People's Democratic Republic of Algeria

Ministry of Higher Education
and Scientific Research

University of Kasdi Merbah – Ouargla

Department of Chemistry

Memory for obtaining a master's degree in chemistry

Specialty: Analytical Chemistry

Under title:

Modeling isotherm adsorption of a dye by montmorillonite

Prepared by:

Bendiff Houssam Eddine

Badgers Anouar Abdelmadjid

Discussed by:

Dekmouche Messaouda	President	**M.C.A**	University of Kasdi Merbah-Ouargla
Hadef Derradji	Examiner	**M.C.A**	University of Kasdi Merbah-Ouargla
Smara Ouanissa	Supervisor	**M.C.A**	University of Kasdi Merbah-Ouargla
Tobbi Wafa	Co-Supervisor	**M.C.B**	University of Hadj Lakhdar Batna

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Dedicated

Thanks to Allah thus provided me with knowledge and strength to do this work.

Thanks to my beloved parents who helped me get through difficulties of life and defeat my fears and who provided all they can to manage a good life and suitable conditions for me.

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Summery:

Pollution of water it become a huge issue for humanity which represent a great danger for the men and the environment.

In this study, an Organo-clay montmorillonite of (Maghnia, Algeria), was used for the removal of sandocryl red from aqueous solution, such as contact time, initial sandocryl red concentration was investigated in batch system. The adsorbent was specified infrared spectroscopy (FTIR) and X-ray. The optimum dosage reached in low concentration of adsorbate.

Montmorillonite has shown that the favourable conditions for obtaining a maximum degree of discoloration are: Concentration of the Montmorillonite suspension equal to 0.2 g / L; pH of the dye solution = 6.40, Stirring speed 3500 rpm; Temperature of the reaction medium $T = 30$ ° C

Keyword: Montmorillonite, Adsorption, clay, days.

ملخص

تلوث المياه أصبح مشكلة كبيرة للبشرية والتي تمثل خطرا كبيرا على الإنسان والبيئة.

في هذه الدراسة ، تم استخدام المونتموريونيت الطين العضوي من منطقة (مغنية ، الجزائر) ، لإزالة الصبغة الحمراء من المحلول المائي ، بتغيير في وقت التلامس بين المونتموريونيت و المحلول الصبغي ، ثم تم التحقيق في التركيز الأولي للصبغ الحمراء و بتراكيز مختلفة تحديد المواد المدمصة بالأشعة تحت الحمراء والأشعة السينية. ووصلت الجرعة المثلى في تراكيز منخفضة.

لقد أظهر المونتموريونيت أن الظروف المواتية للحصول على درجة قصوى من الإدمصاص لصبغة هي: تركيز يساوي 0.2 جم / لتر ؛ و درجة الحموضة لمحلول الصبغة = 6.40 ، وسرعة التحريك 3500 دورة في الدقيقة أما بالنسبة لدرجة حرارة وسط التفاعل فهي $T = 30°$ C درجة مئوية.

الكلمة الدالة : المونتموريونيت ، الإدمصاص ، الطين ، الأصباغ.

Résumé:

La pollution de l'eau devient un problème énorme pour l'humanité, ce qui représente un grand danger pour l'homme et l'environnement.

Dans cette étude, une montmorillonite organo-argileuse de (Maghnia, Algérie) a été utilisée pour éliminer le rouge sandocryl d'une solution aqueuse, par le temps de contact; la concentration initiale de rouge sandocryl a été étudiée en système de traitement par lots. L'adsorbant était fair par la spectroscopie infrarouge (FTIR) et les rayons X. Le dosage optimal atteint en faible concentration d'adsorbat.

La montmorillonite a montré que les conditions favorables pour obtenir un degré maximum de décoloration sont les suivantes: concentration de la suspension de montmorillonite égale à 0,2 g / L; pH de la solution de colorant = 6,40, vitesse d'agitation de 3500 tr / min; Température du milieu réactionnel T = 30 ° C

Mot clé: Montmorillonite, Adsorption, argile, jours.

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SYMBOLS

- **A** : Refers to the absorbance
- I : Intensity of the incident ray
- $\boldsymbol{I_0}$: Intensity of the transmitted ray
- $\boldsymbol{\varepsilon}$: The absorption coefficient which is a constant for an absorbing species and a given transition (L / mol.cm)
- **C** : The molar concentration of the absorbing species (mol / L)
- **T** : Transmittance
- $\mathbf{k_F}$: Freundlich constant
- $\boldsymbol{q_e}$: Amount of adsorbed solute per unit mass of adsorbent at equilibrium (mg / g);
- $\mathbf{q_m}$: Amount needed to cover the area of one gram of adsorbent in a monomolecular layer of solute (mg / g);
- $\mathbf{c_e}$: Solute concentration of the solution at equilibrium (mg / L);
- **x**: Amount of adsorbed solute (mg);
- $\boldsymbol{m}$: Mass of the adsorbent (g).

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INTRODUCTION

Pollution of water is probably as old as the settlement of humanity. However, the volume of water that covers the surface of the planet remains constant via its natural cycle of evaporation, condensation and precipitation. The quality used by human does not exceed 1% of the total water, it continues to deteriorate and sometimes even irreversibly.

Population growth combined with economic and industrial development that mean the demand for water continues to increase therefore its pollution. The industrial sector is a major factor affecting the quality of water, especially the textile industry. The dyes, represent a real danger for the human and his environment, because of their stability and their low biodegradability due to their aromatic molecular structure [1].

Adsorption is a phenomenon that can manifest itself between the surface of a solid and the molecules of the surrounding medium. This phenomenon is used to retain unwanted molecules existing in a fluid or to recover the precious elements [2]. Industrial applications generally use only the physical adsorption property of materials because this phenomenon does not change the molecular structure of the adsorbate. In addition to that, it is reversible, which makes it possible to recover the adsorbed molecule, thus regenerate the adsorbent [3].

In general, the use of activated carbon in the adsorption process is very demanding because of its high adsorption capacity and large surface area [4, 5]. However, this process is very expensive. For this reason, much attention has been focused later on the use of new adsorbents based on abundant natural materials more respectful to the environment such as clays [6], zeolite [7], olive pomace [8], wheat bran [9], sawdust [10] and phosphates [11-13].

Our study focuses on the elimination of a basic textile dye which is sandocryl red, by natural clay montmorillonite waste from the region of (Maghnia, Algeria).

The objective of our work is to valorize this local material with low concentration of elements which is usefull for the treatment of aqueous effluents loaded by dye.

We evaluated the influence of the following parameters on dye adsorption:

- The type, granulometry and mass of clay;
- The concentration of the dye solutions and the contact time between the adsorbent(Montmorillonite)and adsorbate (sandocryl red);
- Temperature and pH of the reaction medium.

For this study, we will adopt the following plan:

Theoretical part:

There is a bibliographical synthesis, organized into three chapters:

- The first chapter deals with the theory of adsorption.
- In the second chapter, we give the origin, main characteristics and areas using the montmorillonite as well as an overview of Algerian natural montmorillonite (Maghnia).
- The third chapter is devoted to the generalities on dyes.

Experimental part:

It includes two chapters:

- In the first chapter the equipment and methods of characterization are presented, a description of equipments and products used, in addition the experimental protocol used.
- In the second chapter presents the results obtained and their discussions concerning Characterization of Maghnia’s montmorillonite.

In conclusion, we will highlight all the essential results obtained during this study and the prospects for the future.

BIBLIOGRAPHY SYNTHESIS

I. Theory of adsorption

I.1. Definition

Adsorption is a physico-chemical phenomenon by which a chemical species can accumulate on the surface of a solid. This is a process of the utmost importance as regards the behavior of both inorganic and organic substances in natural waters. The term "adsorption" was first used by Kayser in 1881 to describe the increase in the concentration of gas molecules on adjacent solid surfaces [14].

Thus, adsorption is used to designate the accumulation of chemical species at the interface between a liquid phase and a solid surface. It is the retention on the surface of the adsorbent (solid), molecules or ions present in the aqueous or gaseous phase. It can occur on organic matter (activated carbon), clays, carbonates, iron oxides and hydroxides and on silica [15].

The surface interactions between the adsorbent and the adsorbate strongly depend on the chemical nature of the constituents involved. The adsorbed quantities depend not only on the surface of the materials but also on the temperature and concentration [16].

I.2. Types of adsorption

Depending on the energies involved, two types of adsorption can be distinguished; Physical adsorption and chemical adsorption.

I.2.1. Physical adsorption

Adsorption is called physical when it is due to forces of physical interactions between the atoms, or groups of atoms of the solid and the adsorbate molecules. This type of adsorption is based on the mutual attraction of the adsorbent and adsorbate molecules under the action of Van Der Waals forces, which are due to the movement of electrons inside the molecules that can generate instantaneous dipole moments.

A small local dipole can induce on another molecule another instantaneous dipole oriented so that the interaction between the two dipoles is attractive [17, 18].

I.2.2. Chemical adsorption

The chemisorption is essentially the result of the establishment of ionic type bonds between the cations (or anions) of the adsorbate and the negative (or positive) charges of the surface of the adsorbent material. The ion or atom thus fixed is at a very distance. Close to the surface of the solid and one tends to consider it as belonging to the solid.

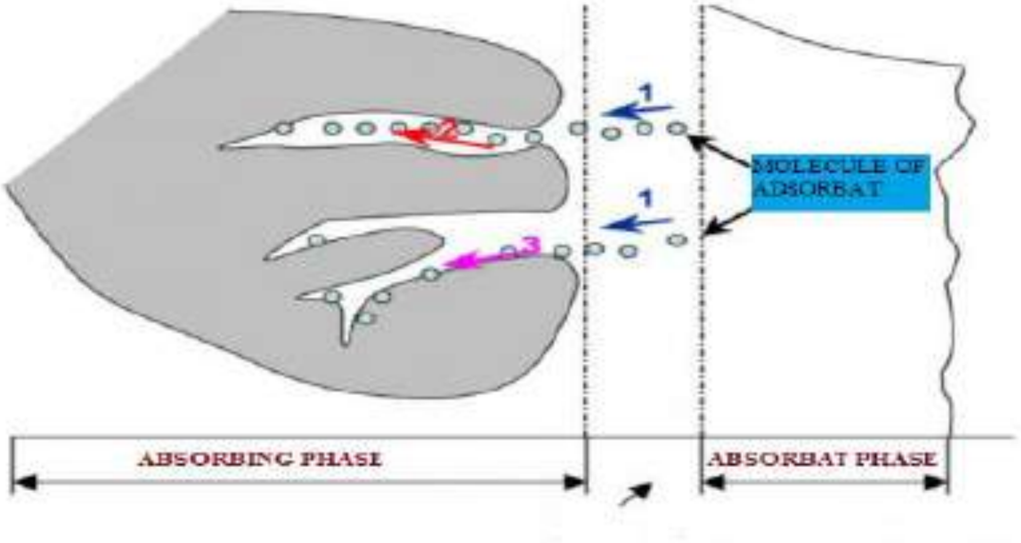
This situation gives this type of specific adsorption a high energy and the phenomenon is no longer reversible from the thermodynamic point of view. It is thus referred to a specific adsorption of high affinity (energy greater than 50 KJ.mol-1) [15].The criteria for differentiating these two adsorption modes are summarized in Table 1.

Table 1: Differences between chemical adsorption and physical adsorption.

	Chemical adsorption	**Physical adsorption**
Nature of interactions	Strong bond, great adsorbent / adsorbent affinity (ionic forces)	Weak links (Van der Waals forces)
Adsorbed amount	Determined by the number ofsurface sites (monolayer maximum)	Possibility of overlay several layers of adsorbed atoms (Multilayer)
Character of the surface	Heterogeneous: the sites are not equivalent to the point ofenergy view	More or less homogeneous
Characteristic of the phenomenon	Specific	Not specific
Adsorption heat	> 50 kJ/mol	<50 kJ/mol
Adsorption rate	Sometimes slow because of the great energy barrier activation	Fast unless there is broadcast in micropores
Reversibility of the phenomenon	limited	Very marked
Mobility of species adsorbed	limited	Very long

I. 3. Mechanism of adsorption

Figure 1: Diagram of the transport mechanism of an adsorbate within a grain:1-External diffusion; 2-Internal diffusion (in the pores); 3-Surface scattering.



