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Intitulé

Traitement d'un colorant alimentaire par adsorption

Soutenu devant le jury composé de:

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Dedication:

To every student who seeks science, to every researcher who walks the path of knowledge, to every teacher who taught his students honestly, to everyone who wrote a book, wrote a page, translated a line, explained a word… In order to spread knowledge, to everyone who contributed to this, even with a kind word.

kamel Deia

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Index

Index :

Chapter III) physicochemical methods of analysis

Chapter IV) the experimental study

Figures list

Figures list:

Chapter I) : generalities about adsorbents and dyes

Chapter II): Adsorption

Chapter III) physicochemical methods of analysis

Chapter IV) the experimental study

General introduction

General introduction :

It is no hidden to anyone, that water for humans, living creatures and the entire earth means life itself, and it is not possible to imagine the existence of life without water, and all our activities, industries and food depend entirely on its availability.

But due to the great expansion of industrial activities that the world is witnessing today and the various pollutants that come from it, obtaining clean water has become extremely difficult, on the one hand, and on the other hand, environmental degradation caused by polluted water has become a real problem that cannot be ignored.

Dyes are one of the most common water pollutants, as textile dye alone accounts for from 17 to 20% of industrial pollutants.[1] of course, dyes are not only used in the textile industry, but are used in almost all industries, from paper and plastic manufacturing to the food that we eat, and all of them are not without color, So the pollution caused by it will be in huge quantities, but the problem does not lie in the quantities, but in the effects resulting from that, Due to the presence of toxic chemicals used in the manufacture of dyes, exposure to these substances has devastating effects on living organisms and human health, in addition to distorting the landscape. and its impact on the ecological balance.

Therefore, treating pollution with dyes is essential and extremely important, and there are several ways to do this, including filtration and sedimentation processes, ion exchange, adsorption, aerobic and anaerobic treatment, and other physical and chemical methods.

Due to the fact that the pigments have a great ability to dissolve in water, adsorption is considered one of the most common and effective methods of treating the pollution resulting from them, and many adsorbent materials are used for this purpose, and the most used is activated carbon because of its properties, in addition to the use of clay as it is one of the most abundant and least expensive materials.

In this note we will study the adsorption of carmine dye on the surface of two different materials: activated carbon and clay, where we will observe how the

adsorption process is affected by changing the dye concentration, the mass of the adsorbents, temperature and pH.

This research was divided into four chapters:

Chapter one: In it we will mention generalizations about activated carbon, clays and dyes.

Chapter Two: In it we will explain the phenomenon of adsorption.

Chapter Three: In it we will talk about the various physical and chemical methods for studying adsorption.

Chapter Four: In it, we will present the experimental study that we will conduct and discuss the results obtained.

Chapter I) : *generalities about adsorbents and dyes*

Chapter I) : generalities about adsorbents and dyes

Introduction:

Dyes are one of the most widespread materials, as they are used in many fields and cannot be dispensed with, but on the other hand, dyes are also considered one of the most important water pollutants, due to the huge quantities of dyes residues that are disposed of in rivers and waterways. The process of treating water contaminated with dyes is very important, and there are several ways to do this, the most famous of which is adsorption, where the phenomenon of adsorption depends on two main components, namely: the adsorbate , which in this case is the dyes, and the second component is the adsorbent , and there are many of them, and the active carbon is the most famous. In addition to the presence of other adsorbents such as clay and others.

In this chapter, we will talk about adsorbents and adsorbats, or more precisely, we will talk about activated carbon, its forms, uses and methods of manufacturing it. We will also talk about clay, its types, structure and uses, and in this chapter we will learn about dyes, their types and uses, and their classifications and the effects of pollution by dyes, and we will take an example of food dyes, which is carmine dye.

I-1) Activated carbon :

I-1-1) Definition :

Activated carbon is a mostly amorphous solid that has an extremely large internal surface area and a highly developed internal pore structure. It is these unique properties that are responsible for its absorbent properties. The activated carbon structure is best described as a twisted network of layers of carbon, tied casually.[2]

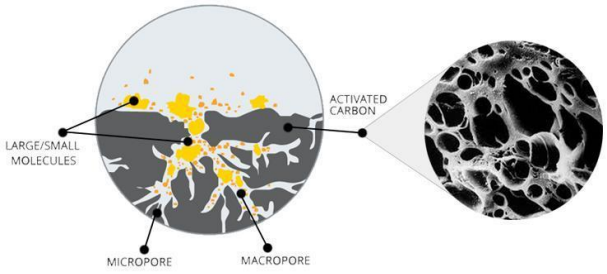


Figure **I.1** : **Adsorption process on activated carbon**

I-1-2) Types of activated carbon:

- **Granular Activated Carbon:**

GAC are irregularly shaped particles that are formed by grinding and sieving. These particles range in diameter from 0.2 mm to 5 mm. It has the advantages of being harder and longer life than activated carbon powder, and it can be reactivated and reused many times. GAC is used in both liquid and gas phase applications [3]

figure I.2 : Granular Activated Carbon

- **Powdered Activated Carbon:**

PAC generally contain particles with a diameter of less than 0.1 mm, although coarse .1 and fine grades are available. The advantages of powdered activated carbon are lower processing costs and flexibility in operation. The dose of the activated carbon powder can be increased or decreased easily according to the different process conditions, and the activated carbon powder is mainly used for liquid phase absorption. The wet active carbon powder is not regenerated due to the problems associated with carbon recycling [3]

figure I.3 : Powdered Activated Carbon

I-1-3) The difference between carbon and activated carbon:

There are many differences between carbon and activated carbon (Charcoal and Activated Charcoal) , including the difference in the method of production, structure and areas of use, and the following table summarizes some of these differences: [4]

table The difference between carbon and activated carbon

Parameters of comparison	Charcoal	Activated Charcoal
Process	Charcoal is obtained by burning wood, or other organic materials, at high temperatures and in the absence of oxygen.	Activated charcoal is the residue obtained by burning carbon-rich materials at high temperatures, with the addition of other substances.
Heating temperature	Compared to the temperatures required to burn and produce activated charcoal, the heat needed to burn charcoal is lesser.	More heat is needed for the production of activated charcoal in comparison to standard charcoal .
Properties/ Structure	standard charcoal has properties such as low density and low porosity, bad conductivity of heat and electricity.	Activated charcoal has a greater surface area, and that makes it an excellent absorbent in comparison to standard charcoal.
Purpose/Uses	Charcoal is used in areas such as cooking products and some medicines.	Activated charcoal is used in many fields such as water treatment, gas purification, some medical uses, and others.
Porous structure	The internal structure of standard charcoal makes it less porous in comparison to activated charcoal.	the considerable surface area of activated charcoal makes it highly porous.

I-1-4) Manufacture of activated carbon:

I-1-4-1) Carbonization :

" is the process of taking a carbon-rich piece of material and converting it to pure carbon through heating. This heating process, called pyrolysis, comes from an ancient technique for making charcoal. Very dense carbonaceous material is used in the beginning, because the end result needs to be extra-porous for activated carbon purposes. Carbon-rich material is placed in a small (relative to the amount of material) furnace and cooked at extreme temperatures topping 2000 degrees Celsius. What remains is usually 20-30 percent of the beginning weight, and consists of mostly carbon and a small percentage of inorganic ash."[5]

I-1-4-2) Gas Treatment :

Commercially used physical activation is a two-step process that involves the process of carbonization (pyrolysis) in a neutral atmosphere and then activation in atmospheric oxidation gases such as steam, carbon dioxide, nitrogen, or air mixtures with an increase in temperature in the range of 800-1100 ° C. This method with the ability to produce activated carbon has a porous structure with good properties, and it is an inexpensive way to prepare activated carbon and it is considered an environmentally friendly method because it is free of chemicals. However, the main disadvantages of the activated carbon's physical activation process are the long activation period, low absorption capacity and high energy consumption.[5]

I-1-4-3) Chemical Treatment:

Chemical activation is usually used for raw materials that contain cellulose, such as wood, sawdust, or fruit peels. In the chemical activation of the active carbon preparation, the activation takes place in the presence of chemicals at high temperatures, where the activation can occur at temperatures ranging from 400 to 900 degrees Celsius, these activating agents with deep penetration into the carbon structure lead to the development of small pores in the carbon The activated carbon, thus increasing its surface area, ultimately the activated carbon is obtained from repeated washing of the resulting mixture[5]

I-1-5) Uses of activated carbon:

- ✓ **Medical applications :**

Activated carbon is widely used to treat drug overdoses and poisonings. Additionally, activated carbon capsules or tablets can be purchased to relieve problems such as indigestion and diarrhea.

- ✓ **Industrial applications :**

Activated carbon is used in a wide range of industrial applications. Like metal finishing, activated carbon is the primary refining agent to remove impurities from metals such as nickel.

- ✓ **Agricultural applications:**

Farmers use activated carbon in animal and agricultural production, with activated carbon acting as an additive to animal feed, a natural pesticide, and disinfectant.

- ✓ **Environmental applications:**

Due to its high surface area and absorbency potential, activated carbon has a wide range of environmental uses. It is useful in treating groundwater and wastewater.

- ✓ **Cosmetic applications**

Activated carbon is now a popular ingredient in shampoos, toothpaste, and face masks. It also locks in toxins and pollutants so that they can be washed off easily.

- ✓ **Water Purification**

One of the main uses for activated carbon is water purification. activated carbon filters are used in all treatment plants, large and small, to remove impurities from drinking water, either on a large scale or at the house .

