W.I. (2003).Preparation of Size-Controlled TiO₂ Nanoparticles and Derivation of Optically Transparent Photo catalytic Films.
- [32] Yamada, A.; Sasabe, H.; Osada, Y.; Shiroda, Y.(1989). Concepts of Hybrid Materials, Hybrid Materials—Concept and Case Studies. ASM International, OH.
- [33] Thomas, S.; Weimen, Y., 2009. Advances in Polymer Processing: From Macro to Nano scale. CRC Press, Woodhead Publishing Limited, Washington, DC, pp. 6571.
- [34] Niizeki, N. (1986). What are hybrid materials? Sensor Tech.6 (2), 42-44.
- [35] Sanchez, C.; Ribot, F. (1994). Design of hybrid organic-inorganic materials synthesized via sol–gel chemistry. New J Chem 18: 1007 – 1047.
- [36] Sanchez, C.; de A.A.; Soler-Illia, G.J.; Ribot, F.; Lalot, T.; Mayer, C.R.; Cabuil, V. (2001).Designed hybrid organic-inorganic nano-composites from functional nano building blocks.
- [37] Singh, A.; Verma, N.; & Kumar, K. (2019). Hybrid composites: a revolutionary trend in biomedical engineering. Materials for Biomedical Engineering.
- [38] Chadwick, A.V.; He, J.; Hess,M.; Horie, K.; Jones, RG.;et al. (2007) Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials. Pure and Applied Chemistry .
- [34] Ashby, M.F.; Brechet, Y.J.M.; 2003.Designing hybrid materials. Acta Mater. 51, 58015821.Bauer, T.W., 2007. An overview of the histology of skeletal substitute materials. Arch.Pathol. Lab. Med.
- [40]Wiesner,U.(2012).Hybrid Polymer-Inorganic Nanostructures Polymer Science: a Comprehensive Reference, 10 Volume Set. 7: 129-140.
- [41]Ding, S.Y.; & Wang, W. (2013). Covalent organic frameworks (COFs): from design to applications. Chem. Soc. Rev., 42(2).
- [42] Gomez-Romero, P.(2001).Hybrid Organic-Inorganic Materials–In Search of Synergic Activity.
- [43] Smaldone, R.A.; Forgan, R.S.; Furukawa, H.; Gassensmith, J.J.; Slawin, A.M.Z.;Yaghi, O.M.; Stoddart, J.F.A. Chem. Int. Ed. Engl.2010, 49, 8630

- [44] Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Metal-organic frameworks: functional luminescent and photonic materials for sensing applications. *Chem.Soc. Rev.* 2017, 46, 3242–3285.
- [45] Fleker, O.; Borenstein, A.; Lavi, R.; Benisvy, L.; Ruthstein, S.; Aurbach, O. Preparation and properties of metal organic framework "activated carbon composite materials".
- [46] Soni, S.; Bajpai, P.K.; Arora, C. (2019). *Metal-organic Framework: Synthesis, Properties and Application*.
- [47] Hüsing, N.; Hartmann, S. *Inorganic–Organic Hybrid Porous Materials*. Chapter 3.
- [48] IUPAC, *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book") (1997). Online corrected version: (2006) "transition element.
- [49] Petrucci, R. H.; Harwood, W.S.; Herring, F. G. (2002). *General chemistry: principles and modern applications* (8th ed.). Upper Saddle River, N.J: Prentice Hall. pp. 341–342.
- [50] Housecroft, C. E.; Sharpe, A. G. (2005) *Inorganic Chemistry*, 2nd ed, Pearson Prentice-Hall, pp. 20–21.
- [51] Khandelwal, B.L. *Inorganic Chemistry of Transition Elements*. Director Disha Institute of Management and Technology Satya Vihar, Narhada-Chandakhuri Marg, Tehsil Arang Raipur – 492 101.
- [52] Matsumoto, P.S. (2005). Trends in ionization energy of transition-metal elements. *Journal of Chemical Education* 82 (11): 1660–1661
- [53] Hogan, C.M. (2010). "Heavy metal" in *Encyclopedia of Earth*. National Council for Science and the Environment.
- [54] McMurry, J.E. (1992), *Organic Chemistry* (3rd ed.), Belmont: Wadsworth.
- [55] Uppuluri, V.; Mallavadhani, N. F. "1,4-Diazabicyclo [2.2.2]octane". In *Encyclopedia of Reagents for Organic Synthesis*, 2010, John Wiley & Sons, Ltd.
- [56] D. H. Ripin; D. A. Evans (2002). "Pka's of Nitrogen Acids" (PDF).
- [57] Laus, G.; Kahlenberg, V.; Wurst, K.; Lorting, T.; Schottenberger, H. *CrystEngComm.*, 2008, 10, 1638.
- [58] Oxalic acid - SAX's dangerous properties of industrial materials. 11 ed. New-York : Wiley-Interscience ; 2005: CD-ROM.
- [59] Othmer, O. *Encyclopedia of chemical technology*. New York, Londres, John Wiley and sons, 1981, vol.16, pp.618-636
- [60] Oxalic acid dihydrate - International Chemical Safety Cards. IPCS, CEC, ICSC 0707, 2009.