During the adsorption of a species on a solid, the transfer of material instead of the fluid phase to the active sites of the adsorbent, this process takes place in three steps:

- The transfer of external material by molecular diffusion through the boundary layer of fluid around the adsorbent grain.
- The transfer of microporous internal matter: the molecules migrate inside the macro-porous and mesoporous of the adsorbent, from the surface towards the interior of the grain;
- The transfer of microporous internal matter: the molecules diffuse into the microporous [15].

I.4. Factors influencing adsorption

In the case of adsorption in the liquid phase, a large number of factors are likely to have an influence on the adsorption process [19-21], among which are distinguished the factors related to:

I.4.1. Thenature of the adsorbent

- Specific surface.
- The density and nature of the functional groups on its surface.
- The distribution of pore size.

I.4.2. Thenature of the adsorbate

- Its molecular mass.
- Its polarity.
- Its solubility.
- The size of the molecules.
- The nature of the functional groups (acidic or basic).

I.4.3. Theoperating conditions

- The concentration of adsorbent and adsorbate.
- The temperature of the solution.
- The presence of competitive species for the same adsorption sites; (case of mixtures).
- The pH of the medium.
- The contact time between the adsorbent and the adsorbate.
- The stirring speed.

I.5. Adsorption balance isotherms

When an adsorbent and an adsorbate are brought into contact, an equilibrium thermodynamics settles between the adsorbed molecules on the surface of the adsorbent and the molecules present in the fluid phase. The adsorption equilibrium isotherm is the characteristic curve, at a given temperature, of the amount of adsorbed molecules per unit mass of adsorbent as a function of the concentration of solute in the fluid phase. The shape of this curve makes it possible to make assumptions about the mechanisms involved: adsorption in monolayer or multilayer, interactions between adsorbed and non-adsorbed molecules.

I.5.1. Classification of adsorption isotherms

The classifications of the most known isotherms are:

I.5.1.1. Giles classification

The evolution of the adsorbed quantities as a function of the equilibrium concentration differs according to the structural nature of the solids, so that in 1974 Giles [22] proposed a classification of adsorption isotherms in aqueous solution. Four main classes called S, L, H, C, based on the shape of the initial part of the isotherm were listed.

I.5.1.1.1.Class L

Class L isotherms show, at low concentration in solution, a downwards concavity which reflects a decrease in free sites as the adsorption progresses [23].

The Langmuir model indicates a flat adsorption of bifunctional molecules [24]. The ratio of the concentration in the aqueous and adsorbed solution decreases as the concentration of the solute increases. Thus describing a concave curve, this curve suggesting a gradual saturation of the adsorbent [25].

I.5.1.1.2.Class S

The isotherms of this class have, at low concentration, a concavity turned upwards. The adsorbed molecules promote the subsequent adsorption of other molecules (cooperative adsorption). This is due to molecules that attract by Van Der forces Waals, and group together in islets in which they pile up against each other [23].

I.5.1.1.3.Class H

The initial part of the isotherm is almost vertical, the adsorbed quantity appears important with almost no concentration of the solute in the solution. This phenomenon occurs when the interactions between the adsorbed molecules and the surface of the solid are very strong [23].

I.5.1.1.4. Class C

The isotherms of this class are characterized by a constant partition between the solution and the substrate up to a plateau. Linearity shows that the number of free sites remains constant during adsorption. This means that sites are created duringadsorption. This implies that isotherms of this class are obtained when the solute molecules are able to modify the texture of the substrate by opening pores that had not been previously opened by the solvent [23]. The shape of each type of isotherm is shown in Figure 2.

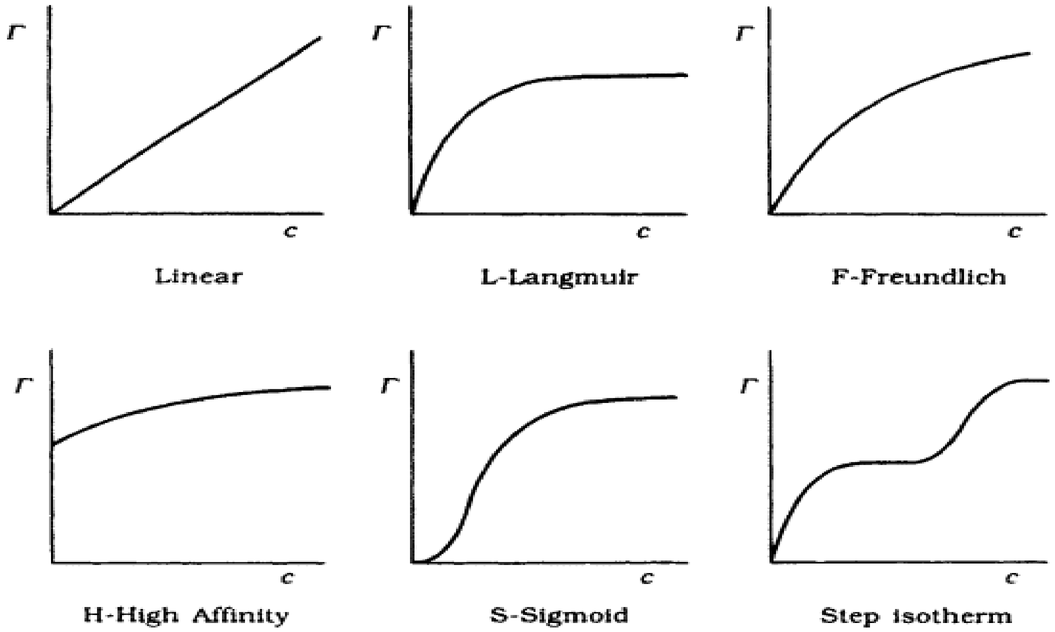


Figure 2: System of isotherm classification.

I.5.1.2. Classification of I.U.P.A.C

According to the classification of I.U.P.A.C, the adsorption-desorption isotherms can be grouped into six classes (Figure 3).

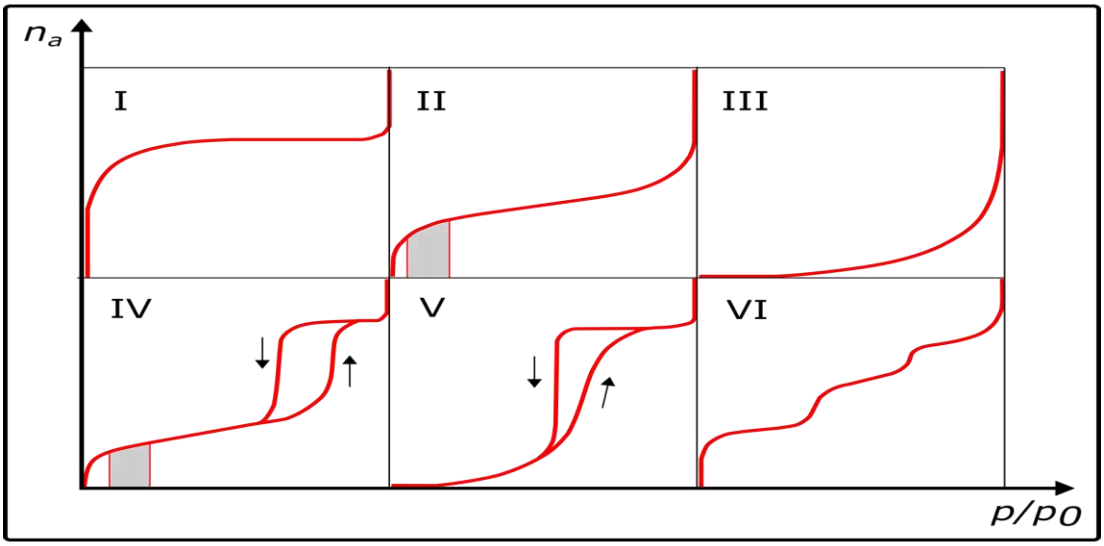


Figure 3: System of isotherm classificationof I.U.P.A.C

- The adsorption equilibrium of type I adsorption is characteristic of an absorbent whose microporous volume is particularly high. The saturation of the adsorption sites is gradual from low concentrations and the shape of the isotherm is characterized by a long plats indicating low formation of multilayers.

- The adsorption equilibrium isotherms of type II and III are observed in the case of adsorbents having a large macroporous volume. The adsorption is first monolayer then multilayer to capillary condensation, which translates the existence of strong intermolecular interactions compared to the interactions between the adsorbate molecules and the solid.
- In the case of liquid phase adsorption, the majority of the isotherms encountered are of type I or II.
- The Type IV adsorption equilibrium isotherm is associated with rather mesoporous adsorbents. The presence of two levels can result from the formation of two successive layers of adsorbate on the surface of the solid. When the interactions between the adsorbate molecules and the surface of the adsorbent are stronger than those between adsorbate molecules, the adsorption sites of the second layer begin to be occupied only when the first layer is completely saturated.
- Type V adsorption equilibrium isotherms are characteristic of microporous adsorbents with multilayer formation at low concentrations. As with the Type III isotherm, this behavior is representative of stronger interactions between the adsorbate molecules than between the adsorbate and adsorbent molecules.
- The type VI isotherm is associated with layer-by-layer adsorption on a highly uniform surface [26].

I.6. Modeling of adsorption isotherms

Numerous mathematical models to represent the adsorption isotherms have been developed, those whose use is the most widespread are the models of Langmuir and Freundlich because their mathematical expression is simple and they allow to correctly represent equilibrium isotherms adsorption in aqueous phases in the majority of cases.

I.6.1. The Langmuir model

The first fundamental theory of solute adsorption on solids was proposed by the American physicist Irving Langmuir in 1918. The development of the Langmuir representation for an adsorption isotherm is based on a number of assumptions:

- The adsorbed species is fixed on a single well-defined site;
- Each site is able to fix only one adsorbed species;
- The adsorption energy of all sites is identical and independent of the presence of species adsorbed on neighboring sites (homogeneous surface and no interactions between speciesadsorbed).

The adsorption phenomenon is considered dynamic. It results from the equilibrium between two inverse phenomena: the fixation of the solute on the solid and the desorption of the adsorbed solute which leaves the surface of the adsorbent

$$\boldsymbol{q_e = \frac{x}{m} = \frac{q_m . k_L . c_e}{1 + k_L . c_e}} \quad \ldots\ldots\ldots\ldots \ (\mathbf{1})$$

Or:

- $\boldsymbol{q_e}$: Amount of adsorbed solute per unit mass of adsorbent at equilibrium (mg / g);
- $\mathbf{q_m}$: Amount needed to cover the area of one gram of adsorbent in a monomolecular layer of solute (mg / g);
- $\mathbf{c_e}$: Solute concentration of the solution at equilibrium (mg / L);
- x: Amount of adsorbed solute (mg);
- $\boldsymbol{m}$: Mass of the adsorbent (g).

In the case of low adsorption, the term $\mathbf{K_L c_e}$ tends to 0 because it is much less than 1, and can be neglected. In this case, Langmuir's relation is written:

$$\mathbf{q_e = q_m . K_L . c_e} \qquad (2)$$

In the case of a large quantity of adsorbed solute, $\mathbf{K_L c_e}$ becomes much greater than 1, the surface of the solid is completely saturated and the equation is reduced to:

$$\mathbf{q_e = q_m} \qquad (3)$$

The linearization of the Langmuir equation makes it possible to deduce the maximum quantity qm and the constant $\mathbf{K_L}$[27].

$$\mathbf{\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_L . q_m . C_e}} \qquad (4)$$

We multiply equation (4) by (C_e) we obtain equation (5)

$$\mathbf{\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L . q_m .}} \qquad (5)$$

I.6.2. TheFreundlich model

The Freundlich isotherm is one of the oldest equations describing adsorption (1906). This empirical isotherm describes with satisfaction the adsorption of the solute on energy heterogeneous surfaces (case of the non-ideal adsorption) and in solutions diluted.

Freundlich speculated that the binding energy or heat of adsorption decreases exponentially with increasing saturation of the surface of the solid, an assumption that may be closer to reality than the Langmuir model.

The Freundlich equation is:

$$q_e = \frac{\mathbf{x}}{m} = \mathbf{k_F C_e^{\frac{1}{n}}} \qquad (6)$$

Or:

$\mathbf{k_F}$: Freundlich constant which gives a rough indication of the adsorption capacity of adsorbent. As$\mathbf{k_F}$: increases, the adsorption capacity increases.