- ✓ **Air and gas purification**

Activated carbon removes odors, pollutants and volatile organic compounds from the air by trapping gas molecules and removing them efficiently, as activated carbon filters are used for this purpose.[6]

I-2)the Clay:

I-2-1) Definition:

Clay is small particles (less than 0.002 mm) formed as a result of natural factors and rock erosion, consisting mainly of alumina and silica, and it is found in most types of soil, and we can find it in different colors depending on the materials in it, and the clay has many uses in different fields.

figure I.4 :some types of clay

I-2-2) Clay minerals:

I-2-2-1) Definition:

Clay belongs to a certain group of minerals called clay minerals, which are secondary minerals based on aluminum silicate and some other minerals, most of which have a crystalline shape, and they all consist of thin layers of regular shape.[7]

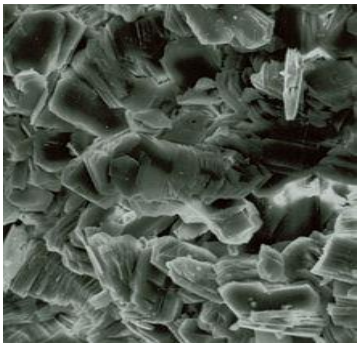


figure I.5 :Kaolinite structure Ref:wikipedia

I-2-2-2) Characteristics of clay minerals:

- **The structure of clay minerals:**

The size and shape of the clay minerals are determined by an electron microscope. The structure of the clay minerals varies according to their type, so we find, for example, well crystallized kaolinite in the form of well-formed six-sided flakes, often with prominent elongation in one direction. We find some of them in the form of tube units, and we find some in the form of irregular shaped scales that are grouped together in irregular groups. [8]

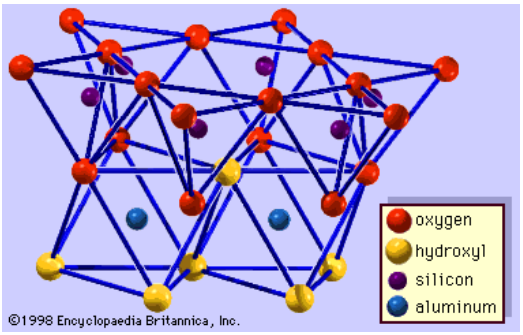


figure I.6 :Crystal structure of clay Ref : Encyclopedia Britannica

- **ion exchange :**

Due to the imbalance in the positive or negative charge balance of clay minerals, it is able to adsorb some cations and anions and keep them around the outer part of the structural unit through ion exchange, and the exchange capacity depends on the size and nature of the particles and the pH value, and the ion exchange of clay is one of the most important its characteristics . It specifies the physical properties and economic use of clay minerals. [8]

- **Clay-water relations:**

Clay minerals have the ability to absorb water due to their ability to expand. This water can be removed by heating to temperatures ranging from 100 to 200 degrees Celsius. [8]

- **High temperature reactions:**

At high temperatures, the mineral structure of the clay can be modified and new phases formed. Information about high temperature reactions is important in the ceramic industry.[8]

- **Interaction of clay with organic matter:**

The ability of clay to interact with organic materials can be used to detect some of its minerals, for example the mineral montmorillonite can be identified by x-ray after treatment

with glycerol, as well as there are organic materials that give the clay a distinctive color when interacting with it, which makes it easy to identify.[9]

I-2-2-3) Classification of clay minerals:

Clay minerals have been divided into two main groups:

- **Amorphous:**

It is called the Allophene group, as it appears amorphous when exposed to x-rays, as its building blocks are present together in an irregular shape, and Allophene is a fine white substance consisting mainly of silica, alumina and water.[7]

- **Crystallized:**

So that it is divided according to the number of layers and the type of the crystal system, and it includes three groups:[7]

✓ **The first group:**

Silicon tetrahydra is linked to the aluminum octahidra plate, forming clay minerals of type 1: 1 such as kaolinite and halocite.

✓ **The second group:**

the association of two silicon tetrahydra plates with the aluminum octahidra plate, forming clay minerals of the 1: 2 stratigraphic type. Examples include smectite and illite.

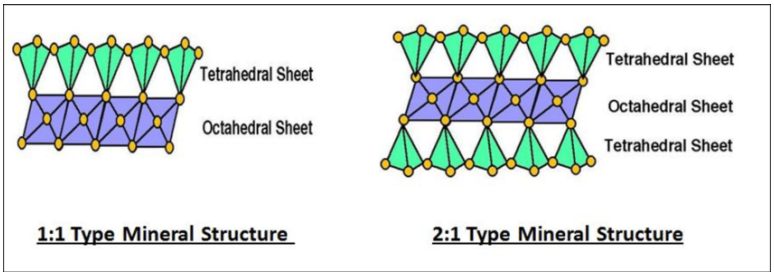


figure I.7 : Type mineral structure 1: 1 and 1: 2

- ✓ **The third group:**

It consists of an octagonal plate of aluminum located between two units of type 1: 2. To form the lamellar clay minerals of the overlapping stratigraphic type 1: 1: 2. The chlorite group, for example .

I-2-2-3) Naming clay minerals:[9]

- **Allophene :** It includes all amorphous clay minerals regardless of composition.
- **kaolinite group**: It includes three distinct minerals: kaolinite, nacrite, and dicite.
- **The haylocyte group:** It is found in two types, one of which has the same chemical composition as kaolinite, and the other contains a greater percentage of water in its composition, and the first is called methaaloysite, and the second is called Endelite.
- **Montmorillonite group:** This group is characterized by the property of expansion when absorbing water, and it includes a type rich in iron called nontronite, and a type rich in magnesium called soaponite.
- **Vermiculite group:** It is characterized by the property of expansion, but it is in a lesser proportion compared to Montmorillonite., and its grains are larger.
- **Ellite group:** its composition does not show expansion properties, and it includes all clay minerals that resemble mica.
- **Chlorite group:** its difficult to distinguish from kaolin. It consists of single layers of biotite and layers of brosite, and is characterized by a uniform structure.

I-2-3-1) Clay applications:

Clay has many applications in different fields, including:[10,11]

- **Farming:**

Clay soil particles are compact in nature, therefore, not all plants can be grown with them. However, clay soil can be used to grow many types of plants by adding different types of gypsum and compost. These plants can then benefit from the clay's nutrients and moisture content.

- **Building:**

  Since ancient times, clay soil has been used in construction due to its properties, as it has been used in buildings and the manufacture of heat-resistant furnaces and many other structures.

- **Ceramic:**

After adding water to the clay soil, a malleable substance is formed. They can be used to make utensils, tubes and other useful things that can be used for household purposes. Clay is also used to make ceramic tiles that can be used for floors and walls.

- **Pottery:**

The use of clay in pottery was known since ancient times, when the clay was mixed with water and then a thick lump was formed. Then the thick mass is formed into various other pots and shapes. The cast structures are then inserted into the oven, where the clay must be heated slowly so that the moisture does not remove too quickly.

- **Medical:**

In the field of folk medicine, the minerals of clay soil have been used to treat stomach disorders and wound inflammation, and clay soil contains minerals with antimicrobial properties that are effective in killing antibiotic-resistant bacteria, and clay minerals can also be used to produce inexpensive medicines to treat infections.

- **Using clay as an adsorbent:**

Due to the unique properties of clay and its ability to exchange ions and its abundance in nature, it is considered one of the most common adsorbents. Clay can remove approximately 70% of water waste in a water removal system. Clay is also used to remove various minerals, organic compounds and pigments.[11]

I-3) the dyes:

I-3-1) Historical glimpse:

People have known dyeing since ancient times, and there is evidence of the diversity of natural products that use dyes, and dyed fabrics were found in the graves of the ancient

Egyptians, which indicates the experience of the Pharaohs in dyeing since the third millennium BC, as well as archaeological evidence showed the use of dyeing more than 5000 years ago, especially In India and the Middle East. The dye was most often obtained from plants, animals, or minerals, without or with minor modifications. Plants were the main source of pigments and were extracted from roots, fruit, bark, leaves and wood ,nowadays, countless types of high-quality synthetic dyes have appeared, which have contributed to the development of many industrial and food fields.[12]

I-3-2) Definition of dye:

A dye is a substance that may be organic or inorganic compounds, natural or synthetic used to change the color of something, and it has many types and classifications depending on the method of manufacture and field of use[13]

figure I.8 : Some types of dyes

I-3-3) Classification of dyes:

I-3-3-1) By origin:

- **Natural Dyes:**

  Pigments from vegetable, animal and mineral sources. All dyes, until 1856, were extracted from plants, flowers, plant roots, insects, shellfish, and minerals. The problem with making natural dyes is that no two batches can be obtained with identical hues and strengths in any way. Also, color fastness varies widely between natural dyes.[12]

- **synthetic dyes :**

  In 1856 Dr. Perkins discovered by chance the first industrial dye when he was trying unsuccessfully to produce one of the chemical compounds, and industrial dyes are dyes that are produced in an industrial or synthetic way, as these materials have a high

degree of purity, and they include more than 12 groups, including the azo dye. And nitros and others, and it is distinguished by its ability to give a large number of harmonious and bright colors, and industrial colorants are divided into two main groups, the standard shapes which include powder, granules and liquids, and the second group is called the forms with special use and it includes the paint.[14]

I-3-3-2) Chemical classification:[15]

_ Azo colorants

_ Thiazole dyes

_ Indigoid colorants

_ Benzodifuranone dyes

_ Formazan dyes

_ Phthalocyanine colorants

_ Cyanine colorants

_ Xanthene colorants

_ Acridine dyes

_ Indamine, indophenol and lactone dyes

_ Stilbene dyes and fluorescent brighteners

_ Anthraquinone colorants

_ Quinacridone pigments

_ Quinophthalone dyes

_ Aminoketone and hydroxyketone dyes

_ Diphenylmethane and

_ triarylmethane colorants

_ Nitro and nitroso colorants

_ Azine, oxazine and thiazine colorants

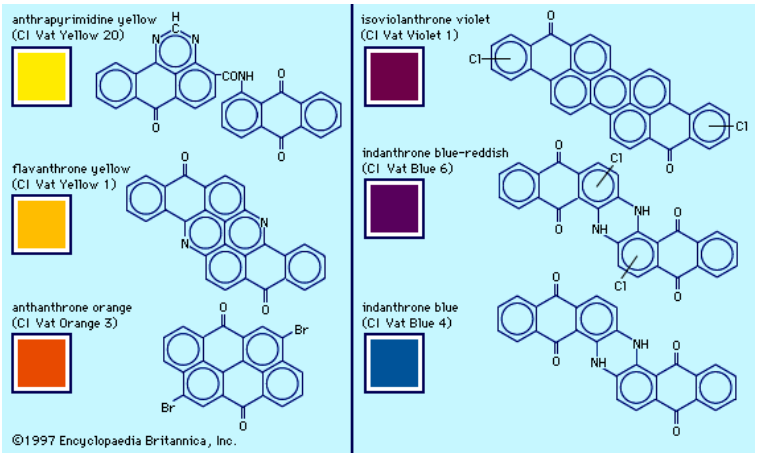


figure I.9 : Examples of anthraquinone pigments . Ref : Encyclopedia Britannica

I-3-3-3) Classification of dyes Based on Application:[16]

- ✓ **Acid Dye :** Acid dyes are very soluble in water, and have better light fastness than basic dyes. Acid dyes are effective for textile fibers such as silk and wool, as well as for nylon and modified acrylic fibers.

- ✓ **Basic dyes :** Basic dyes are used to dye wool, leather, and paper.

- ✓ **Mordant Dye :** These dyes can be applied or fixed to wool or any other textile material with the help of an auxiliary chemical.

- ✓ **Direct dyes :** Direct dyes for cotton, silk and nylon. These dyes are mainly used in products that contain fewer washes, such as shirts, curtains, and the like, as these dyes are easily applied from an aqueous solution, so it is called a direct dye.

- ✓ **AZOIC DYES :** It is usually a dye for all natural fibers and is not sold as a "final dye" but in the form of its ingredients (insoluble azo base and fast color coupling compound) that combine on the fibers to produce an azo dye with exceptional stability properties.

- ✓ **VAT DYES:** These dyes are used especially in dyeing cellulose fibers to give the best properties of color stability.