- [61] Record in the GESTIS Substance Database of the Institute for Occupational Safety and Health.
- [62] Hüsing, N. (2006). Porous Hybrid Materials. *Hybrid Materials*, 175–223.
- [63] Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Metal-organic frameworks: functional luminescent and photonic materials for sensing applications. *Chem. Soc. Rev.* 2017, 46, 3242–3285.
- [64] Di Gianfrancesco, A. (2017). Technologies for chemical analyses, micro structural and inspection investigations. *Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants*, 197–245.
- [65] ZENKHRI, L. (2018). Synthèse, structure cristalline et réactivité de nouveaux matériaux inorganiques poreux. *Chimie des matériaux*. Université Kasdi Merbah –Ouargla.
- [66] Introduction to Fourier Transform Infrared Spectrometry.(2001).Thermo Nicolet Corporation.
- [67] Bouyahia, F. (2013). Synthèse et modification d'un matériau méso poreux type MCM-48; Application à l'adsorption d'un polluant organique. Université des Sciences et de la Technologie d'Oran Mohamed BOUDIAF.
- [68] Abd Al-Aziz, M. (2019). Introductory Chapter: Infrared Spectroscopy - A Synopsis of the Fundamentals and Applications.
- [69] Shodhganga .chapter 2: characterization techniques.
- [70] <http://mathias.borella.fr/2-1-La-spectroscopie-infrarouge.html#nb2-4>
- [71] C. Jelsch, M. Teeter, V. Lamzin, V. Pichon-Pesme, R. H. Blessing and C. Lecomte. Accurate Protein crystallography at ultra high resolution: valence Electron distribution in crambin. *Proc. Nat. Acad. Sci. USA.*, 97 3171-5176 (2000).
- [72] V, S. Lamzin, R. S. Morris, Z. Douer, K. S. Wilson and M. Teeter, *J. Biol. Chem.*, 274 ; 20753-20755 (1999).
- [73] Rousseau, J.J. (2000). *Cristallographie géométrique et radiocristallographie*.
- [74] Bouacida, S. (2008). Synthèse, caractérisation structurale, stabilité thermique et propriétés physiques des composés hybrides à base d'étain et d'amines. Doctoral thesis. Université Mentouri - Constantine, Faculté des Sciences Exactes, Algeria.
- [75] Partha Samanta, Aamod V. Desai, Sumanta Let, and Sujit K. Ghosh. (2019). *Advanced Porous Materials for Sensing, Capture and Detoxification of Organic Pollutants toward Water Remediation*. Department of Chemistry, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pashan, Pune 411008, India.