The Freundlich equation can be represented in a linear form as follows [27]:

$$\mathbf{\ln q_e = \ln k_n + \frac{1}{n} \ln C_e} \qquad (7)$$

The shape of the isotherm will depend on the value of 1/n, which represents the adsorption intensity and gives us crucial information as to the mechanisms governing the adsorption of the compound on the adsorbent. According to the value of 1/n, the following cases are distinguished [28]:

- 1/n = 1: the isotherm is linear of type C;
- 1/n> 1: the isotherm is convex of type S;
- 1/n <1: the isotherm is concave type L;
- 1/n << 1: the isotherm is of type H.

n is between 2 and 10, the adsorption is good (easy);

n is between 1 and 2, the adsorption is moderately difficult;

n is less than 1, the adsorption is low. In this case, a large mass of adsorbent is used to recover an appreciable fraction of the solute [29].

II .Clays

Several researches and scientific works are oriented towards the development of low-cost treatment processes in terms of protection of natural environments and improvement of water quality through the use of natural materials such asclays which are characterized by a large surface area, excellent cation exchange property, wide availability in nature and are capable of same time removing organic and inorganic pollutants. [30, 31]

The fields of application of clays are multiple: In its raw state, its most important application, after heating above 1000 ° C, is the production of ceramics (porcelain ,pottery ... etc.). In the modified state, clay is used in the paper industry, cosmetics, in the pharmaceutical industry (Manufacture of drugs, such as Smecta) and in the degradation of polluting compounds. To a lesser extent, clay is used in many other industrial processes such as the manufacture of paints, the construction of roadsin public works, and the manufacture of cells (for storage of radioactive waste).

II.1. Generality on clays

The clay particles result from the physical or mechanical disintegration of the rocks, followed by a chemical transformation.

Clay, a natural material that usually contains phyllosilicates (layered silicates). It can also contain materials that induce no plasticity (for example quartz) and / or organic matter: these are associated phases. [32]

Phyllosilicates are one of the main components of the earth's crust, they have been extensively studied by X-ray diffraction which is the fundamental tool for their identification [33] and whose structure gives these materials – comparatively to other types of soils or rocks - very specific properties for their interaction with water. The fact we speak about these minerals implies that one selects a certain category according to their behaviour, the character clay is related to four types of standard: [34]

- **Division:** minerals must be in very small sizes of less than 2 μm.
- **Facies:** their dissymmetrical particles with lamellar tendency can slide theon top of each other, which gives them plasticity, this form also favours the trapping of liquid molecules, in particular water.
- **Dispersion:** these species must be able to constitute the colloidal suspension more or less stable with water, the interfacial properties must therefore playa big role.
- **Chemical constitution:** they are silicates because only these compounds seem to be able to be characterized by the properties which have just been evoked.

The clays are always accompanied by impurities, [35] they are consequently constituted by various substances in the form of particles of very small sizes:

- ❖ Oxides and hydroxides of silicon: (quartz and cristobalite).
- ❖ Ferriferous minerals: Fe_2O_3hematite, Fe_3O_4magnetite.
- ❖ Carbonates: calcite$CaCO_3$, $dolomite CaMg(CO_3)_2$.
- ❖ Aluminum oxides and hydroxides: Gibbsite$Al(OH)_3$.
- ❖ Organic materials.

II.2. Structure and chemical properties of clays

Due to their physical and physicochemical properties, clays play a fundamental role in the processes involved in soils. These properties result, at thefundamental characteristics of clays (chemical composition, structure and morphology) and the physicochemical conditions in which they occur.

By their consequences on the phenomena at the interfaces, the size, the shape and the specific surface are the most important morphological characteristics. [36]

They depend on the granulometry, the mineralogical structure and the distribution of the charges, the granulometry gives the clays properties similar to those ofcolloidal substances, the structure of clays-organized into layers spaces of variable dimensions-leads to the characteristics and propertiesfollowing general

- Very large surface area [37] (sum of external and internal surfaces), clays developing the largest specific surfaces will have important sorption properties, enhance their frequent involvement in soil studies.
- Possibility of insertion into the layers spaces of metal ions, organic molecules and water in quantity sometimes are important.
- The presence of electric charges (37) will condition the physico-chemical reactivity of the constituents with ions in solution or other constituents (able to ionize organic molecules).

The clay minerals are alumino-silicates (oxides of silicon and aluminum) belonging to the family of phyllosilicates more or less hydrated under form of finely divided particles whose size is in the order of a micrometer.

These phyllosilicates are composed of a succession of leaflets composed themselves of a stack of:

- Mainly siliceous tetrahedral layersSiO_4 (the thickness is 3Å oxygen occupies the vertices of the tetrahedron and the center is occupied by Si or Al). [38]

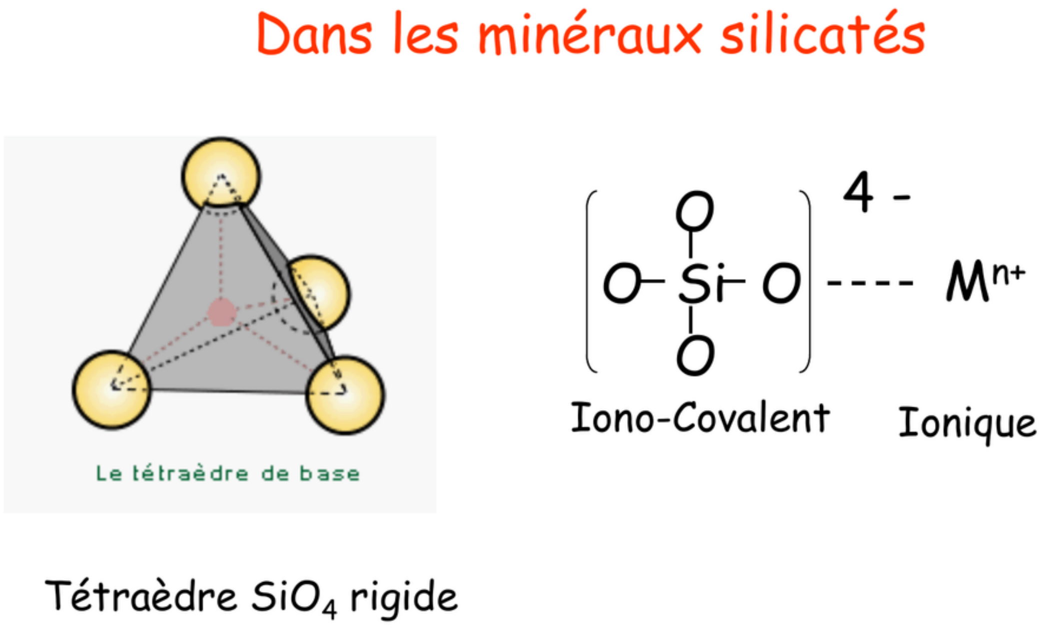


Figure4 : Structural elements: the tetrahedral.

- Predominantly aluminous octahedral layers $Al(OH)_6$(whose thickness is 4Å, the octahedrons have their vertices occupied by O or OH and their center is occupied by an Al atom or by Mg).[38]
    - When two cavities out of three of the octahedral layer are occupied by Al^{+3} or another trivalent metal ion, the structure is called dioctahedral.
    - When all the octahedral cavities are occupied by divalent metal ions, the structure is called octahedral. [38]

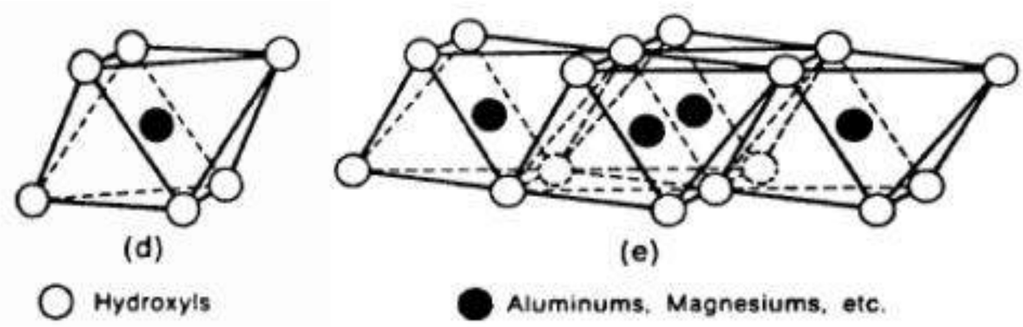


Figure5 :Structural elements: octahedral.

- A characteristic distance, called "interfoliar space" which can be empty or occupied by anhydrous or hydrated cations, can exist isomorphic substances in the tetrahedral layers (Si^{+4}, Al^{+2}, ,Fe^{+3}) and in the layersoctahedral ($Al^{+3}Mg^{+2}$,Fe^{+2},Li^{+}), these substances lead to a positive charge deficit which gives the entire sheet a negative charge and is compensated on the outside of the sheet, by compensating cations. [39]

This crystalline structure of clays induces three physicochemical properties:

- Important internal and external surfaces (700-800 m^2/g for montmorillonite).
- Negative surface charge (at neutral pH), hence the possibility of retaining cations.
- An ability to retain a large number of water molecules between different layers (swelling clays).

All of these properties make clays the most reactive mineral constituents of soils, largely contributing to the physical, chemical and biological properties of soils.

II.3. Classification of clays

The classification of clay minerals depends on several parameters such as the combination of layers (T-O, T-O-T, T-O-T-O), the type of cations in the octahedron and the tetrahedron, the layer loading and the nature of the species in the interfoliar space(cations, water molecules, ...). The simplest and most widely used criterion for classification is the mode of arrangement of the tetrahedral and the octahedral constituting the clays, [40] two major classes are defined: [38]

- Phyletic clays.
- Fibrous clays.

Phyletic clays are the most widespread and the most studied. It is about mineral phyllosilicates formed by the stack of sheets, each sheet (thickness of 7, 10 and 14Å) is itself constituted of several layers.Fibrous clays (interstratified) are minerals in which the layers are alternated or, most often, the interfoliar spaces are different.

Our clay belongs to the class of phyllitous minerals. According to the deficit of the leaflet load, the character and the occupancy rate of the octahedral layer. Three main types of phyllosilicates clays are thus found: [41]

- Type 1/1 (Minerals at 7 Å).
- Type 2/1 (Minerals at 10-15Å).
- Type 2/1/1 (Minerals at 14 Å).

II .3.1.The minerals of the type 1/1 (or TO):

The sheet consists of an octahedral layer and a tetrahedral layer, the characteristic equidistance is about 7 Å, to this type corresponds to the group of Kaolinite. [41].

Kaolinite:

It is the most abundant mineral in the 1/1 phyllosilicates family, [42] often associated with other minerals. The presence of quartz is so systematic, from the geological processes of clay formation. For the same reasons, impurities in the form of oxides, micas and / or feldspars are often encountered. [41]

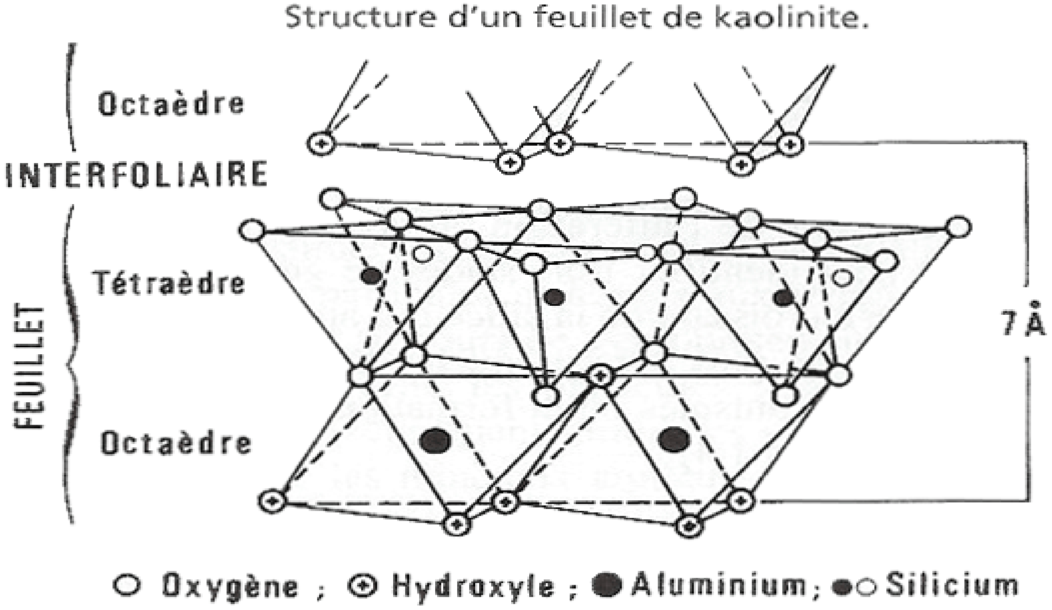


Figure6:schematic of the Kaolinite layer

The elemental sheet is composed of a tetrahedral layer with silicon core (SiO_4) and an octahedral layer with aluminum core $Al\ (OH)_6$, the ion exchange capacity is very low due to a total occupation of the sites. Octahedral which limitsalso the possibilities of ion substitutions. Nevertheless, there remains a possibility of exchange in tetrahedral sites between $Si^{+4}$and Al^{+3}. This substitution causes the appearance of a charge defect which is rebalanced by housing a compensating cation very strongly retained, the specific surface is of the order of 40 m^2/g.[43].