- ✓ **Sulphur dye:** Water insoluble pigments, specially used to obtain faded colors in an economical way. It is specially used to dye cellulose fibers.

- ✓ **Reactive dyes:** Reactive dyes are used when bright dyeing with high luminance and washing fastness is required. It is mainly used to dye cotton, linen and cellulose fiber

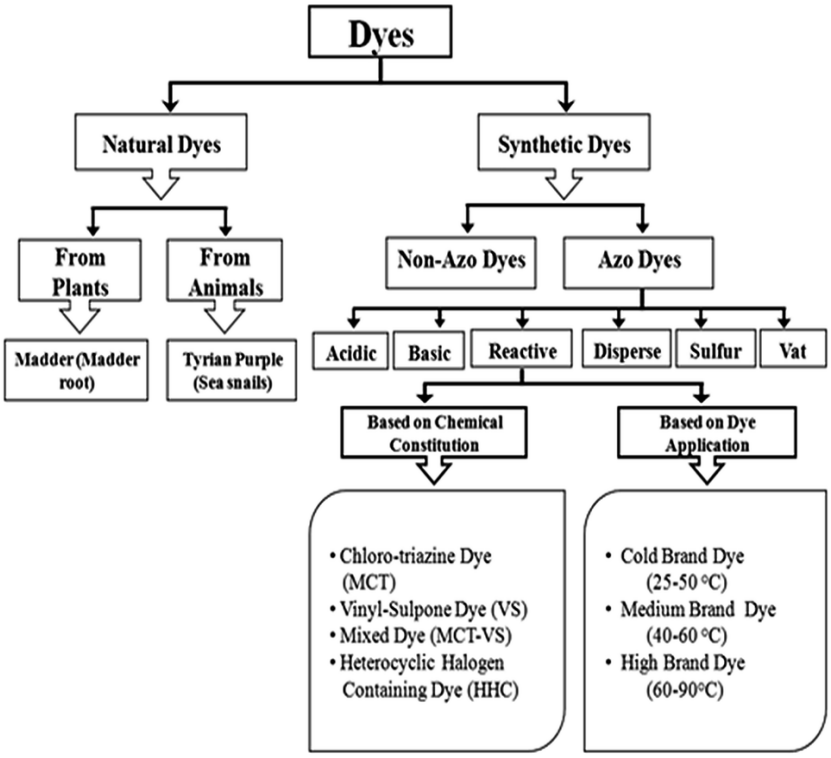


figure I.10 : Classification of dyes

I-3-4) Carmine dye :

Carmine or E120 is a bright red pigment that can be obtained from keraminic acid, which is produced by some scale insects such as cochineal, and is used as a food color for many foods as well as in other industries.[12]

figure I.11 : Carmine dye

I-3-4-1) Uses of carmine dye:

Carmine dye has many uses, as it is used as a food colorant.It includes several products such as meat coloring, drink , various jams and gelatin, candy coloring and many more, It is

also used in cosmetics such as lipstick, and in the textile field, it is used to color fabrics and carpets, and it can also be used in the field of arts and painting.[12]

I-3-4-2) Manufacturing method:

To prepare the carmine, the powder of the bodies of the insect is boiled in ammonia or sodium carbonate solution, and the sediments are removed by filtration ,The alum is added to the clear brine For carminic acid to precipitate red aluminum salt, the color is pure when it is devoid of iron ions, and we can add chloride Tin, citric acid, or gelatin to control the nature of the precipitate. Calcium carbonate is added To alum in order to obtain purple hues.[12]

figure I.12 : Cochineal. Ref: https://chie.xyz/310

I-3-5) The effect of pollution with dyes:[17]

- The color associated with textile dyes causes aesthetic damage to water bodies .It prevents the penetration of light through the water, which leads to a decrease in the rate of photosynthesis and levels of dissolved oxygen affecting the entire aquatic organism.
- Increased demand for biochemical and chemical oxygen (BOD and COD), due to the increased concentration of non-degradable organic matter.
- Dyes act as toxic, mutagenic and carcinogenic agents.
- Affects the food chains, which leads to the transmission of pollution throughout the food chain.
- The use of contaminated dyes in agriculture has a very negative impact on the microbial communities in the soil, In addition to its negative impact on plant growth.
- It causes accumulation of dyes in sediments and soils Its move to public water supply systems.

figure I.13 : Water pollution caused by textile dyes

Chapter II:

Adsorption

Chapter II): Adsorption

The phenomenon of adsorption is one of the most important natural phenomena, and that is because it is used in many industrial fields such as the industries of petroleum, oils, dyes, and others, in addition to that, it is also used in purifying water and air, so the study of adsorption is a very important matter.

In this chapter, we will learn about adsorption, its definition, types, uses, forms of isotherms and methods for their mathematical modeling.

II-1) Definition of Adsorption :

Adsorption is the collect of a substance, whether in the form of atoms, molecules, or ions, which we call absorbent on the surface of another substance called adsorbate , and the cause of adsorption is either due to physical forces or due to the formation of chemical bonds, depending on the type of adsorption, and the reverse process of absorption is called desorption.[18]

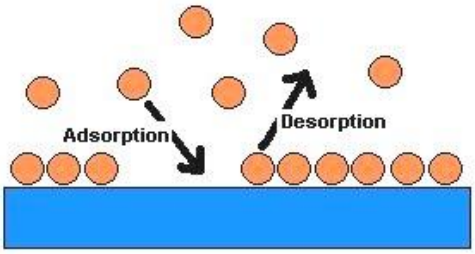


figure II.1 The difference between adsorption and desorption

II-2) The difference between adsorption absorption :

Adsorption is a process that occurs when a gas, liquid, or solute material collects on the surface of another material, forming a molecular or atomic layer (absorbent material). As for absorption, it is the spread of one substance inside another. This means that the main difference is that in adsorption the absorbed particles are attracted to the outer surface of the particle, whereas in absorption they are physically incorporated into the particle structure. In addition, adsorption is an exothermic process while absorption is an endothermic process.[18,19]

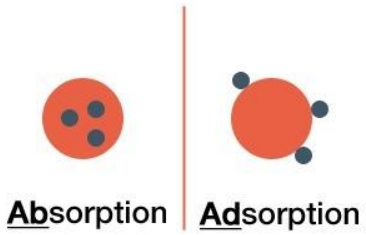


figure II.2: The difference between adsorption and absorption

II-3) Types of adsorption :

II-3-1) Physical adsorption :

It is the adsorption process by which the particles of a substance stick to the surface of another substance through the forces of natural attraction or van der Waals forces, and it is a reversible process, which is similar to the condensation of a substance's vapor on the liquid surface of the same material**.** [18]

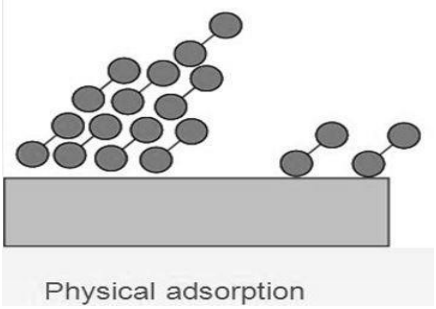


figure II.3: physical adsorbtion

II-3-2) Chemical adsorption:

In this type of adsorption, chemical bonds are formed between the adsorbent and the adsorbat, and thus it is irreversible, and it is characterized by the formation of only one layer of the material molecules that have been adsorbed on the surface. [18]

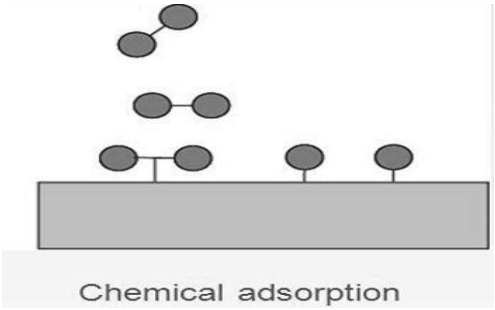


figure II.4: chemical adsorbtion

II-3-3) The difference between physical and chemical adsorption :

Physical adsorption is similar to condensation of gases into liquids and depends on the physical attraction force or van der Waals force between the solid adsorbents and the adsorbed molecules while chemical adsorption depends on the formation of chemical bonds. . Chemical adsorption usually occurs at temperatures higher than those at physical adsorption. Moreover, chemical adsorption is usually a slower process than physical adsorption, and often requires activation energy. In physical adsorption, several layers of adsorbed molecules can accumulate on the adsorption surface while in chemical adsorption only one layer is formed. [20]

II-4) Adsorption applications:

The adsorption process has many applications, whether in the industrial field or in practical applications, and we mention for example:[21]

- ✓ Gas masks.
- ✓ Purify the air from toxic gases.
- ✓ The use of the phenomenon of adsorption to catalyze some chemical reactions.
- ✓ Get rid of pollutants and dyes in solutions.
- ✓ Petroleum refining.
- ✓ Chromatographic separation.
- ✓ Control and absorption of moisture.

II-5) Adsorption isotherm:

The adsorption isotherm is a representation of the amount of material absorbed on a substrate (solid, liquid, or gas) as a function of the equilibrium concentration remaining after adsorption, at a constant temperature. Isotherm is useful for obtaining information on the nature of adsorption.[22]

II-5-1) Types of adsorption isotherms:

Isothermal is classified according to the experimental results into five types, and this classification helps us to know the nature of adsorption, is it monolayer or multilayer, and thus know the mathematical model that describes it.

In these five classifications, the presence of a flat region in the curve indicates a monolayer adsorption.[22]

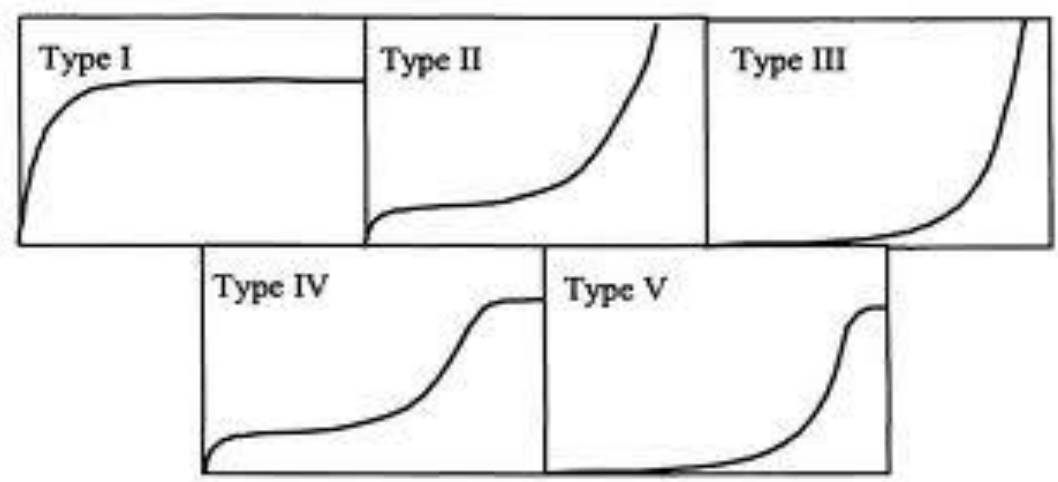


figure II.5: Types of adsorption isotherms .Ref: wikibedia.