CHAPTER II

EXPERIMENTAL PART

Introduction

Amines are known in coordination chemistry for their flexibility of coordination; they can coordinate with according to their functions. Because of their biochemical and pharmaceutical properties; the amino-metal complexes and their derivatives are of definite interest. For that the small amines of all types are very soluble in water. In fact, the ones that would normally be found as gases at room temperature are normally sold as solutions in water [1]. It is in this context that we synthesized, characterized the compose $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$.

I .Departing products

During our work we have used commercial chemicals mentioned in the table II.1

Table II.1. Name and purity of the initialed materials.

<i>product name</i>	<i>Chemical Formula</i>	<i>Molar mass (g/mole)</i>
Nitric acid	HNO_3	63.01
Hydrochloric acid	HCL	36.46
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	46.07
Oxalic acid	$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$	126.02
Squaric acid	$\text{C}_4\text{H}_2\text{O}_4$	114.06
Aluminum Nitrate Nona hydrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	375.1338
Bismuth(III) Nitrate penta hydrate	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	485.07
Cerium(III) Nitrate Hexahydrate	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	326.12
Iron Nitrate Nona hydrate	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	404.00
Nickel(II)Nitrate Hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	290.7949
Barium(II) Nitrate	$\text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	261.34
DABCO	$\text{C}_6\text{H}_{12}\text{N}_2$	112.17
Iron(III) Chloride Hexahydrate	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	270.29568

We initially tried to have simple complexes (mononuclear) from the different metal salts (Cu, Ni, Mn, Fe, Zn , ...) and known amino acids Table II.2.

Table II.2. The experiments carried out at the laboratory level.

Work conditions : ambient temperature and pH<3				
Final Product	Squaric acid	Oxalic acid	M(NO ₃)	Amine C ₆ H ₁₂ N ₂
cloudy white crystals	--	+	Bi(NO ₃) ₃ .5H ₂ O	+
cloudy transparent crystals	-	+	Al(NO ₃) ₃ .9H ₂ O	+
yellow biker crystals	-	+	Fe(NO ₃) ₃ .9H ₂ O	+
-	-	+	Ce(NO ₃) ₃ .6H ₂ O	+
Cloudy Green crystals	-	+	Ni(NO ₃) ₃ .6H ₂ O	+
-	-	+	Ba(NO ₃) ₂ .H ₂ O	+
Crystal	+	-	Al(NO ₃) ₃ .9H ₂ O	+
Crystal	+	-	Fe(NO ₃) ₃ .9H ₂ O	+
Transparent greenish crystals	+	-	FeCl ₃ .6H ₂ O	+

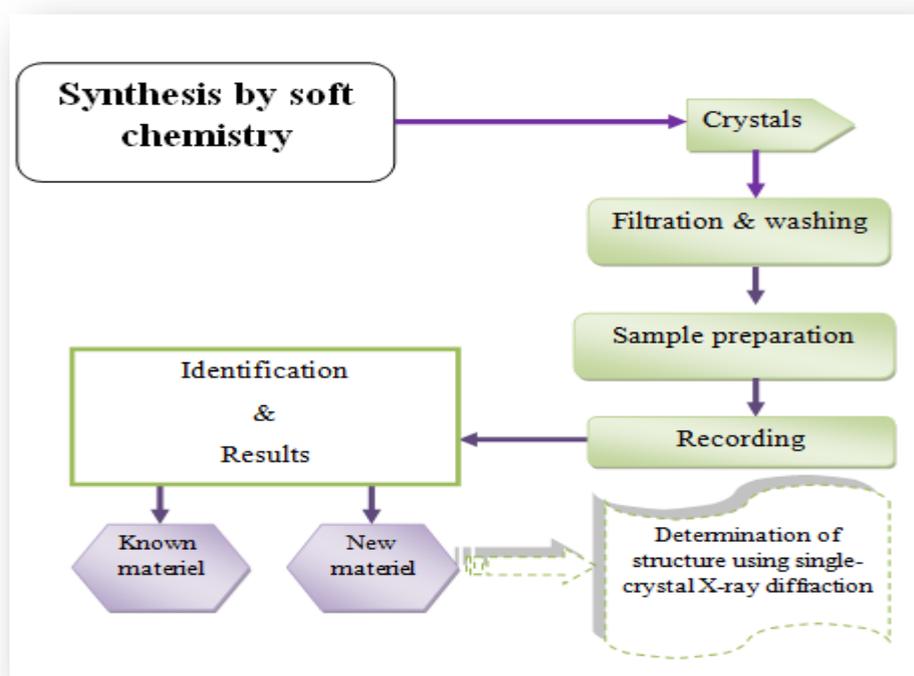


Figure II.1. Experimental protocol followed for the synthesis.