II.3.2.The type 2/1 (or TOT) minerals:

The sheet consists of a layer of octahedral framed by two tetrahedral layers with the second tetrahedral layer being reversed relative to the first, these three layers are linkedbetween them by oxygen atoms. The characteristic equidistance varies from 9.4 to 15 Å depending on the content of the interlayer. To this type correspond the groups of talc,smectites, illites, vermiculites and that of micas, [41] these clays can be found in three different situations: [41]

- No isomorphic substitution.
- Octahedral substitutions.
- Tetrahedral substitutions.

- In the first situation, all octahedral sites are occupied by Mg^{+2} (no isomorphic substitution). As a result, there is no load deficit on the surface. The sheets are then electrically neutral and have a high stability with respect to water, exactly as in the case of T-O clays.
- In the case where there is isomorphous substitution, there is a load deficit (often negative) on the surface of the sheets, which is naturally compensated by compensating cations. The resulting charge deficit is compensated for in the interfoliar space by potassium K^{+} ions which provide strong bonds between the layers and is compensated by introduction into the interfoliar space.

II. 3.2. Type2/1 (or T-O-T) minerals

- **. Montmorillonite**

Of all the existing phyllosilicates, montmorillonite is one of the most widespread on the surface of the globe and therefore also widely used. It was discovered for the first time in 1847 near Montmorillon, in the department of Vienne(France). [44]

In Algeria, the most economically important bentonite deposits are in Oran (western Algeria). We note in particular the career ofMaghnia (HammamBoughrara) whose reserves are estimated at one million tons and that of Mostaganem (M'zila) with reserves of two million tons. [45]

The idealized formula of a unitary mail of montmorillonite can describe: [46]

$$\left[Si_{8-x}\left(Al_{4-y}Mg_{y}\right)O_{20}.OH_{4}\right]^{-(x+y)}M_{(x+y)}.nH_{2}O$$

The complex in square brackets indicates: the macro anion that composes the leaflet.

$\boldsymbol{M(x+y)}$: Is the cation exchangeable in the interfoliarspace

$\boldsymbol{x/8}$: Is the proportion of atom of Si substituted by Al tetrachloride.

$\boldsymbol{y/4}$: Is the proportion of Al in the octahedral layer substituted by Mg.

❖ The structure of montmorillonite has been definitively established from Hofmant's work. Endel and Wilm. Marchal, the leaflet shown in Figure I-7 consists of two layers of silicon-centered tetrahedral between which is an octahedral layer centered on the aluminum. Two layers are separated by the interlayer space whose thickness is of the order of 14A°, thickness which can vary according to the water content (9.8 A° for a montmorillonite s at 110A ° C). [47].

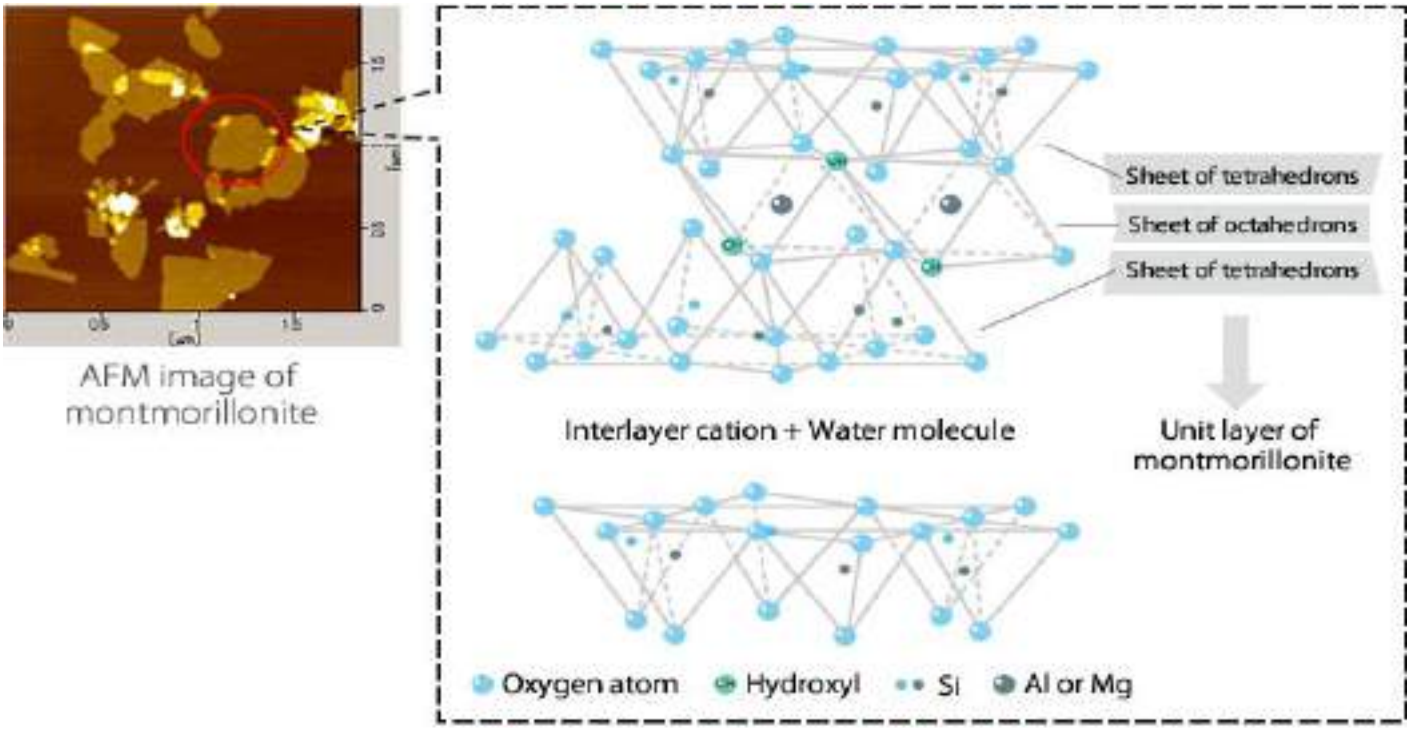


Figure7 :Schematic representation of the structure of amontmorillonite.[47]

- ❖ Montmorillonite is a white clay, usually its density is equal to2.04. It is partially soluble in hydrochloric acid but totally destroyed by sulfuric acid. The most important property is its cation exchange capacity, which varies from 100 to 150 milleequivalents per 100g of clay and its specific surface area (for Maghnia montmorillonite) of 90m^2/ g.
- ❖ Various authors have highlighted three levels of organization in clay systems, particularly montmorillonites. Figure I-7 shows the presentation of the three different levels of organizationcharacteristics of this multi-scale structure of montmorillonite.

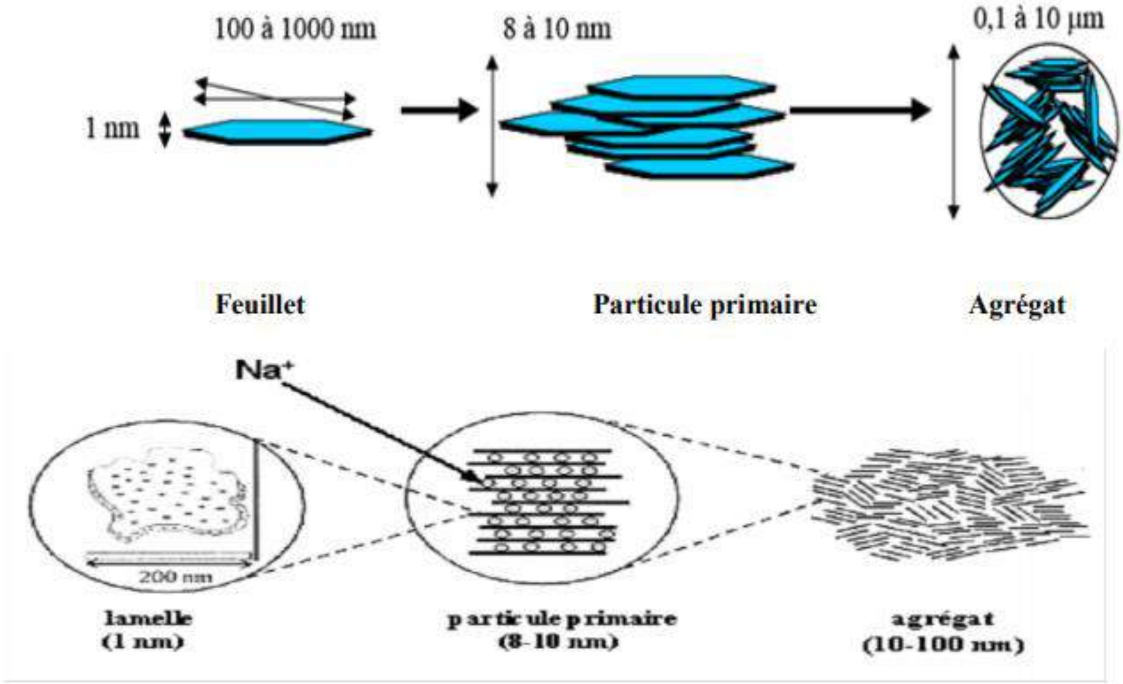


Figure8:Multiscale structure of montmorillonite.

- **The leaflet**

The leaflets are the basic structural units defining the mineralogical nature, the belonging to the type of clay, the physicochemical properties as well as the macroscopic behavior. The leaflet is stacking horizontally successively in the X and Y directions for the half-mesh, it has the shape of a disk or a wafer with dimensions of approximately one hundred and a thousand nanometres in length and ten Angstroms in thickness. These pads are very flexible especially in the presence of water so they are deformable.

- **The crystal**

The phyllosilicates form crystals composed of a stack of layers, their number determines the thickness of the crystal, the crystals consist of a variable number of layers (3 or 4 for smectites up to several tens for chlorites). The smectite crystals are very small (crystallites less than 1 µm) and have a very small thickness (some nm).

- **The particle**

Several crystals can associate to form a particle, the stack of sheets is made by attractive electrostatic forces between the compensating ions and the layers, the thickness is about 8 to 10 nanometres for the primary particle size which has remained almost constant, when a montmorillonite is inflated, the interfoliar space is increased and there are fewer leaves in a particle. [48]

- **The aggregates**

The term "aggregate" represents clays in the powdery state, it's a set of small particles having a more or less rectangular shape called "primary particles" oriented in all directions, and thebecome particles are interconnected by deposits of hydroxides or organic matter.The aggregates range in size from 0.1 to 10 microns as shown in Figure 8. [49].

II.3.3.Type minerals 2/1/1 (or T-O-T-O):

The sheet consists of the alternation of T-O-T sheets and interlayer octahedral layer, this layer neutralizes the charges borne by the T-O-T sheets. The characteristic equidistanceis then about 14 Å, to this type corresponds the group of chlorite. [41].

.The Chlorites

The interfoliar space of the chlorites is not occupied by a compensating cation as in the preceding cases, but by a positively charged layer of hydroxides, the characteristic basal space reaches 14 Å. Chlorites are stable at high temperatures. [50].