Where:

- The first type - monolayer adsorption .
- The second and third types - multilayer adsorption .
- The fourth and fifth types show the phenomenon of gas capillary condensation .

II-5-2) Adsorption isotherm models:

There are several mathematical models that describe adsorption isotherms, depending on the nature of the adsorption:

II-5-2-1) Freundlich Adsorption Isotherm:

In 1909, Friendlich proposed an empirical equation describing the change in the amount of gas that was adsorbed per unit mass of the adsorbent in terms of the change in gas concentration

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Where :

- x/m = adsorption per gram of adsorbent
- P is Pressure, k and n are constants whose values depend upon adsorbent and adsorbate at particular temperature (In liquids, we replace pressure p with a concentration of c)

Freundlich Isotherm accurately describes the relationship of adsorption to pressure (or concentration) at low values, except that it fails to predict the value of adsorption at high pressure We notice from the graph that D increases with increasing pressure P (or concentration C) .[22]

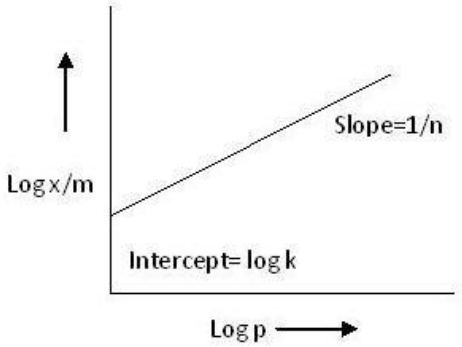


figure II.6: Freundlich Isotherm

II-5-2-2) Langmuir Isotherm:

In 1916, Irving Langmuir published a new model describing the adsorption of gases on a solid surface at constant temperature, a quasi-experimental isothermal derived from a proposed mechanism for the motion of particles. This isotherm was based on various assumptions.It is based on four assumptions:

- ✓ The surface of the adsorbents is homogeneous. All adsorption sites are equivalent
- ✓ The adsorbed molecules do not interact with each other
- ✓ All adsorption occurs through the same mechanism.
- ✓ At maximum adsorption only a single layer is formed: so that no new molecules accumulate on other molecules that have been adsorbed,

Based on the previous theory, Langmuir extracted an equation explaining the relationship between the number of active sites of the surface that undergoes adsorption and pressure or concentration. This equation is called the Langmuir equation. [22]

$$\theta = \frac{KP}{1+KP}$$

Where :

- θ = number of surface sites covered with adsorbed particles.
- P = pressure (substituted for concentration in the case of liquids)
- K = is the equilibrium constant of the adsorbent distribution between the surface and phase of a gas (or liquid).

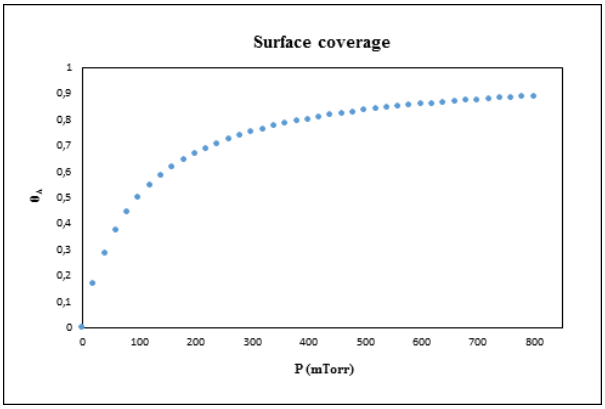


figure II.7: Langmuir Isotherm. Ref: en.wikipedia

II-5-2-3) BET isotherm :

In 1938 Brunauer, Emmett, and Teller developed a theory for the calculation of multilayer absorption (BET isotherm), which remains the most important equation for characterizing porous solids, mainly due to its simplicity, and it is based on the Langmuir isotherm, allowing it to describe monolayer adsorption also.[23,24]

$$\frac{P/P_0}{n(1-P/P_0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}(P/P_0)$$

where :

- n is the specific amount of the adsorbed at the relative pressure P/P0.
- n_m is the monolayer capacity of the adsorbed gas.
- P is the pressure, P0 is the saturation pressure of a substance being adsorbed at the adsorption temperature.
- C is the BET constant which is exponentially related to the energy of monolayer adsorption.

Chapter III)
physicochemical methods of analysis

Chapter III) physicochemical methods of analysis

In this chapter, we will be introduced to the various physical and chemical methods, through which we will study the phenomenon of adsorption, and the clay and activated carbon samples that we used.

This chapter includes the principle of work and areas of use for each of:

- ph meter
- Spectrophotometer
- Diffractometer

III.1)PH meter :

PH, which is a quantitative measure of the acidity or basicity of aqueous solutions or other liquids, translates hydrogen ion concentration values into numbers between 0 and 14. In pure water, which is neutral (neither acid nor alkaline), the hydrogen ion concentration is equivalent to 10-7 grams each Liters, it corresponds to a pH of 7, and a solution with a pH of less than 7 is considered acidic; A solution with a pH greater than 7 is considered basic or acidic [25]

III-1-1) Definition :

A pH meter is a device by which we determine the pH of a solution. It is also called a "potentiometric pH meter" because it measures the potential difference between the pH electrode and the reference electrode. [25]

figure III.1: PH meter

III-1-2) principle:

PH meter, an electrical device used to measure hydrogen ion activity, that is, it measures the acidity and basicity of a solution. The pH meter consists of a voltmeter connected to a pH-responsive electrode and a reference electrode. The pH influence electrode is usually glass, and the reference electrode is usually silver chloride electrode, when the electrodes are immersed in the solution, it works as a battery. The glass electrode develops an electrical potential (charge) that is directly related to the activity of the hydrogen ion in the solution (59.2 millivolts per pH unit at 25 ° C), and the voltmeter measures the potential difference between the glass and the reference electrodes, which is converted into numerical values of the pH. [25]

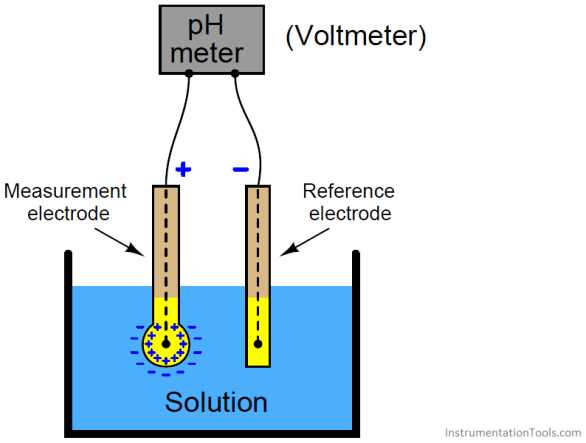


figure III.2: PH meter principle

III-1-3) applications :

- ✓ It is used to measure water quality for municipal water supplies In agriculture industries, it is used to measure the pH of soil.
- ✓ In many chemical and pharmaceutical industries, it is used to measure the pH value of solutions.
- ✓ The pH meter is used in the food industry such as dairy products like cheese, curds, yogurt, etc.
- ✓ The pH measurement is an important factor in detergent production

It is used for monitoring the pH level in water treatment plants and reverse osmosis water purifiers [26]

III-2)Spectrophotometer :

III-2-1) Definition :

A spectrophotometer is an instrument that measures the intensity of light absorbed by a sample solution after passing a light beam through it. this enables us to know some properties of the studied substance, such as concentration.

Spectrophotometers are classified according to the wavelength range of the light source into two types, where the first type uses light above the ultraviolet range (185-400 nm) and the visible range (400-700 nm) of the electromagnetic radiation spectrum, and it is called the UV-visible spectrophotometer, while the second type uses light over the infrared range (700-15000 nanometers) of the electromagnetic radiation spectrum, it is called an IR spectrophotometer.[27]

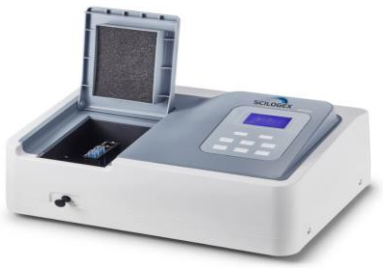


figure III.3: Spectrophotometer

III-2-2)Working principle :

To understand the principle of the device, we must know its components, namely:

It consists of a light source, a collimator (lens), a monochromator (prism), a wavelength selector, a cuvette for sample solution, a photoelectric detector, and a digital display.

In general, we can say that a spectrophotometer consists of two devices, a Spectrometer and a photometer, the spectrometer produces the required wavelength range of light. Where the light source sends a straight beam of light through a lens, then through a monochromator (prism) to divide it into several wavelengths. Then the wavelength selector (slit) transmits only the desired wavelengths, As for the photometer, it determines the amount of light that

the sample has absorbed by comparing it to the amount of remaining light captured by the photometer, and then sends a signal to a digital screen.[27]

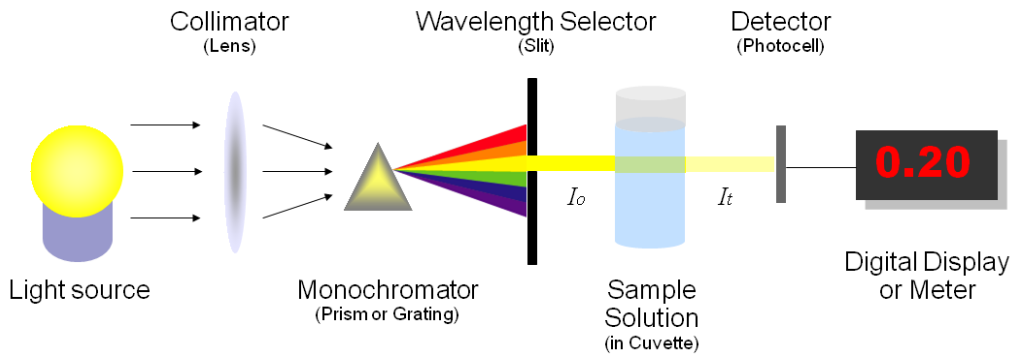


figure III.4: Working principle of Spectrophotometer

And the part of the light that passes through the sample is called the transmittance (T), and it is related to the concentration of the sample and the length of the cuvette. Knowing the light intensity that crosses the sample, we can calculate the transmittance from the following relationship [27]:

$$\textit{Transmittance}\ (T) = \frac{It}{Io}$$

Where:

- $\mathbf{I_t}$ **:** is the light intensity after the beam of light passes through the cuvette
- $\mathbf{I_o}$ **:** is the light intensity before the beam of light passes through the cuvette.