II .Elaboration

To obtain complexes with various architectures and behavior, the experiment was carried out by soft chemistry in solution (25°C - 80°C). The preparation of samples is at room temperature using Magnetic stirring .according to the molar ratio (1:1:1) with a pH<3 for 2 hours. A new mononuclear complex has been formed through extend of the molecular materials and metallic aggregates. Considering the importance of the geometry of the magnetic centers and their environment, a structural study by X-ray diffraction on single crystal has been systematically carried out on the formed complexes. Due to the current circumstances (Covid-19), it was not possible for us to conduct the analyzes, and we were satisfied with discussing the results of the similar study [4].

III. Synthesis

III.1.Synthesis of $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$

We quoted in this reaction, in which is used a squaric acid instead of oxalic acid for the preparation of HPM starting from a solution containing 0.135 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.028 g of Dabco, 0.057 g of squaric acid dissolved in 1.5 ml of ethanol. The pH of the mixture is adjusted to 3 by adding a few drop of 69% nitric acid, gas evolved, once the gas evacuation operation complete (about 2 to 3 minutes) the PFA of 2 ml capacity, is placed in an oven brought to 80°C . The result is the formation of three types of crystals: Dark green cubes of $\text{Fe}(\text{C}_4\text{O}_4) \cdot 4\text{H}_2\text{O}$ [2] and transparent yellow plates of $\{((\text{Dabco_H}_2)^{2+})_2[(\text{Fe(III)Cl}_4)_2(\mu\text{-C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}\}_n$ [3]: these are the first phases that form, gradually, this forms a gel that sticky with the first two phases. The morphological development of gel leads to transparent greenish prisms of the new product $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2) \cdot 2\text{H}_2\text{O}$. The majorities of the faces of these crystals grow with hindrance during the formation process, since they are thwarted by the presence of other phases in their surroundings the neighboring crystallites [4].

III.2.Characterization of $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2) \cdot 2\text{H}_2\text{O}$

When observing the sample under the binocular, using polarized light, crystals of $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2) \cdot 2\text{H}_2\text{O}$, appear to be of very good quality, with well-developed faces. They are sensitive to ambient air, once removed from the stock solution, and resume their transparency if immersed in the stock solution or ethanol.

III.2.1. X-ray diffraction on the single crystal

This phase was characterized by X-ray diffraction on the single crystal. The single crystal selected for the study is in the form of a transparent greenish-yellow prism $580\mu\text{m}$ long, $380\mu\text{m}$ wide $350\mu\text{m}^3$ thick and $1.7550\text{ g}\cdot\text{cm}^{-3}$ density.

III.2.1.1.Data acquisition

The data of the X-ray diffraction by the single crystal of the complex $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2) \cdot 2\text{H}_2\text{O}$ were measured on a Device type 'APEXII, diffractometer, Bruker-AXS 'with a Molybdenum anticathode and radiation ($\lambda=0.71073\text{ \AA}$) by the CCD method rotating images, thin slices using a flat single-ended CCD detector temperature equal to 150 K, and using the 'Bruker APEX2 program for the collection, refinement and data reduction.

III.2.1.2. Resolution and refinement of the structure

After establishing the chemical composition by spectroscopic analysis at energy dispersal, the structure has been resolved in the P21/c space group. The settings of the mesh are recorded in table II.3. The structural model was found by the direct method using the SHELXT software. The crystallographic structure of $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ [4], obtained is shown in Figure II.2 with the ORTEP program.