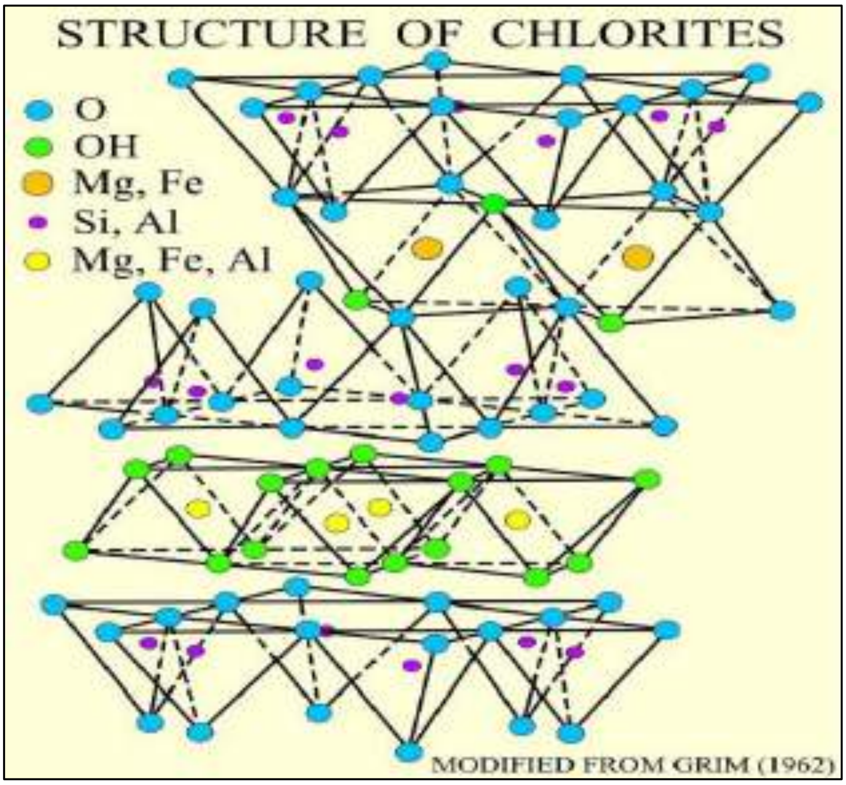


Figure9: schematic of the structure of aChlorites

II.4. The properties of clays

The particular properties of the clay minerals are due to the small size, the sheet structure and the negative charge of the particles, [51] so to define these clay minerals very precisely, we present below the properties themost important clays:

II.4.1. Thecapacity cation exchange

The clays have the property of reversibly (exchangeable) setting cations contained in the surrounding solutions, the cation exchange capacity (CEC)is a very important feature, it is defined as the amount of monovalent and divalent cations (Li^{+} , Na^{+} , K^{+} , Ca^{+2} , or , Mg^{+2}) that can be substituted by compensating cations to compensate for the negative charge of 100 grams of clays. It is conventionally expressed in milliequivalents per 100 grams of clay (meq / 100g). [52] This cation exchange capacity is considered globally and relates to both interfacial space cations, surface cations and leaflet cations.

There are different methods of measuring CEC. In general, a natural montmorillonite is introduced into a solution containing an excess of cations, then an elemental analysis is carried out in order to evaluate the quantity of cation exchanged betweenclay and solution. This method is usually done with NH_4^+, or Ba^{+2}, the dosage is accurate using elemental microanalysis. The remaining cations in montmorillonite define the cation exchange capacity that depends on the clay being studied. [49] In clays there are two main causes of an ion exchange capacity, one internal and the other external.

- **The presence of isomorphic substitutions (internal CEC):**

  The most common is the substitution of Al^{+3} by Mg^{+2} in the octahedral layer, which is the main mechanism of exchange for montmorillonite. For this clay, [38] the distance between the negative sites located at the level of the octahedral layer and the exchangeable cation located on the surface of the sheet is such that the attractive forces are low. Substitutions of Si by Al in the tetrahedral layer are also possible. [54].

- **Border phenomena (external CEC):**

  At the edges of a sheet, the valences of silicon and oxygen in tetrahedral layer on the one hand, aluminum and oxygen in octahedral layer, on the other hand, are not saturated. To compensate for these valences, water molecules hydrolyze and silanol (Si-OH) or aluminol (Al-OH) groups appear which, depending on the pH, can capture or release protons. These can be exchanged with other cations, and the number and nature of the leaflet fillers will be directly related to the pH. [55].

Table 2: Characteristics of minerals.

Ore	Cation exchange capacity (meq / 100g)
Kaolinite	**3-15**
Montmorillonite	**80-150**
Illite	**10-40**
Vermiculite	**100-150**
Chlorite	**10-40**

The cation exchange capacity of montmorillonite is the largest (in the range of 80-150 meq / 100g) among all clay ores due to their high isomorphic substitution in the octahedral and tetrahedral layers, respectively. [56].

II .4.2. The specific surface

Clays are widely used as adsorbents because of their large surface area, [57] which comprises the sum of two surfaces, one external between the particles and the other internal corresponding to the interfoliar space.[57] It is expressed in m^2 per gram of clay, the increase of the surfacespecific gives a greater swelling power and therefore a higher swelling potential.The specific surface seems to be a very important parameter in the precise characterization of the clay. Indeed, the finer the soil, the higher the surface area.

Table 3: The specific surface of some clay minerals. [58].

	Internal surface (m^2/g)	*External surface* (m^2/g)	*Total surface* (m^2/g)
Kaolinite	***0***	***10-30***	***10-30***
Montmorillonite	***600-700***	***80***	***700-800***
Illite	***20-55***	***80-120***	***100-175***
vermiculite	***700***	***40-70***	***760***
Chlorite	***-***	***100-175***	***100-175***

II.4.3. The property of swelling

The swelling of a clay is defined as the separation of the sheets by the entry of water into the interfoliar space, it is done in three successive stages: first, a discrete increase of the interfoliar distance corresponds to the entry of a water between the layers (monolayer state, or monohydrate), then a second layer (bilayer state, or bihydrate), then the spacing of the sheets, the deflating property varies from one clay family to another:

- The 1/1 type clay minerals do not normally have any charges present on the surface, the tetrahedral layer is totally occupied by Si^{+4} and the octahedral layer is completely occupied by Al^{+3} or Mg^{+2} If there is a substitution within a layer, there will always be compensation by substitution in other layers, so neutrality is always maintained. This particular property makes these clays stable andtheir structure - in particular the distance between the sheets - is not affected by the presence of water, they have no capacity to swell.
- In the case of clay minerals of type 2/1, the group of smectites with swelling properties, [56] which are due to the hydrophilic nature of its entire surface. Due to the presence of hydratable cations in the interfoliar galleries, the swelling of the clay will be greater when the cation cations are small andweakly loaded, depending on the type of compensating cation, one classifies the swelling of the leaflets as follows: $Li^{+}>Na^{+}>Ca^{+2}>Fe^{+}>K^{+}$. [49]Two types of swelling can occur within clay materials: interfoliar swelling and interparticular swelling.
- **Interfoliar swelling (crystalline)**

  Crystalline swelling occurs at the smallest scale of the clay structure, it allows an increase in interfoliar distances of 0.96 to 2 nm and it depends on the number of layers of water molecules adsorbed between two adjacent layers [60] (This is the case of smectites such as montmorillonite and chlorites).

The water penetrates inside the particles and is organized in layersmonomolecular, the interfoliar swelling is very important.

- **Interparticular swelling (osmotic)**

  Also called osmotic swelling or macroscopic swelling, macroscopic with respect to water that takes a macroscopic scale, it occurs when the hydration energy is sufficient to cross the potential barrier due to attractive electrostatic forces between the layers.[68,66] Unlike interfoliar swelling, swellinginterparticle has a rather limited extent, but affects all clays. [54]

II - 5) Modified clays

In order to enhance the natural materials, the clay minerals can be modified to improve their adsorbent properties, these modifications, which are physicochemical types based mainly on ion exchange, generally lead, according to the nature of the modification, not only obtaining hydrophobic adsorbents, but also heterogeneous catalysts. We can mention the exchange of ionswith organic or inorganic cations: the grafting of organic compounds, the activation with acid, the calcination ... etc.

II . 5 .1.activated clays

Acid activation is a useful method for the behavior of clay materials as catalysts, [62, 63] it starts with the adsorption of acid on the solid surface to lead to the substitution of exchangeable ions by protons which arethen diffused to active sites of the activated solid where chemical reactions occur (replacement of structural cations Al^{+3}>, Mg^{+2}>, $Fe^{+3}$by H^{+}). This treatment creates a mesoporosity with significant changes in texture andstructure. [64].

Several works have been published on the application of these new generations of adsorbent materials, they are not only used in the water depollution but they also find their application in the industry as catalysts or catalytic support. [65, 66].

II .5. 2.Organophilic clays

The organophilic treatment is a cationic exchange, the inorganic compensating cations naturally present in the interfoliar space of the clay are replaced by organic cations carrying alkyl chains (surfactants), and the surfactants most commonly used are the alkyl amine ions. During the exchange reaction, the polar head of the surfactant replaces the cation and the surfactant is housed in the interfoliar space thus making the clay organophilic andincreases the interfoliar distance and the adsorption affinity of organic molecules. The literature shows that there is a great tendency to use organophilic clays, their first application (55%) is the field of nanocomposites, and their second application is the adsorption processes. [64].

III. The dyes

III.1. Historical

The evolution of the dyestuff industry has been closely linked to the discovery of the killer (aniline, basic dye) by William Henry Perkin in 1856 and fuchsin by Verguin in 1858. Today there are more than 10,000 dyes , this large number required the establishment of a classification system, an index of dyes in English was developed by the "Society of dyers and colorists" and by the "American Association of Textile".Chemists and colorists "noted (color Index C.I.), which describes the essential characteristics of each dye and a description of the main areas of use [68].

III.2. Definition

The dyestuffs are an assembly of chromophore groups, auxochromes and conjugated aromatic structures (benzene rings, anthracene, perylene, etc.). TheseThe groups are able to transform white light in the visible spectrum from 380 to 750 nm, into colored light by reflection on a body, or by transmission or diffusion.Table 4 shows chromophore and auxochromes grouped by decreasing intensity [68].

Table4: Principal chromophore and auxochromes groups classified by increasing intensity

Chromophoric groups.	Auochrome groups
Azo (-N = N-)	Primary amine (Amino -NH_2)
Nitroso (-N = O or -N-OH)	Secondary amine (Methylamino - $NHCH_3$)
Carbonyl (> C = O)	Tertiary amine (Dimethylamino -N $(CH_3)_2$)
Vinyl (-C = C-)	Hydroxyl (-HO)
Nitro (-NO2 or = NO-OH)	Alkoxyl (-OR)
Thiocarbonyl (> C = S)	Electron donating groups

Methine (-CH =, -CR =) Azomethine (-CH = NH)	NH_3, -COOH, -SO_3H. Iodin (I^-) Bromo (Br^-)

The use of a coloring matter must meet a number of criteria [69]:

- Abrasion resistance.
- Photolytic stability of colors.
- Resistance to chemical oxidation and microbial attack.

III.3. Uses and Applications of Dyes [70]

- In industry:
  - Textile: fur, leather (textile for clothing).
  - Plastics (pigments).
  - Building: paints (pigments).
  - Pharmaceutical (dyes).
  - Cosmetics.
  - Agricultural (food coloring).
  - From the printing press (ink, paper).

III.4. Classification of dyes

The dyes can be classified according to a chemical classification or a dye.The chemical classification is a function of the chemical structure of the dye, specifically the nature of its chromophore group [71].

The dye classification is based on the mode of use and application of the color, which in turn depends on the auxochrome group. Table 5 groups the dyes according to the two types of classification.

Table5: Classification of dyes

Chemical classification	Dye Classification
Anthraquinone dyes Indigo dyes Xanthene dyes Phthalocynin Nitrosated and nitrosated dyes	Acidic or anionic dyes Basic or cationic dyes The vat dyes Direct dyes Mordant dyes Reactive dyes Insoluble azo dyes Disperse dyes

III.5. Dyes and their environmental impacts

Many dyes are visible in water even at very low concentrations ($<1mg.L^{-1}$). Thus, they contribute to the pollution problems associated with the generation of a considerable amount of wastewater containing residual dyes [72]. The release of these waste waters into the ecosystem is a dramatic source of pollution, eutrophication and non-aesthetic disturbance in aquatic life and therefore presents a potential bioaccumulation hazard that can affect humans through transport through the sea. Food chain.

III.5.1. Bioaccumulation

If an organism does not have specific mechanisms, either to prevent the resorption of a substance or to eliminate it once it is absorbed, then that substance builds up. Species at the high end of the food chain, including humans, are exposed to levels of toxic substances that may be up to a hundred thousand times higher than the initial concentrations in water.

III.5.2. Toxicological aspect

Dyes are compounds that are difficult to biodegrade by microorganisms, they are toxic and harmful to humans and animals.