Transmittance is related to absorption by the expression [27]:

$$\textit{Absorbance}\ (A) = -\log(T) = -\log\left(\frac{It}{Io}\right)$$

Where :

***Absorbance*(*A*):** the amount of photons that is absorbed.

Using absorbance and using Beer-Lambert's law, we can calculate the concentration of a sample, where:

$$A = \varepsilon \,.l\,.c$$

Where :

- ***A* :** is the measure of absorbance (no units)
- **ε :** is the molar extinction coefficient or molar absorptivity (or absorption coefficient)
- ***l* :** is the path length
- ***c*:** is the concentration.

III-2-3)Applications :

Spectrophotometers have many applications, whether in the fields of physics, chemistry, biochemistry, etc., and the following are some of these applications[28]:

- ✓ Qualitative analysis :where a spectrophotometer can determine the type of chemical compounds, based on the fact that each substance or compound has a specific absorption spectrum.
- ✓ quantitative analysis :a spectrophotometer can be used to measure the unknown concentration of a compound by measuring the absorption of light.
- ✓ Enzyme assay :In biochemistry, enzymes can be recognized by the absorption spectrum.
- ✓ Determination of molecular weight :the molecular weights of small particles can be determined in this way.
- ✓ With spectrophotometry, it is possible to determine the temperature of the formation of a compound and determine the rates of reaction.

III-3)X-ray diffraction:

III-3-1) Principle :

Diffraction is the irregularity that occurs when waves encounter something. a common phenomenon in everyday activities, the most common type of diffraction in X-ray crystallography is known as Bragg diffraction, which is defined as the scattering of waves from a crystal structure. Depending on the nature of diffraction, waves will experience constructive or destructive interference with other waves. Therefore, some diffracted waves will appear stronger and others will appear weaker, and this mostly depends on the wavelength of the incident beam, and the structure of the sample. Information about the

three-dimensional structure of the crystal lattice of a solid is obtained by measuring the angle of incidence of diffracted waves, observing the changes when changing the wavelength of light and the direction of the crystal, and comparing it with reference data.[29,30]

The Bragg diffraction can be described by the following equation:

$$n\lambda=2d\cdot\sin\theta$$

where:

- n is an integer determined by the order given,
- λ is the wavelength of x-rays
- d is the spacing between the planes in the atomic lattice
- θ is the angle between the incident ray and the scattering planes.

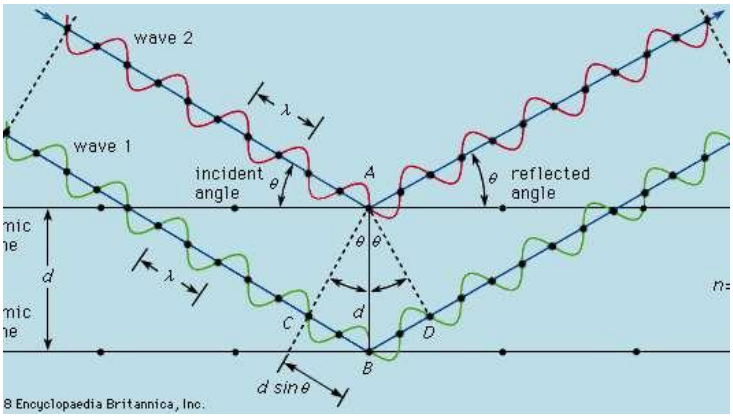


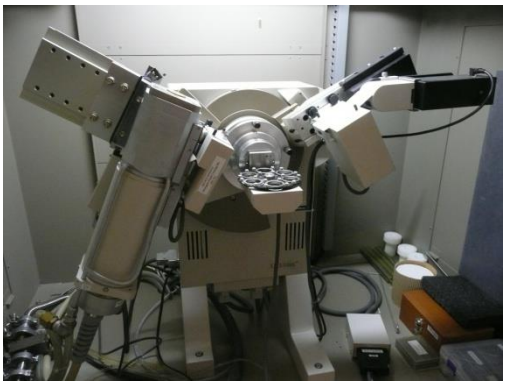
figure III.5: X-ray diffraction Principle Ref: Encyclopedia Britannica

III-3-2)Diffractometer:

A diffractometer is a device that determines the structure of a material by analyzing the diffraction pattern when it interacts with a beam of light. A diffractometer consists of a radiation source, slits to adjust the shape of the beam, a sample, and a detector.

An X-ray source is the basis of any XRD device. , and it is very important that the beam intensity remains constant throughout the entire analysis, otherwise defective data will be obtained. The detector is another important component of X-ray diffractometer. There are two methods for obtaining the diffraction pattern, depending on the type of detector. The first

is called a continuous scan, in which the detector is set in a circular motion around the sample, and the second and more widely used method is known as a step scan. Instead of moving the detector in a circle around the entire sample, stage scanning involves collecting data at one fixed angle at a time,[29]



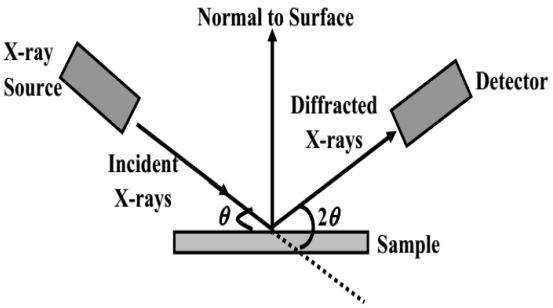


figure III.6: Diffractometer

III-3-3)Applications:

X-ray diffraction is widely used in many applications such as [31]:

- Identification of unknown crystalline materials such as metals and inorganic compounds.
- Characterization of crystalline materials
- Identification of fine-grained minerals such as clay and mixed layers that are difficult to visually identify
- Determine the dimensions of the unit cell
- Measure the purity of the sample

Chapter IV)
The experimental study

Chapter IV) the experimental study

In this chapter, the experimental methodology for studying the adsorption of carmine dye on activated carbon and on clay will be explained, where we will present the tools, devices and materials needed to conduct this study, in addition to explaining how to take and analyze samples, and the effect of changing concentration, temperature and pH will also be studied. And its effect on the adsorption capacity, and all the results obtained will be shown.

IV-1)Devices and materials used:

- **Devices and tools:**
  - Pipettes
  - Beakers
  - Test tubes
  - Balance
  - Funnel
  - volumetric flask
  - Filter paper
  - syringe
  - Test tube rack
  - oven
  - centrifuge
  - ph meter
  - Spectrophotometer
- **Materials:**
  - Activated carbon powder
  - Carmine dye powder
  - HCl and NaoH
  - clay
  - distilled water

IV-2)Spectral properties of adsorbents:

Here we will show previous results to reveal the crystal structures and vibrational energy state of clays and activated carbon particles by XRD and IR devices.

IV-2-1) X-ray diffraction:

The device used is an Xpert Pro (Panalytical) diffractometer using CuKα radiation from copper (λ = 1.5418Å). This diffractometer is equipped with a high temperature chamber (HTK16 Anton Paar) which makes it possible to follow the evolution of the crystal structure during heat treatment.

The spectrum presented in (figure IV.1) make it possible to identify the structure of the adsorbent.

Figure. IV.1 shows the diffractogram of the raw clay, according to the XRD diagram obtained, the clay has a mineralogical composition and inter-layer distances practically identical to bentonite

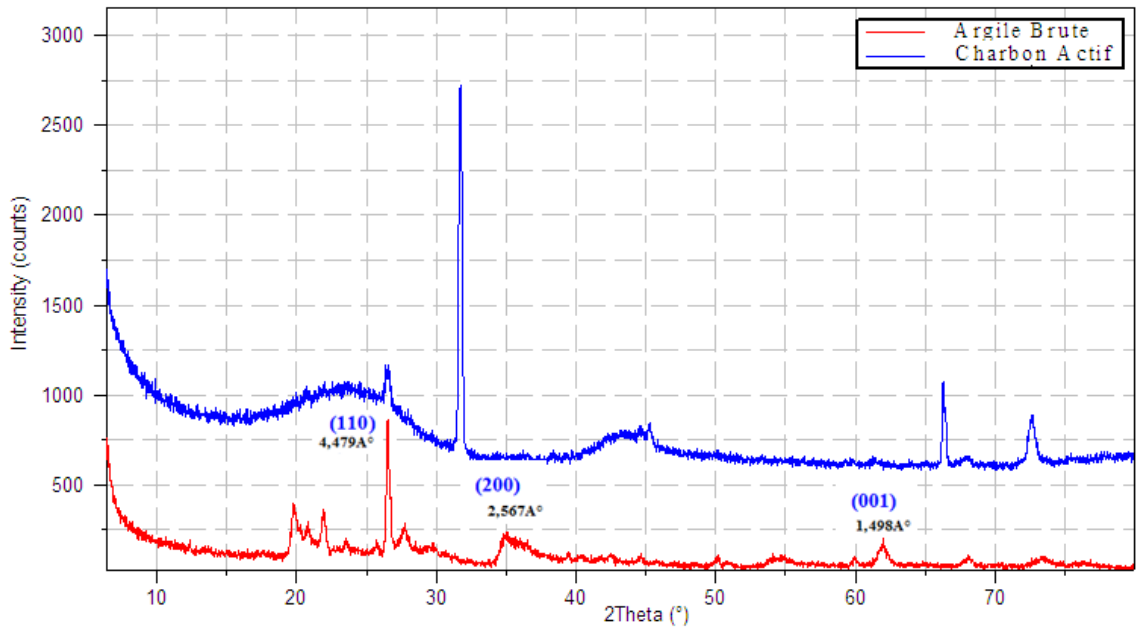


figure IV. 1: Diffractogram of raw clay and activated carbon

Table IV.1: Chemical composition of raw bentonite (Maghnia deposit). [32]

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
%	54.92	16.92	1.95	0.02	4.29	0.71	1.23	0.73	0.05	0.13

From figure IV.1 we can see: Bentonite is characterized by four peaks, the first is located at 15.037 Å (001) and the other three are at 4.479Å (110), 2.567 Å (200) and 1.498Å (001) [33]. This diffractogram shows that the non-clay minerals present in varying amounts from one sample to another are mainly quartz with characteristic reflections at d001 = 3.35 Å and 4.28 Å, calcite (d001 = 3.21 Å), and feldspars (d001 = 4.06 Å) [34].

We also observe in the same figure IV.1 the XRD diffractogram of the activated carbon the presence of a large peak (2Θ = 32 °) indicating to amorphous structure . [35]

IV-2-2)Fourier transform infrared spectroscopy (FTIR):

The raw clay and the activated carbon, dried at 100 ° C / 24h, were analyzed by infrared fourier transform spectroscopy on a SHIMADZU FTIR-8000 spectrometer. The two solids were prepared as a solid mixture (KBr mixture) and analyzed by absorption

The FITR tests confirmed that the analyzed materials have a crystalline structure

The spectra obtained are illustrated by (figure IV.2.) We note:

- Raw clay:

- Two absorption bands located between 3200-3800 cm-1 and between 1600-1700 cm-1:
- The band that spans between 1600-1700 cm-1 may be attributed to the valence vibrations of the OH group of the constituent water, in addition to the binding vibrations of the adsorbed water located at 1646.
- An absorption band centered on 3620 cm-1 is due to the valence vibrations of the OH groups bound to the octahedral Al cations (Al-OH-Al) [4].
- The Si-O bond is characterized by:
- The intense band located between 900-1200 cm-1 and center around 1008.9 cm-1 corresponds to the valence vibrations of the Si-O bond [36].