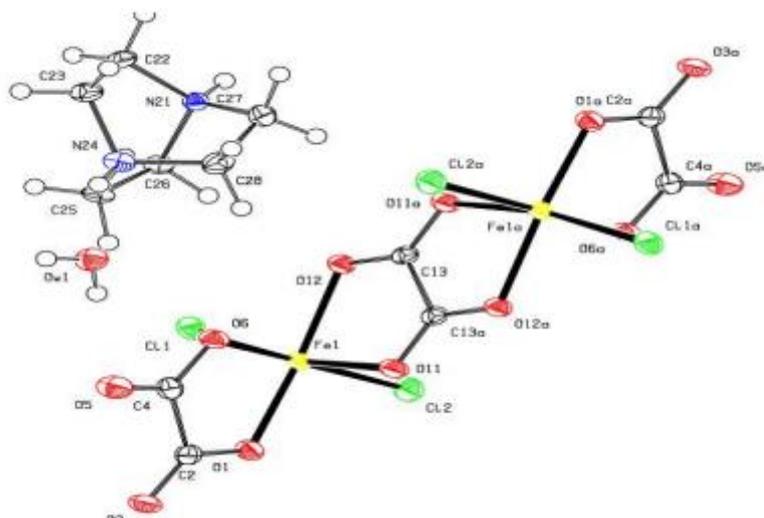


Figure II.2. Representation of the molecule with the ORTEP program.

The model was refined with full matrix least square methods based on F^2 (SHELXL-2014) [5]. All non-hydrogen atoms have been refined except for the hydrogen atoms bonded to nitrogen which were introduced into the model structural analysis by the analysis of Fourier difference maps, the H atoms were finally included in their calculated positions. A final refinement on F^2 with 3376 unique intensities and 202 parameters converge to the values of the rehabilitation factors: $\omega R (F^2) = 0.0804$ ($R (F) = 0.0341$) for 2958 reflections observed with $I > 2\sigma (I)$ and GoF (Goodness-of-fit) = 1.176. Finally an absorption correction of the multi scan type was performed with a coefficient $\mu = 1.409$ and $T_{\min} = 0.472$, $T_{\max} = 0.611$. Molecular graphs were produced using drawing programs (Diamand [6], Mercury [7] and Ortep3).

Table II.3. Cristallographique data on the cell $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$.

Crystallographic data	
Empirical formula	$\text{C}_6\text{C}_{14}\text{Fe}_2\text{O}_{12} \cdot 2(\text{C}_6\text{H}_{14}\text{N}_2) \cdot 2(\text{H}_2\text{O})$
Chemical formula	$\text{C}_{18}\text{H}_{32}\text{C}_{14}\text{Fe}_2\text{N}_4\text{O}_{14}$
Molecular weight	$781.97 \text{ g}\cdot\text{mol}^{-1}$
The cell $\text{Fe}_2\text{Cl}_4(\text{C}_2\text{O}_4)_3(\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$[4].	
Crystal system	Monoclinic
HM space group	P21/c
Hall space group	-P2ybc
Group number	14
a(Å)	9.2690 (5)
b(Å)	13.7360 (8)
c(Å)	11.6667 (7)
α(°)	90.0000
β(°)	92.567 (3)
γ(°)	90.0000
V(Å³)	1483.90(15)
Z	2
M	1.409 mm^{-1}
D	$1.750 \text{ g}\cdot\text{cm}^{-3}$
F(000)	800
Crystal size	0.580 x 0.380 x 0.350 mm
Crystal color	Yellow

Theta range for data collection	2.966 to 27.480°
h_min,h_max	-12.11
k_min,k_max	-17.17
l_min,l_max	-15.9
Reflections collected\unique	10777\3376[R(int) ^a = 0.0215]
Reflections [I>2σ]	2958
Completeness to theta_max	0.994
Absorption correction type	multi-scan
Max.and min.transmission	0.611 , 0.472

III.3. Description of the structure

The asymmetric unit of the complex is presented in figure II.3, with a system of atomic numbering. It consists of a trivalent iron cation, coordinated in two-anion octahedral Cl^- , and three oxygen from the oxalic anion, a molecule of water and a di-protonated DABCO cations; Or one atom of iron, two of chlorine, nine of carbon, seven oxygen, sixteen hydrogen.