III.5.2.1. Toxicity to human health

Several research studies on the toxic effects of dyes on human health have been developed [73]. Indeed, researchers have shown that amine dyes are often able to cause skin irritation and dermatitis. Similar effects with production of eczema and ulceration have been observed in dyeing plant workers in the triphenylmethane series. Allergic reactions, asthma sometimes and especially eczematous dermatitis have been observed with various azoci and anthraquinone amine dyes.

Amine-based synthetic dyes lead to carcinogenic risks, urinary tumors and especially benign and malignant bladder tumors [74]. In 1913, for the first time, it was realized that there was a connection between the production of aniline and the appearance of bladder cancer: these diseases particularly affected German workers [75].

Other studies have reported that develops a number of adverse reactions in certain individuals such as purity, edema, urticaria, asthma and rhinitis. Azoic dyes are also responsible for the appearance of epatomas in humans [76].Metalliferous dyes can cause damage to sewage systems and disruption of biological treatments in sewage treatment plants because of theirhigh toxicity [77].

III.5.2.2. Toxicity to aquatic environments

A number of dyes are toxic to the aquatic environment causing the direct destruction of communities living there [78].

- Fuchsin, in concentrations greater than 1 mg / L, has a slowing effect on the vital activity of algae [79].
- Discharges from the dyeing and textile factories are at the origin of various pollutions such as: the increase of the BOD5 and the COD, decreasing the capacity of refresh of the rivers and delaying the activity of photosynthesis [80].

III.5.2.3. Toxicity to fish

Fish is a very good model of the toxicity test, not only because it is a good indicator of general water conditions, but also because it is a source important diet for humans. For example, analysis of the available toxicity data for more than 3,000 products sold by member companies of the dye association, in relation to fish, indicates that approximately 98% have lethal LC50 values greater than 1 mg/L. The remaining 2% is broken down into 27 different chemical structures, including 16 basic dyes, of which 10 aretriphenylmethane type [81].

EXPERIMENTAL PART

CHAPTER I

EXPERIMENTAL MATERIALS AND METHODS

I.1. Introduction

The purpose of this chapter is to present the materials and methods used in our study. We used different techniques to characterize the adsorbent and we have analytical methods and an experimental protocol to obtain a good quantification of results.

Due to that we have access to state environment laboratory and materials and here are the materials we used in our work.

The aim of our work to study the optimal dosage adsorbent for the equivalent concentration for the adsorbate.

I.2. Equipment and Materials:

I.2.1 Equipment used:

- **Analytical balance**
  - Name: KERN ABS 220-4N
  - Weighingrange : Maximum 220g – minimum 0.0001g
  - Calibration certificat : DKD KERN 963-101
  - Error range : $\pm 0.3\ mg$
- **Magnetic agitator**
  - Name: Stuart US151
  - Stirrer Speed, RPM: 100-2000
  - Max stirring capacity: 15L
  - Dimensions :172×248×107(W×D×H)

- **Spectrophotometer**
  - Name: UviLine 9400
  - Light Source: Xenon
  - Optical resolution: 4nm

- Display: graphic display with backlit,320×240 pixel
- Temperature Range: use: 10°C to 35°C / Storage –25°C to 65°C
- Dimensions: 404×197×314 mm(W×H×D)

➢ Centrifuge

- Name: Hettich EBA21
- Frequency: 50-60 Hz
- Capacity: 6× 50ml
- Speed/RCF: n=18000 $\min^{-1}$/ RCF 23907
- Dimensions: 247×275×330mm (H×W×D)

Centrifuge manufacturers generally describe how fast the centrifuge is going by **RPM**. Regardless of its size, is revolving at that rate. The force applied to the contents varies by the size of the centrifuge rotor.

In this case is measured in**RCF** force x gravity or g-force. This is the force exerted on the contents of the rotor, resulting from the revolutions of the rotor. And we can calculate it by RPM by this equation **RCF** = $1.1118 \times 10^{-5} \times r \times \text{rpm}^2$. And the r stands for the rotor radius in centimeters.

I.2.2 Materials:

- The clay Montmorillonite.
- Deionized water with conductivity less than 5 µS/cm.
- The dye RED sandocryl.

I.2.2.1 The adsorbent

Characterization of sodium Montmorillonite and Interposed of Montmorillonite.

- **Specific surface and porosity**

  The Brunauer-Emmett-Teller (B.E.T) method allowed us to access the specific surface area ofsodium montmorillonite and inter-bedded montmorillonite.

- **Diffraction X-ray**

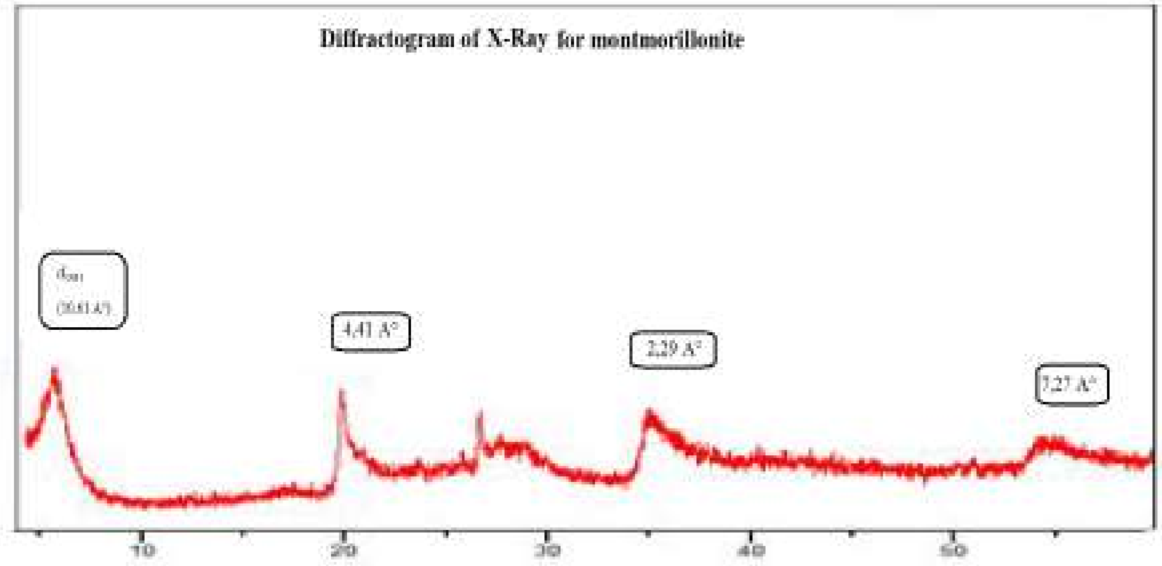


Figure10 : Diffractoganm **of X-ray for** montmorillonite.

The clay diffraction graph (mont-Na) shown in the figure reveal the presence of clay minerals and crystalline phases essentially in the form of tectosilicates (at $2\Theta = 20°$ (4.42A°), chlorite at $2\Theta = 35°$(2, 39 A°), kaolin at $2\Theta = 60$ ° (7.27 A°)).

The widening of the d_{001} peak that characterizes montmorillonite is representative of the order of the leaflets, which could be explained by the bursting of the material layers, which makes the interfacial surface more exposed. This phenomenon is called the delamination of the sheets of the material (no stacking between the sheets). [82].

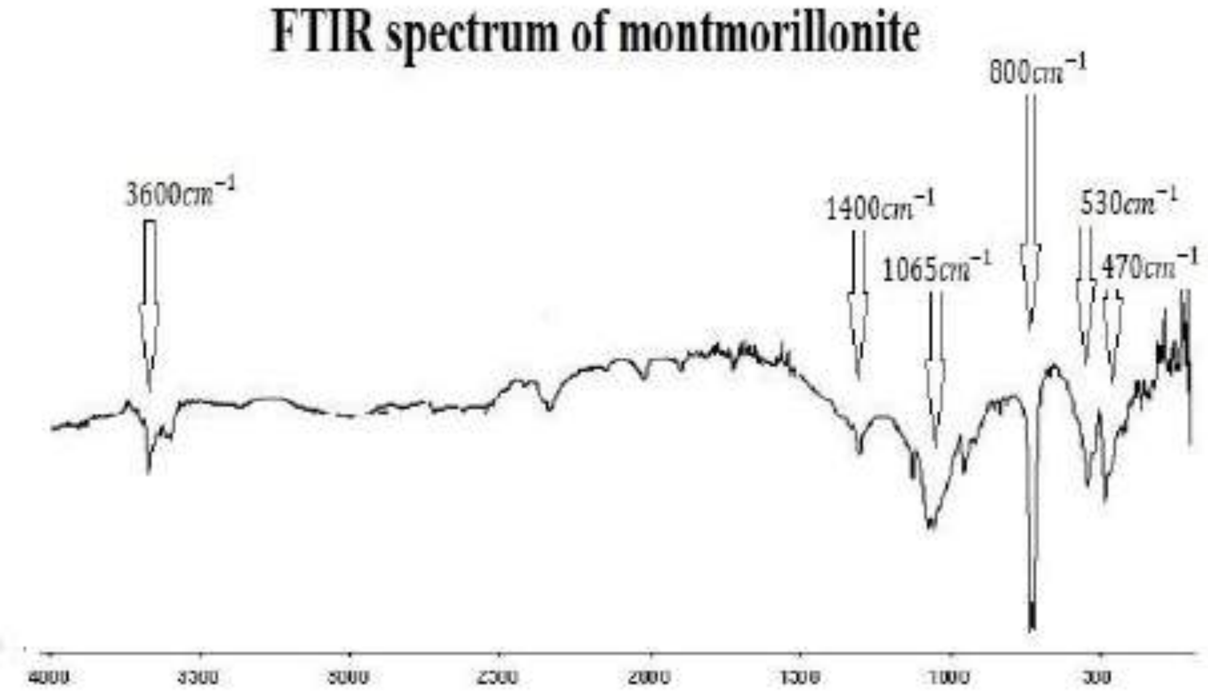


Figure 11:FTIR spectrum of montmorillonite

- **FTIR spectrum**

The spectra show the absorption bands (3600, 1400, 1065, 800, 530, and 470 cm^{-1}) that correspond to the Si-O, Al-O and Ca-O vibrations.

The presence of calcium associated with carbonates is related to the presence of calcite and this has been confirmed by thermogravimetric analysis.

The absorption bands (1065, 1047, 917, 530 and 470 cm^{-1} are assigned to SiO4.

The bands corresponding to the Al-Al-OH groups are observed at 800 cm^{-1} . At 620 cm^{-1} , the vibrations attributed to Al-O groups associated with SiO 2 are observed.[82].

The FTIR spectrum has two bands at 3546 $cm^{-1}$and 1700 cm^{-1}, which respectively correspond to the OH groups of the silanol groups (Si-O-H) and to the water molecules.

I.2.2.2.The adsorbate:

The adsorbate we used in our study is a basic textile dye which is the red sandocryl supplied by the textile company ALCOVEL Akbou (Algeria) which the formula is shown in Figure and the main properties are summarized in the table. .

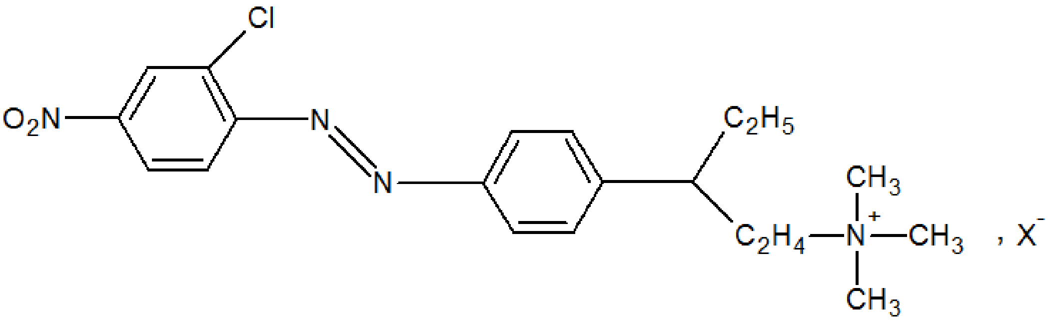


Figure 12: The developed formula of sandocryl red

Table6 : Characteristics of the red sandocryl dye.

Name commercial	Raw Formula	Type	Wight molar (g/mole)	λ_{max} (nm)
Basic red Cl 18	$C_{20}H_{26}N_4O_2Cl$	cationic	389.5	530

I.3. Operational mode:

I.3.1. UV Visible characterization methods

Molecular absorption spectroscopy is based on the measurement of the transmittance T or absorbance A of solutions contained in transparent cells having an absorption path length equal to 1. In general, between the concentration of an absorbent analyte and the absorbance, there is a linear relationship expressed by the BeerLambertequation ;

$$\boldsymbol{A = Log\frac{I_0}{I} = \varepsilon.I.C = -logT}$$

or

A: Refers to the absorbance.