- The bands between 795 and 748 cm-1, coming from the Si-O-Al bond, also give way to a band around 778.4 cm-1

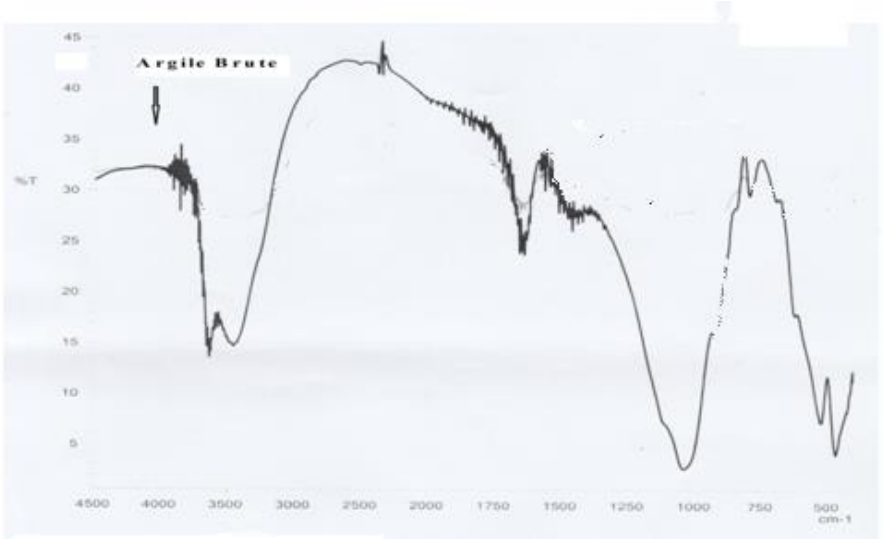


figure IV.2:IR spectrum of raw clay

IV-3) Physical and chemical properties of Carmine dye:

Carmine is a bright red pigment that can be obtained from carminic acid, which is produced by some scale insects such as cochineal. Carmine pigment is used in the manufacture of food colorings, medicines and cosmetics, and many other uses[12].

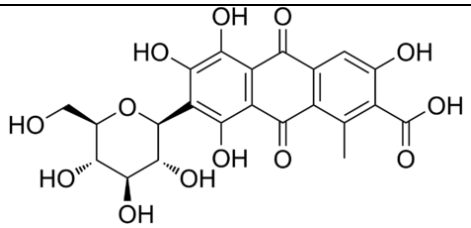
Carmine dye	
Molecular Formula	$C_{22}H_{20}O_{13}$
Structure	
Molecular Weight	492.4g/mol
Synonyms	➢ carminic acid ➢ Cochineal Dye ➢ Natural Red 4 ➢ C.I. 75470

Table IV.2: properties of Carmine dye[37]

IV-4) Preparation of the standard solution of carmine dye:

A solution of carmine dye with a concentration of 1250 mg/l was prepared by dissolving 625 mg of dye powder in 500 ml of distilled water, then dilating the resulting solution to obtain standard solutions of 5 ml volume, with concentration ranging from 62 mg/l to 625 mg/l.

IV-4-1)Plotting the calibration curve:

Using a spectrophotometer, the absorbance of the primary dye solution was measured and the maximum wavelength was obtained, i = 493 nm. Then we measured the absorbance of the dilute standard solutions at the previous wavelength to obtain the calibration curve, which represents the absorbance in terms of changing concentrations, where the following relationship was obtained:

$$Abs=0.001C+0.008$$

Where :

- Abs :Absorbance
- C : concentration (mg/l)

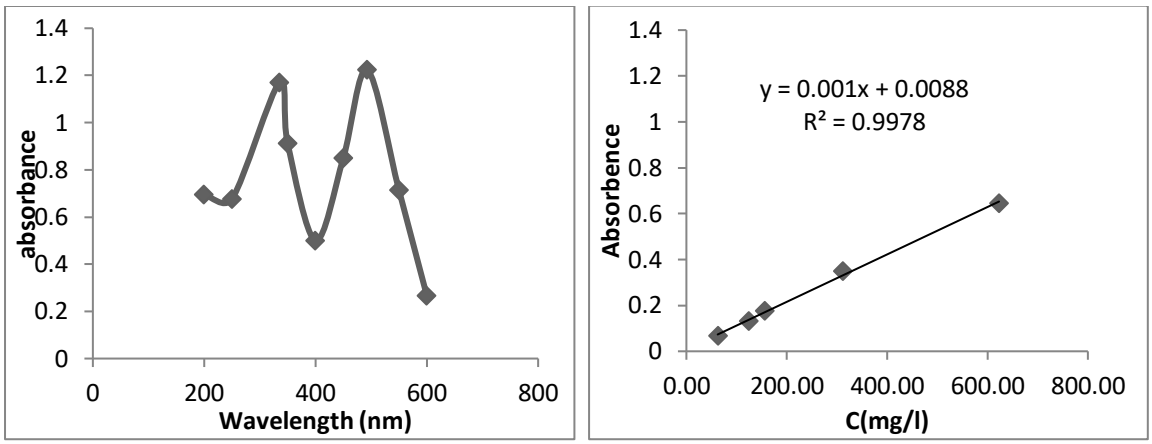


figure IV.3:Absorbance and calibration curves

IV-5)the used relations:

✓ Adsorption Calculation:

$$Qe = (C0 - Ce) \times \frac{V}{m}$$

Where :

- Qe: adsorption ratio (mg/g)
- C0: Initial concentration (concentration of dilute standard solutions) (mg/l)
- Ce: equilibrium concentration of the liquid phase (the residual concentration of the dye in the solution after equilibrium) (mg/l)
- V: the volume of the solution in the sample (L)
- m: Adsorbent mass(g)

We can extract Ce from the calibration curve or calculate it from the Beer-Lambert equation:

$$Abs = \varepsilon . l . c$$

Where :

ε : is the molar absorption coefficient in L/mol.cm

l: is the optical path length in cm

In the case of the dye we used, we calculate Ce:

$$Ce=\frac{Abs}{\varepsilon .l}\ (mol/l) = Ce\ (mol/l)\times 492.48\times 1000\ (mg/l)$$

- ✓ **Calculate the Decolorization (T%):**

$$T\% = \frac{(C0-Ce)}{C0}\times 100$$

IV-6) Study of the factors affecting the adsorption process:

The factors whose effect on adsorption has been studied are the effect of initial concentration, the effect of pH, the effect of temperature, the effect of contact time.

This was done by preparing standard solutions in a volume of 5 ml of dye solution with varying concentrations from 62 mg / l to 625 mg / l with a mass of adorbents (activated carbon and clay) ranging from 0.1 g to 0.006 g per 5 ml of the previous solutions and then, studying The effect of changing the previously mentioned factors. where:

- The effect of the initial concentration is studied by measuring the adsorption ratio when we put a fixed mass of adsorbent with different concentrations of dye.
- The effect of contact time is studied by measuring the adsorption rate of the previous solutions in different time periods.
- The effect of changing the pH is studied by measuring the adsorption rate of the previous solutions at different values of pH, and in order to change the pH values we use a solution of HCl and NaoH
- The effect of temperature is studied by measuring the adsorption rate at variable temperatures.

IV-6-1) Initial concentration effect:

To do this, we put a fixed mass of activated carbon, m = 100 mg, in each of the standard solutions of the dye with different initial concentrations (625, 312, 62 mg) and a volume of 5 ml at a constant pH and temperature, and after the end of the experiment the samples are

placed in a centrifuge for 4 minutes at 2500 rpm, Then we filter the solutions and measure the absorption ratio with a spectrophotometer and calculate the adsorption ratio after that, and the same previous steps for the bentonite clay. The following figure shows the results:

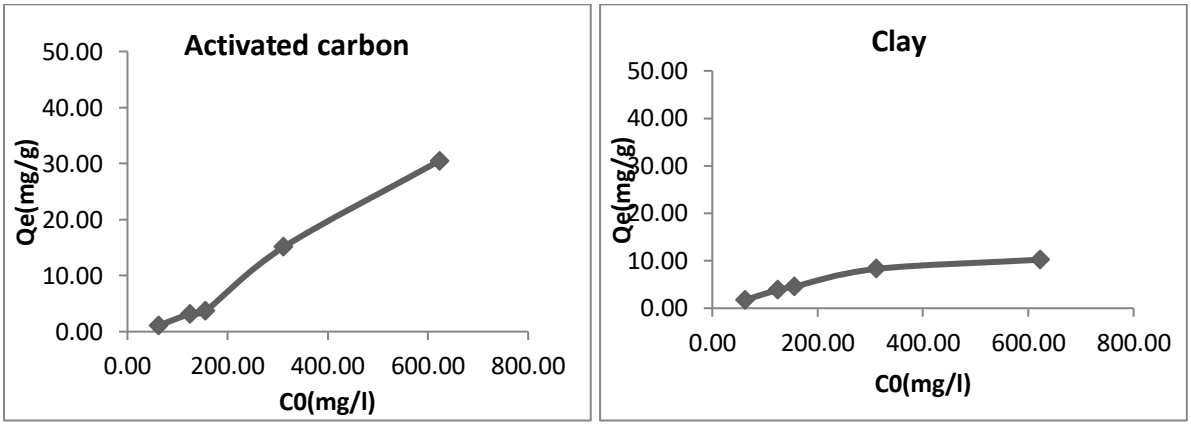


figure IV.4: Initial concentration effect

Where we note that the higher the initial concentration, the greater the adsorption capacity to reach a maximum value at the highest concentration (30 mg/g for activated carbon and 10 mg/g for clay, and that is at a concentration of 623 mg/l).

We can also note the difference in the adsorption capacity between activated carbon and bentonite clay, as it is greater in the first than in the second.

This result is due to the fact that the large concentration of the dye in the solution necessarily means a larger number of its molecules, which will increase the number of collisions between it and the surface of the adsorbent material and thus enhance the chance of its bonding to its surface, unlike low concentrations. In addition, the large adsorption capacity of activated carbon compared to clay is due to its large surface area, which can absorb more pollutant particles than clay.

IV-6-2)The effect of contact time:

To measure the effect of contact time, we prepared the solutions in the same way as before, where we put a fixed mass of activated carbon m = 100mg with different concentrations of dye, ph value and temperature constant, and we took the results during different time periods

(2, 4, 6, 8, 24 h), where the lowest concentration corresponds to the lowest period of time, and the same for clay. After placing the samples in a centrifuge, filtering them and measuring the absorbance, we obtained the results represented in the figure.