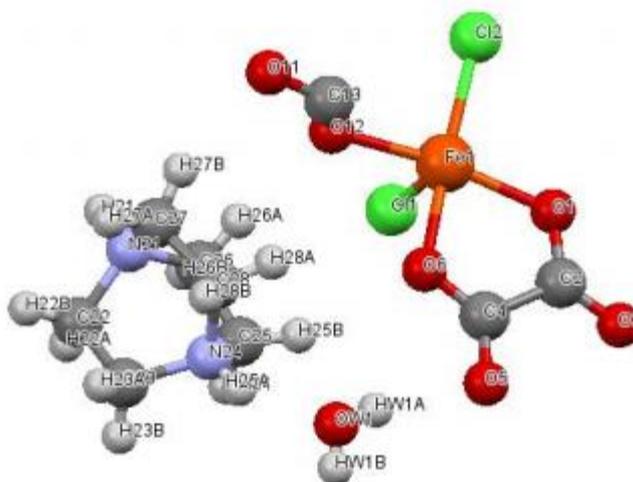
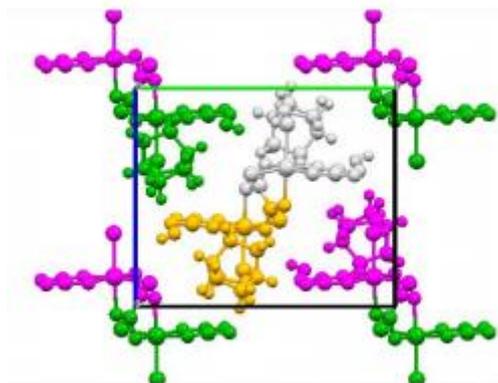
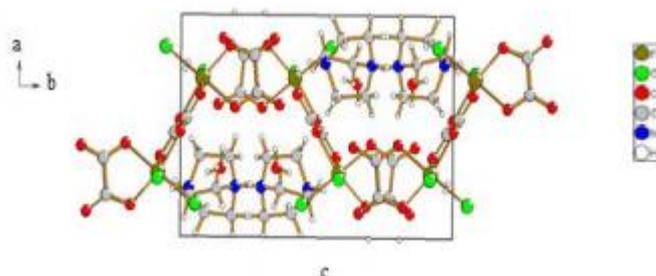


Figure II.3. The asymmetric unit of $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$.

The compound consists of two iron atoms, three oxalate ligands (two are crystallographically similar), a water molecule and cation of dabco. The elementary cell of the $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ [4] complex consists of entities isolated from $[\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3]^{-2}$, diprotonated DABCO and H_2O . It contains four units asymmetric. Atoms of iron Fe1 and Fe2 are found in co-ordination six linked to atoms of oxygen and chlorine with an octahedral geometry (figure II.4, figure II.5). Function carboxylate forms a chelation by the atoms O1 and O6 giving the ligand the mode of bidentate chelate coordination.



FigureII.4. The elementary cell $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ represented by symmetry operations projected along the axis a.



FigureII.5. The elementary cell $\text{Fe}_2\text{Cl}_4 (\text{C}_2\text{O}_4)_3 (\text{C}_6\text{H}_{14}\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ [4] represented by symmetry operations projected on the axis c.

Conclusion

During this chapter a hybrid compound based on iron and amine and squaric acid has been synthesized in water (soft chemistry). This phase was characterized by x-ray diffraction on a single crystal.

This compound has organic cations, anions (a complex of minerals and iron), and two molecules of water. The structure has been resolved in the $P21 / c$ space group.