I: Intensity of the incident ray.

I_0 : Intensity of the transmitted ray.

ε : The absorption coefficient which is a constant for an absorbing species and a given transition (L / mol.cm).

C: The molar concentration of the absorbing species (mol / L).

T: Transmittance.

I .3.2. Preparation of solutions:

At first we start to prepare mother solution of concentration equal to 50 mg / L or (50 ppm) was prepared by dissolving 200 mg of red sandocryl in a 4 liter of distilled water. Then, solutions of lower concentrations (10, 20, 30, 40 mg / L) were prepared by diluting the mother solution in distilled water.

I.3.3.The measuring process:

The analysis were carried out on a Visible UV spectrophotometer the samples are analyzed at the maximum wavelength λ_{max} corresponding to the maximum adsorption of the dye. λ_{max} is determined after scanning wavelengths between 400 and 800 nm on a sample of dye solution at different concentrations.

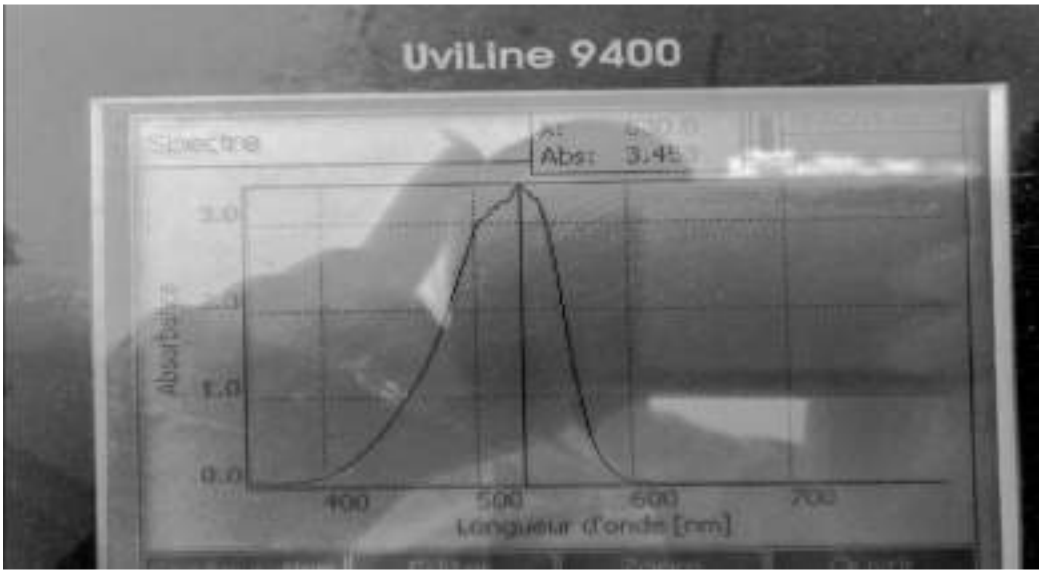


Figure 12: Visible spectrum of sandocryl red

I.3.4 Preparation of calibration solutions

Concentration standard solutions range from 1 to 10 mg / L were prepared by dilution of a Mother solution of 50 mg / L is been analyzed at the wavelength (λ equals 531 nm) corresponding to the maximum absorption of sandocryl red.

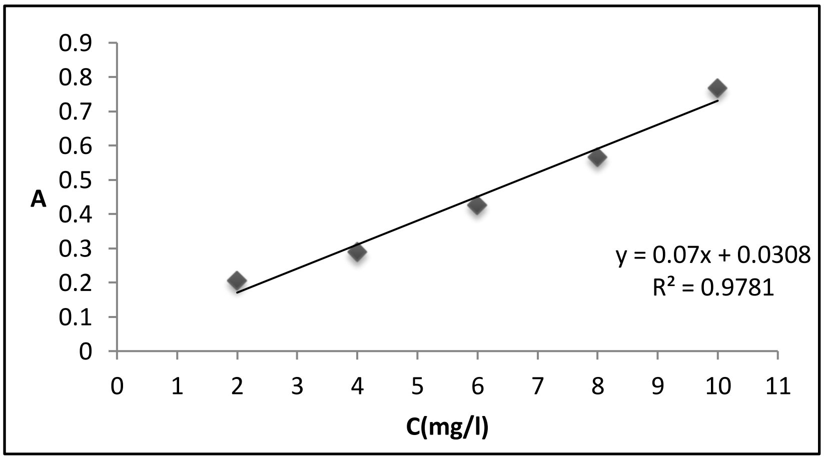


Figure 13: Calibration graph

I.4.Studied parameters:

For the experiment temperature always was the ambient temperature T=30°C ± 3°Cand the pH was fixed during the whole experiment investigated the influence of the following parameters on the amount of dye adsorbed by the different Montmorillonite samples:

- The adsorbate-adsorbent contact.
- The mass of the adsorbent.
- The initial concentration of the adsorbate.
- The stirring speed was on low speed.

I.4.1. Experimental protocol:

The adsorption tests were carried out in Erlenmeyer flasks covered with caps in order to avoid the contamination of our solutions by other elements and the modification of the pH.

For each contact time, a certain quantity of montmorillonite is introduced into an Erlenmeyer flask with 100 ml of the dye solution at a given C0 concentration (mg / L).

The heterogeneous mixture is subjected to permanent magnetic stirring using a magnetic bar, on a agitation plate, to ensure contact between the absorbent and the adsorbent.

After a stirring time given 24h, a volume of 10 mL of the solution is taken and centrifuged at 5000 rpm for 5 minutes. The residual concentration is monitored by UV-Visible spectrophotometry after establishment of a calibration curve.

After determining the equilibrium time, the same experimental protocol was followed for the study of other influencing parameters on adsorption.

CHAPTER II

RESULTS AND DISCUSSION

II. Adsorption experiment

II.1.The influence of clay dosage on different dyes concentration

Our work is on the influence of different clay dosage on initial dyes concentration and the effect of the dosage in different concentration of dyes.