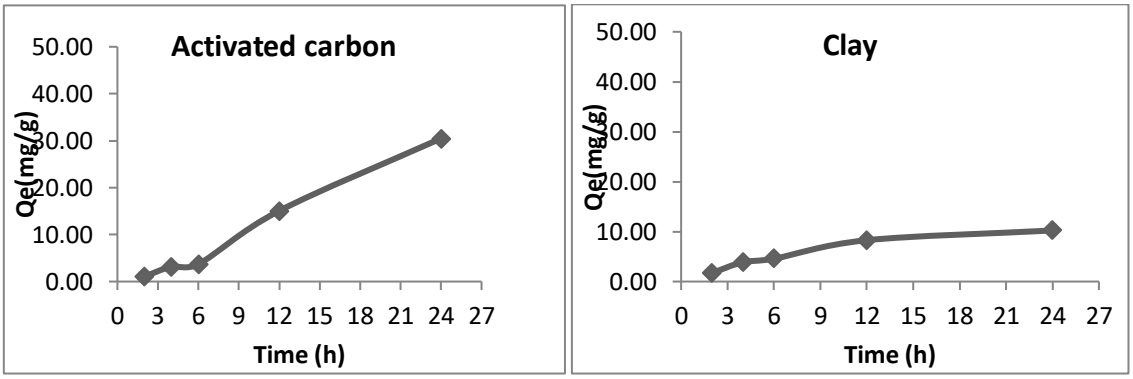


figure IV.5: effect of contact time

As the contact time increases, the adsorption capacity increases, and we also notice a similarity in the adsorption capacity between activated carbon and bentonite clay in the range of low dye concentrations, but soon the contrast appears between them in the range of large concentrations and the longer contact time.

This is due to the fact that the adsorption process does not occur immediately, since in porous materials adsorption occurs first on the available sites on the outer surface, and then on the surface of the inner pores, which takes longer time.[18]

IV-6-3)The effect of changing the pH:

To do this, we put a fixed mass of activated carbon m = 0.025 g in 5 ml of the dye solution at a constant concentration of 155 mg/l, at a constant time and temperature, and at different pH values (4; 6 and 10), and in the same way for the clay. After placing the samples in a centrifuge, filtering them and measuring the absorbance, we obtained the results represented in the figure IV.6.

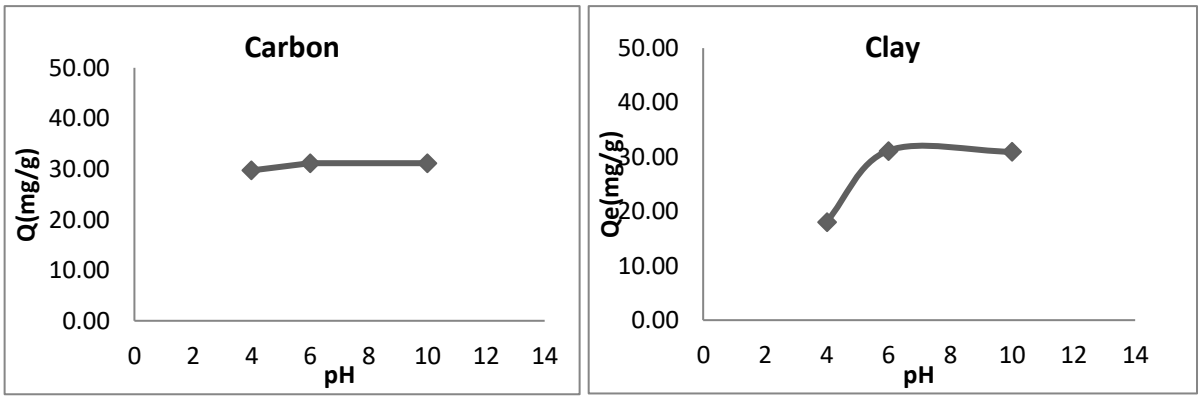


figure IV.6:The effect of changing the pH

Where for clay, we can observe an increase in the adsorption capacity with an increase in the pH value and that is in the range [4,6] and then tends to settle at a value close to 30 mg/g in the moderate and basic range, As for activated carbon, the adsorption capacity appears to be more stable with the change in pH, as the value of the adsorption capacity in the acidic, moderate and basic ranges is close to 30 mg/g, with a slight increase in it in the acidic range. In addition, there is a discrepancy in the adsorption capacity between carbon Activated and bentonite clay and that are in the acidic range where they are greater in carbon compared to clay.

The reason for the weak adsorption capacity in the acidic field is due to the presence of hydrogen ions H+ in a large amount that competes with the dye molecules for adsorption sites, In addition, bentonite clay is more affected by these ions due to the properties of clay that differ from activated carbon in terms of the nature of the charges on its surface. we note the absence of this effect with the absence of hydrogen ions in the moderate and basic range where the adsorption capacity is large and more stable.

IV-6-4)The effect of changing the temperature:

To measure the effect of temperature on the adsorption process, we prepared standard solutions with a volume of 5 ml and with different concentrations, and we put a different mass for each solution, where the lowest mass of carbon corresponds to the lowest concentration of the dye solution, and we put the previous solutions at different temperatures (25 30 35 35 40 45 degrees) where the lowest temperature corresponds to the lowest concentration, and in the same way with the bentonite clay.

After placing the samples in a centrifuge, filtering them and measuring the absorbance, we obtained the results represented in the figure **IV.7** .

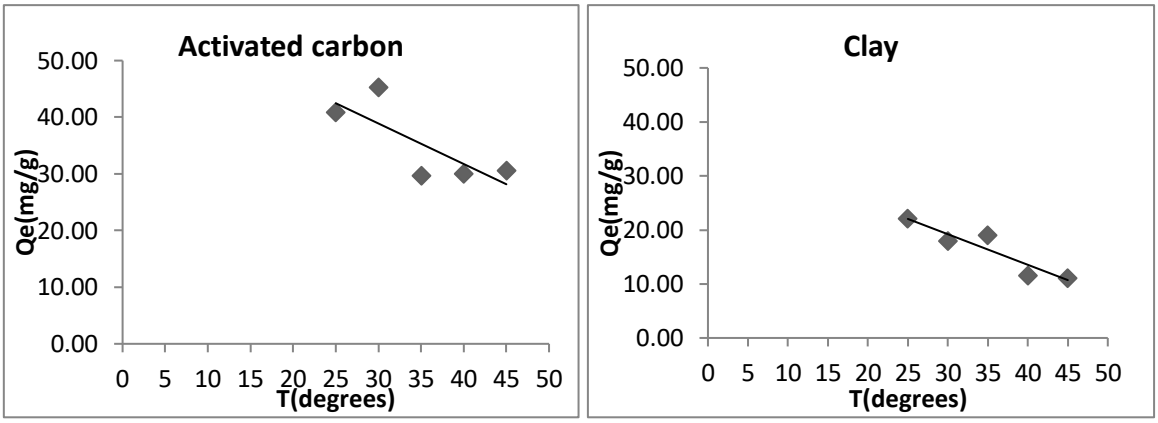


figure IV.7:The effect of changing the temperature

Where from the general form of the curve, we can notice that the adsorption capacity decreases with increasing temperature, where it was 22 mg/g at 25 degrees to reach 11 mg/g at 45 degrees, this is for clay, as for activated carbon, the maximum adsorption capacity was 45 mg/g at a temperature of 30 degrees to reach 30 mg/g at 45 degrees, and we can also note the discrepancy in the adsorption capacity between activated carbon and bentonite clay as it is larger in carbon compared to clay.

The reason for the decrease in the adsorption capacity with increasing temperature is due to the fact that the adsorption process is an exothermic process, in addition, the molecules at high temperature have a high kinetic energy [18] , which reduces the chance of them collecting on the surface of the adsorbent material.

IV-6-5) Decolorization Ratio (T%):

In order to identify the most efficient adsorbent material in removing color, is it activated carbon or clay, we will determine the percentage of color removal for both of them and then make a comparison, and in order to do this we will use the same data from the experiment through which we determined the effect of the initial concentration (a fixed mass of the adsorbent with variable dye concentrations) and we get the following figure:

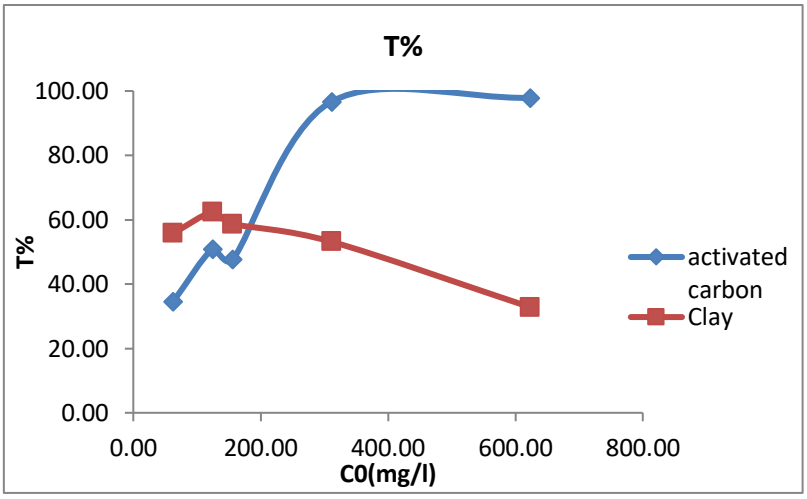


figure IV.8: Decolorization

Through the curve, we can make several observations:

for activated carbon, we note that its efficiency in removing the dye increases with increasing its concentration to reach 97% at the highest concentration.

for clay, we can notice in general that its efficiency in removing the dye decreases with the increase in the initial concentration of the dye , where it was at its highest value 62% at a concentration of 125 mg/l to decrease to 32% at the highest concentration of 623 mg/l.

We can also note that the curve is divided into two parts: the range of minimum concentrations, which ends at a value close to 200 mg/l, and the other range is the range of major concentrations, which starts from the previous value and ends at the maximum concentration of 623 mg/l. Where we can see that the decolorization efficiency for bentonite clay is high in the first range compared to activated carbon, While the opposite is in the second range, where the efficiency of the clay decreases significantly in exchange for the significant increase in the efficiency of activated carbon.

This is due to the large surface area of activated carbon that allows it to absorb a large amount of colorant, while the surface area of clay is less than it is in carbon and therefore it absorbs a smaller amount of dye. as for the range of small concentrations, the clay's high efficiency in removing color may be due to the charges on its surface that cause ion exchange with the dye molecules [8], which quickly run out to return its efficiency to decline with large concentrations.