It crystallizes in the non-Centro symmetric space group $Fdd2$ of the orthorhombic system. The structural determination allowed us to highlight the presence of cationic layers that develop along the b axis and alternate.

BIBLIOGRAPHICAL REFERENCES

[1][https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_\(Organic_Chemistry\)/Amines/Properties_of_Amines/Basic_Properties_of_Amines](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Amines/Properties_of_Amines/Basic_Properties_of_Amines)

[2] Lee, C. R. .; Wang, C. C. .; Wang, Y, Acta Cryst., Sect. B: Struct. Sci. 52, 966. 1996.

[3]Fist, M.; Troyanov, S.; Kemnitz, E. "A Binuclear Chloroferrate Anion with Octahedral Metal Coordination: Octachloro(μ -oxalato)diferrate(III), $[(\text{FeCl}_4)_2(\mu\text{-C}_2\text{O}_4)]^{4-}$ ", Inorg. Chem., 35, 3067.(1996).

[4]Zenkri, L.(2018).Synthèse, structure cristalline et réactivité de nouveaux matériaux inorganiques poreux .Thèse de Doctorat. Université Kasdi Merbah – Ouargla.

[5] SHELXL-2014.

[6] Brandenburg, K. (2006). DIAMOND. Version 2.1C.Crystal Impact GbR, Bonn, Germany.

[7] CCDC (2002). Mercury. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.

**GENERAL
CONCLUSION**

General Conclusion

The main objective of the studies carried out during this work was the structural study, and the search for new properties (porous materials) for these new hybrid compounds based on a metal and an organic matrix based on amine and acid squaric. The physico-chemical analysis method used, namely the X-ray diffraction on a single crystal. The preparation of these compounds was carried out by main method, synthesis by aqueous method, the aim of this work was to prepare a hybrid porous materials containing inorganic (Aluminum, iron, barium...) substances, and organic (DABCO) entities, and the oxalic acid, by following the “soft chemistry” base in order to characterize them physically and chemically.

Abstract: The hybrid porous materials can be used for the waste water treatment for the presence of their pores .in this study ,we focused on the preparation of porous organic inorganic material following the soft chemistry base .the preparation of HPM involve and consist of combination of organic part (amine , oxalic acid ,acid squaric)and inorganic part(metal) predissolved in distilled water; where in microscopic level the crystals obtained are selected for single X-ray diffraction analyzing .

Keywords: Hybrid materials, organic-inorganic porous materials, colorants, water pollution, MOF.

Résumé: Les matériaux poreux hybrides peuvent être utilisés pour le traitement des eaux usées pour la présence de leurs pores. Dans cette étude, nous nous sommes concentrés sur la préparation de matériau inorganique organique poreux suivant la base de la chimie douce. La préparation de HPM implique et consiste en une combinaison d'une partie organique (amine, acide oxalique, acide squarique) et d'une partie inorganique (métal) préalablement dissoute dans l'eau distillée; où au niveau microscopique les cristaux obtenus sont sélectionnés pour une analyse par diffraction des rayons X.

Mots clés : Matériaux hybrides, matériaux poreux organiques-inorganiques, colorants, pollution de l'eau, MOF.

الخلاصة: يمكن استخدام المواد الهجينة المسامية لمعالجة مياه الصرف الصحي لوجود مسامها. في هذه الدراسة ركزنا على تحضير المواد العضوية غير العضوية المسامية بإتباع أسس الكيمياء اللينة يتضمن تحضير و تكوين المواد الهجينة المسامية من مزيج من جزء عضوي (أمين ، وحمض أكساليك ، وحمض سكواريك) و جزء غير عضوي (معدن) مذاب مسبقاً في الماء المقطر ؛ حيث يتم اختيار البلورات التي تم الحصول عليها على المستوى المجهرى لتحليل حيود الأشعة السينية الفردي لتحديد بنية المادة

الكلمات المفتاحية: المواد الهجينة ، المواد العضوية غير العضوية المسامية ، الملونات ، تلوث المياه ، الهيكل المعدني العضوي