IV-7) Adsorption isotherms:

Adsorption isotherms help us know the nature of adsorption, is it monolayer or multilayer (or is it physical or chemical adsorption), for this purpose we will use solutions with different concentrations ranging from 62 mg/l to 625 mg/l with a variable mass of adsorbent, and after obtaining the results we will draw a graph of the two functions:

LogCe=f(logCe) and $\frac{1}{Qe}$ **=f(**$\frac{1}{Ce}$**)**

From the curves, we will get the values of the constants of the two adsorption isotherms that we will use:

IV-7-1) Freundlich isotherm:

$$\textbf{Log Qe=log Kf+}\frac{1}{n}\textbf{ log Ce}$$

IV-7-2) Langmuir isotherm:

$$\frac{\mathbf{1}}{\boldsymbol{Qe}} = \frac{\mathbf{1}}{\boldsymbol{Qm}} + \frac{\mathbf{1}}{\boldsymbol{K}} \times \frac{\mathbf{1}}{\boldsymbol{Qm}} \times \frac{\mathbf{1}}{\boldsymbol{Ce}}$$

Where:

Ce: Equilibrium solute residual concentration (mg / L).

Qm: Maximum adsorption capacity (mg / g).

k: Adsorption equilibrium constant for the solute / adsorbent pair (L / mg).

kf and n: Constants characteristic of the efficiency of an adsorbent with respect to a given solute

We get the following curves:

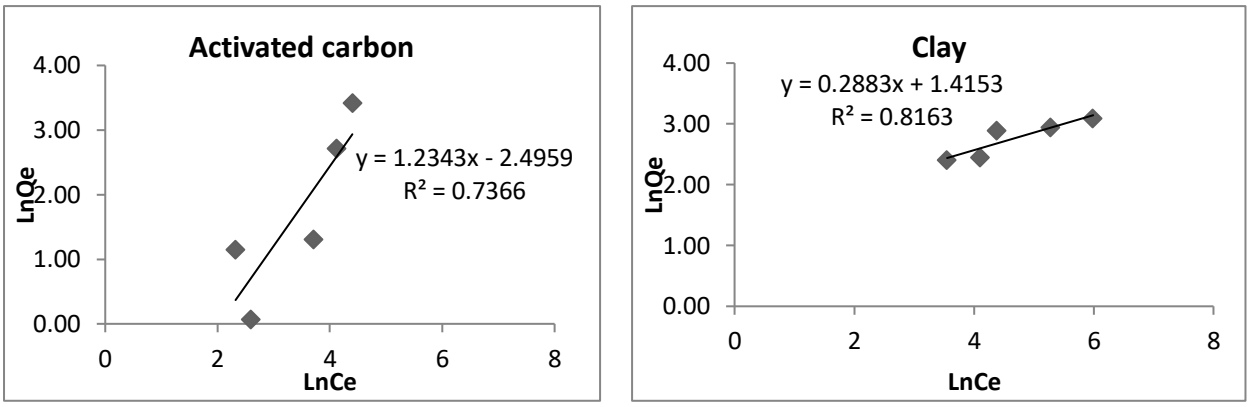


figure IV.9:Freundlich isotherm

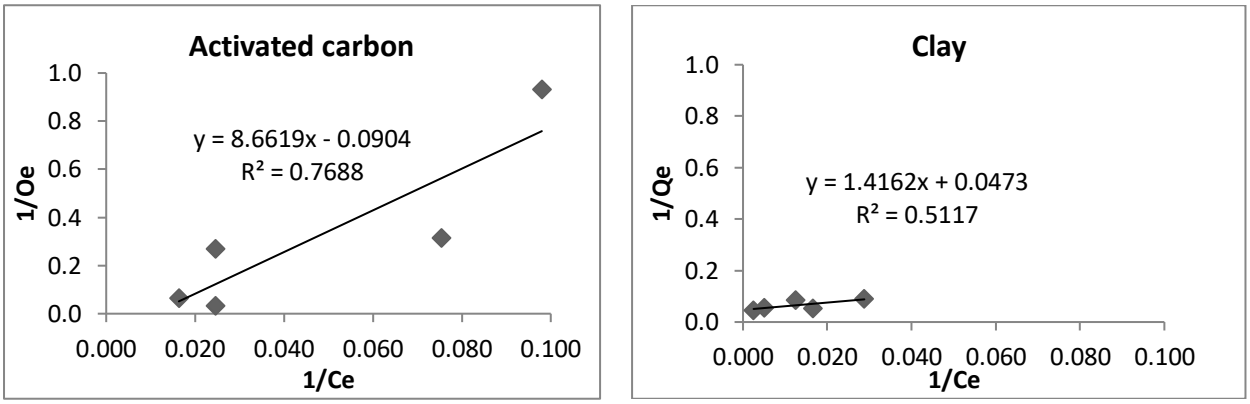


figure IV.10:Langmuir isotherm

Through these curves, we were able to obtain the constants of the Langmuir and Freundlich isotherms, which are represented by the following values:

- ✓ **Freundlich isotherm:**

$$\textbf{Log Qe=log Kf+}\frac{1}{n}\textbf{ logCe}$$

Clay :	Activated Carbon :
Kf=4.11	Kf=0.082
$\frac{1}{n}$=0.288	$\frac{1}{n}$=1.234
R² =0.816	R² =0.736

- ✓ **Langmuir isotherm:**

$$\frac{1}{Qe} = \frac{1}{Qm} + \frac{1}{K} \times \frac{1}{Qm} \times \frac{1}{Ce}$$

Clay :	Activated carbon :
K=0.033	K=0.01
R^2=0.511	R^2=0.768

After calculating the correlation coefficients and the constants of the Freundlich and Langmeier equation, we can say:

In both cases, for either the Freundlich or the Langmeier isotherm and for either activated carbon or clay, the previous two models do not describe adsorption fully (based on correlation coefficients), which can be justified for the Freundlich isotherm, by the fact that it describes adsorption very precisely at small concentrations. , while it fails in large concentrations.[22]

But in all cases, we can determine which of the two models is more appropriate to describe adsorption, as:

For clay, we can notice that the correlation coefficient of the Frendlich model is 0.816 while in the Langmeier model it is 0.511, and this means that the first is more suitable to describe the adsorption of carmine pigment on the clay, and that means that the adsorption is multi-layered or physical, which characterizes the irregular surfaces.

For activated carbon, we find that the correlation coefficient for the Freundlich model is 0.736, while in the Langmeier model it is 0.768. This means that the Langmire model is more suitable to describe the adsorption of carmine dye on activated carbon, as this model describes the monolayer adsorption, which characterizes homogeneous surfaces.

Conclusion

Conclusion

Conclusion:

In this research, we studied the adsorption process of a food dye, carmine dye, on the surface of activated carbon and bentonite clay, and we determined the efficiency of each of them under different initial conditions, where we studied the adsorption capacity at different initial concentrations, at different temperatures, at different values of pH and also in different time periods, and we also describe adsorption through two isotherm models, which are Freundlich model and Langmeier model.

The results showed with regard to the effect of changing the initial concentration of the dye, that the adsorption capacity increases with the increase in the initial concentration. In addition, studying the effect of contact time on the adsorption process showed similar results, as the adsorption capacity increases with increasing contact time, reaching its maximum value and remaining stable with time, these results are applicable to both activated carbon and clay.

With regard to the effect of temperature, the study showed results that are identical to previous studies, as the adsorption process is negatively affected with an increase in temperature, meaning that the adsorption capacity decreases with increasing temperature, which distinguishes exothermic processes, and this is in both activated carbon and clay.

As for the effect of pH, the results showed some difference between activated carbon and clay, as the former is more efficient in removing dye compared to clay,that in the acidic range, but in the moderate and basic range, there does not seem to be a significant effect on the adsorption process, as it remained stable and at its maximum value, and that is for both adsorbent.

With regard to the effect of changing the type of adsorbent , which is inferred by the extent of its efficiency in removing color, there is no result that can be generalized to all cases, as the clay is characterized by a great efficiency in adsorption compared to activated carbon, within the range of small concentrations of the dye solution, and on the contrary, We find that activated carbon is more efficient than clay in the range of large dye concentrations. Therefore, activated carbon and clay can be considered as excellent adsorbents, depending on the initial conditions.

Regarding the most suitable adsorption isothermal models, we find that Freundlich model is more suitable for clay, while the Langmeier model is more suitable for activated carbon.

Conclusion

In the field of water treatment, it is good to know the characteristics of pollutants, their type and concentration, as this helps us to know the type of adsorbents that we use to remove them. As for dye pollution, we can use clay instead of activated carbon as an adsorbent at low concentrations, and we know that clay is more abundant. and less expensive.

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الملخص:

في هذا البحث, قمنا بدراسة امتزاز صبغة الكارمن على سطح الكربون المنشط وطين البانتونيت, حيث قمنا بعرض بعض المعومات العامة عن كلا مادتي الامنزاز وعن الأصباغ, والطرق الفيزيائية والكيميائية لتحليلها, إضافة إلى ذالك, قمنا بشرح مبسط لظاهرة الامتزاز ثم قمنا بدراسة مختلف العوامل المؤثرة عليها, والمتمثلة في تأثير التركيز الابتدائي لمحلول الصبغة, تأثير درجة الحرارة, الأس الهيدروجيني وزمن التلامس. وتوصلنا إلى النتائج التي تفيدنا في مقارنة كفاءة كل من الكربون المنشط وطين البانتونيت في إزالة الملون, إضافة إلى معرفة إمكانية وصف الامتزاز من خلال ايزوثارم فرندليش ولانغماير.

الكلمات المفتاحية: الامتزاز, الكربون المنشط, الكارمن, الطين.

Abstract :

In this research, we study the adsorption of carmine dye on the surface of activated carbon and bentonite clay, where we present some general information about both adsorpents and dyes, and physical and chemical methods for their analysis, in addition, we have a simplified explanation of the adsorption phenomenon and then we study the various factors affecting it , represented by the effect of the initial concentration of the dye solution, the effect of temperature, pH and contact time. And we reached the results that benefit us in comparing the efficiency of each of activated carbon and bentonite clay in removing color, in addition to knowing the possibility of describing adsorption through Freundlich and Langmeier isotherms.

Keywords : Adsorption, Carmine , Activated carbon, Clay.

Résumé:

Dans cette recherche, nous étudions l'adsorption du colorant carmin à la surface du charbon actif et de l'argile bentonite, où nous présentons des informations générales sur les matériaux d'adsorption et les colorants, et les méthodes physiques et chimiques pour leur analyse, de plus, nous avons une explication simplifiée du phénomène d'adsorption puis nous étudions les différents facteurs qui l'affectent, qui sont l'effet de la concentration initiale de la solution colorante, l'effet de la température, du pH et du temps de contact. Nous avons obtenu des résultats qui nous sont utiles en comparant l'efficacité du charbon actif et de l'argile bentonite à éliminer la couleur, en plus de connaître la possibilité de décrire l'adsorption par les isothermes de Freundlich et de Langmeier.

Mots clés : Adsorption, Carmine, Charbon active, L'argile.