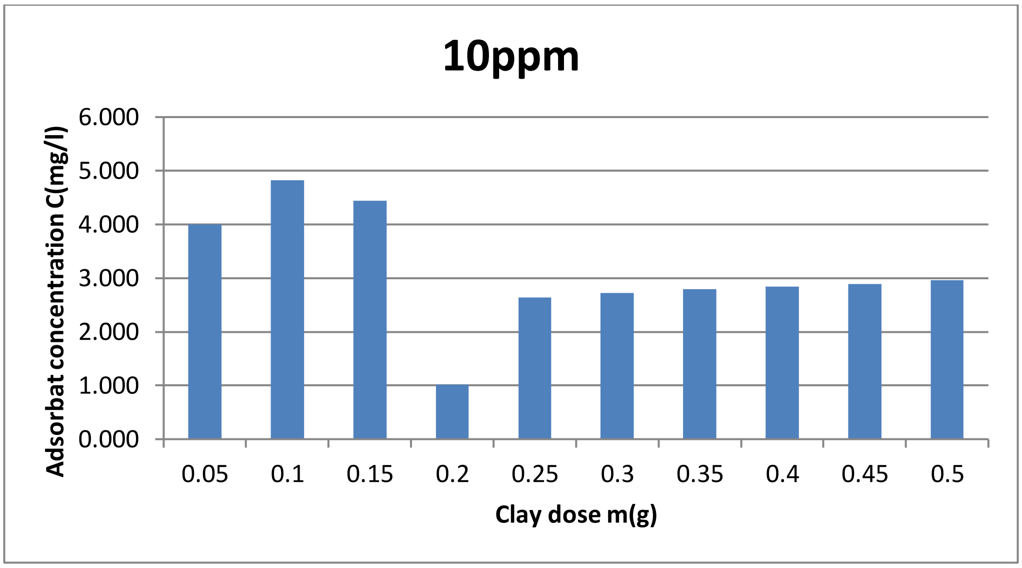


Figure14: Influence of clay dosage in 10ppm dye concentration

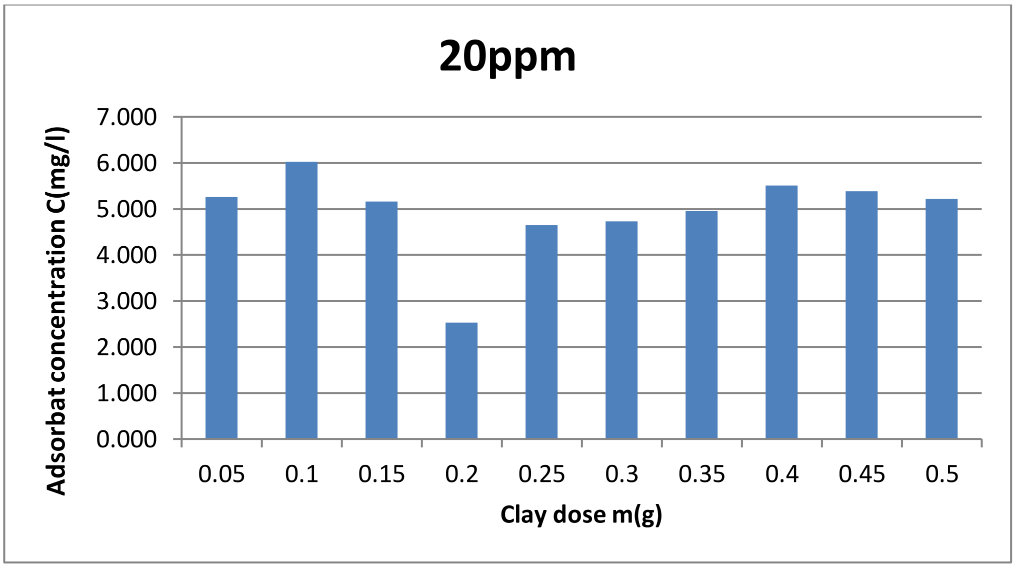


Figure15: Influence of clay dosage in 20ppm dye concentration

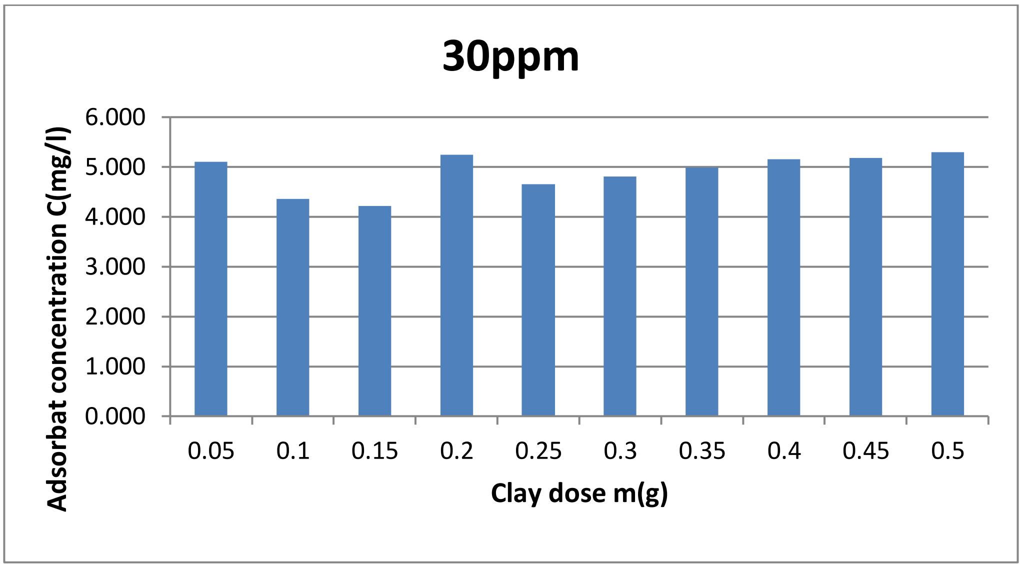


Figure16: Influence of clay dosage in 30ppm dye concentration

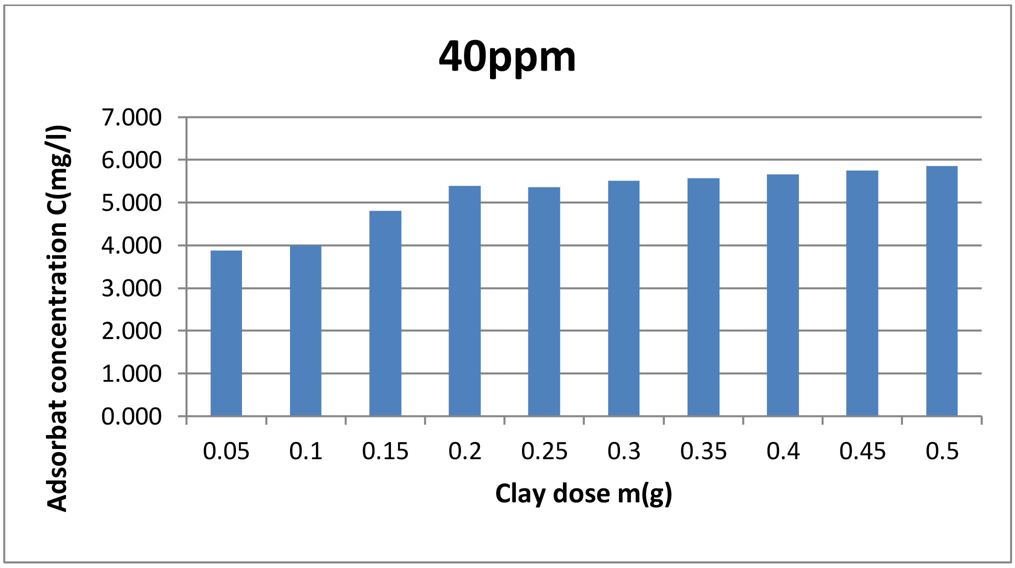


Figure 17: Influence of clay dosage in 40ppm dye concentration

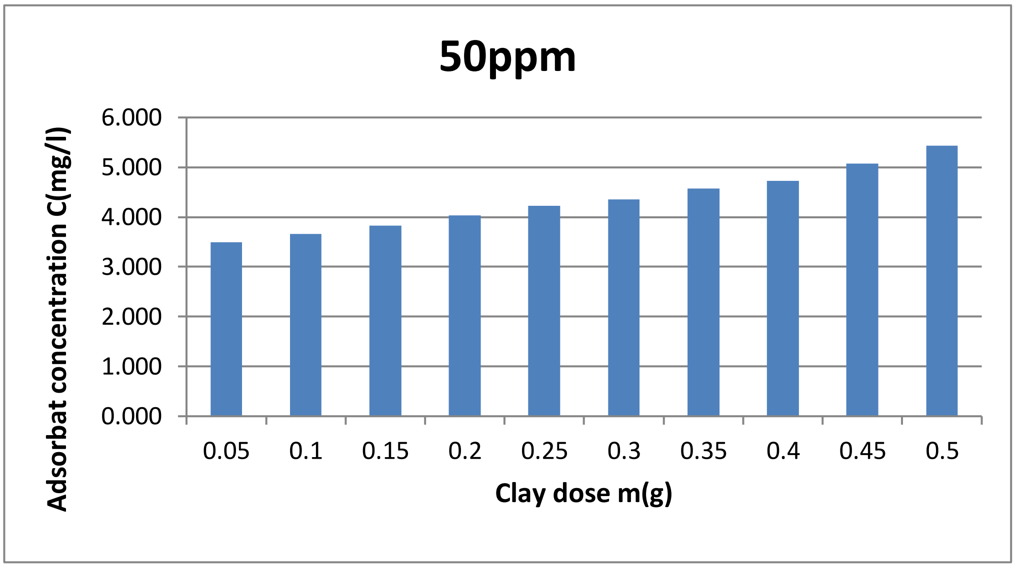


Figure 18: Influence of clay dosage in 50ppm dye concentration

Due to above graphs the shows the relation between the clay dosage and dyes concentrations we get conclusion that 0,2g is the optimal dosage of clay for all dyes concentrations.

II.2. Modeling of isotherm adsorption

The isotherm adsorption are important for the description of any interaction between the adsorbate molecules and the surface of the adsorbent.

For the analysis of our results we used the models of Langmuir and Freundlich

II.2.1.The models of Langmuir

The following figure and table shows the linearization for the experimental data according to the Langmuir model.

Table 7: Values ofLangmuir linear equation

C_0	**C_e**	**x**	**$x/m = q_e$**	**Ce/q_e**
10	1,014	0,8986	4,493	0,2256
20	2,529	1,7471	8,7355	0,2895
30	5,251	2,4749	12,3745	0,4243
40	5.386	3.4614	17.307	0.3112
50	4.029	4.5971	22.9855	0.1752

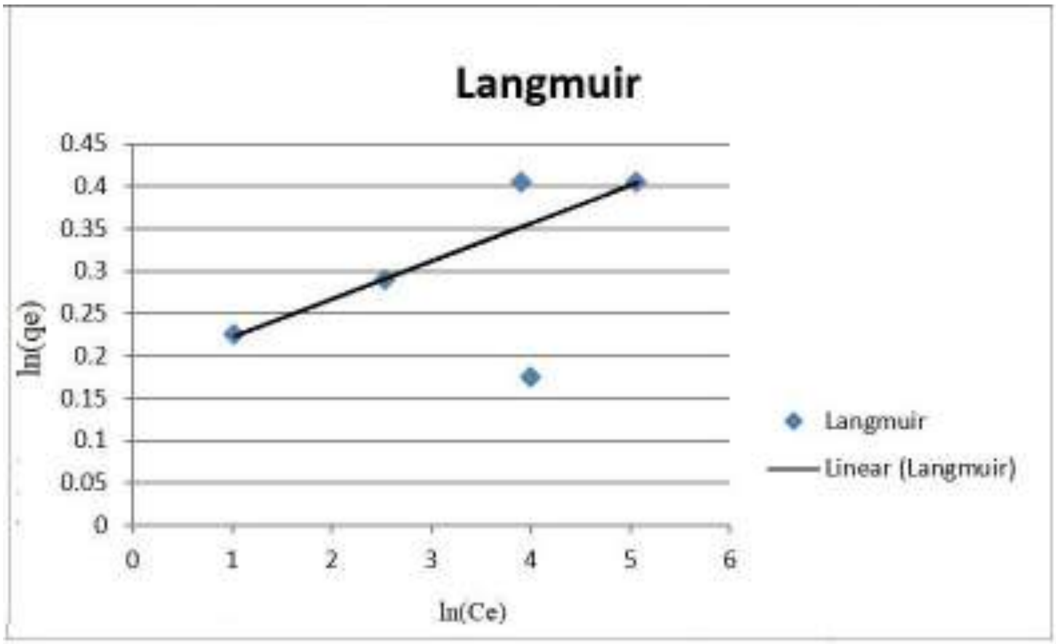


Figure19: Experimental Modeling results according to the Langmuir model

Table 8: Langmuir Parameter Values

Parameters	Value
R^2	0.998
q_m	21.2769
K_L	0.2701

R_L	**10mg/l**	0,7850
	20mg/l	0,413
	30mg/l	0.5942
	40mg/l	0.4074
	50mg/l	0.4789

We find that R_L value is between 0 and 1. and it is fully noted that the adsorption is favorized at low concentrations given the R_L values which decrease when the dye concentration increases. Therefore, the Langmuir model is verified for the Sandocryl Red, indeed, the correlation coefficients found are close to 1 and the errors are small.

In this sutation we will only use 10,20 and 30ppm for the next modiling

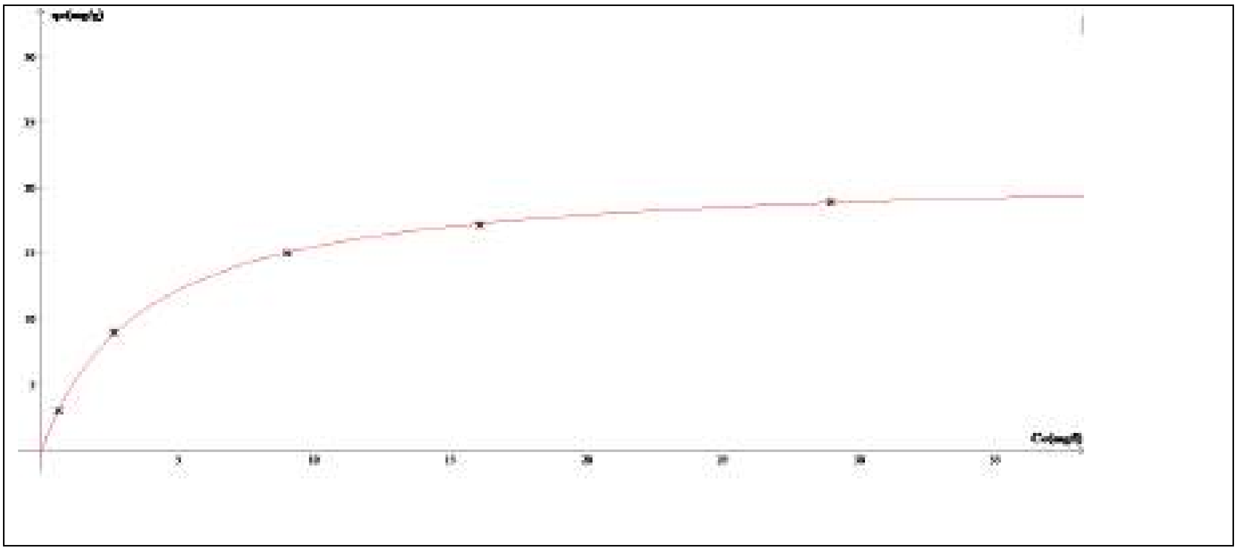


Figure20:isothermal adsorption Freundlichmodelof RS on clay with theexperimental points

II.2.2. Themodels ofFreundlich

The following figure and table shows the linearization for the experimental data according to the Freundlich model.

Table 9: Values of Freundlich linear equation

C0(mg/L)	**Ce(mg/L)**	**x** (mg)	**x/m = qe**	**ln(Ce)**	**ln(qe)**
10	1,014	0,8986	4,493	0,01390291	1,50252063
20	2,529	1,7471	8,7355	0,92782397	2,16739518
30	5,251	2,4749	12,3745	1,65841853	2,5156379

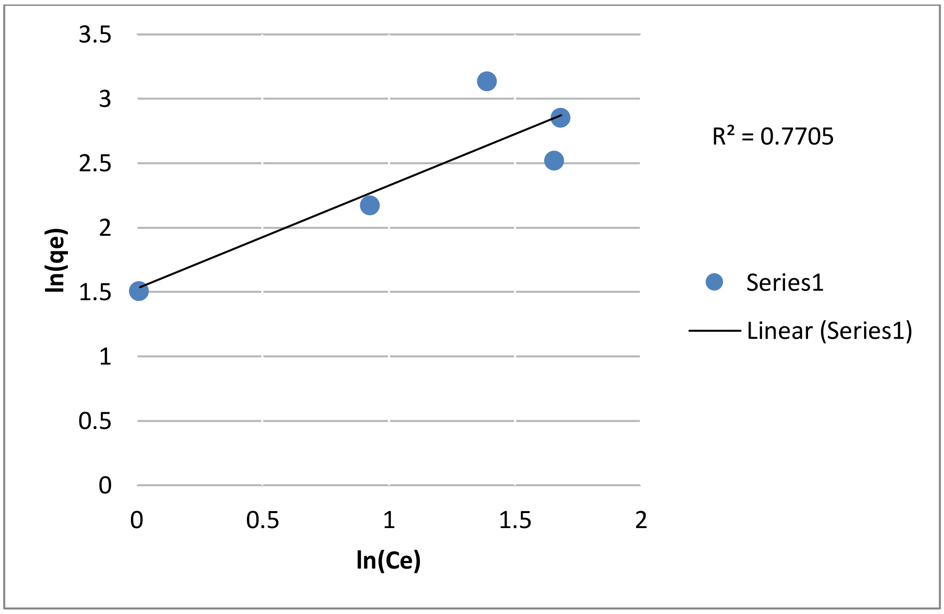


Figure21: Experimental Modeling results according to the Freundlichmodel

Table 10: Freundlich Parameter Values

Parameters	Value
$\mathbf{R^2}$	0.770
1/n	0.62
n	1.61
$\mathbf{K_L}$	4.5859

The values of 1/n obtained from modelization Freundlich equal to 0,62 which is less than 1 what indicate that the adsorption intensity type L, in this case n=1,62 is restricted between 1 and 2, and we can conclude that adsorption is moderately difficult

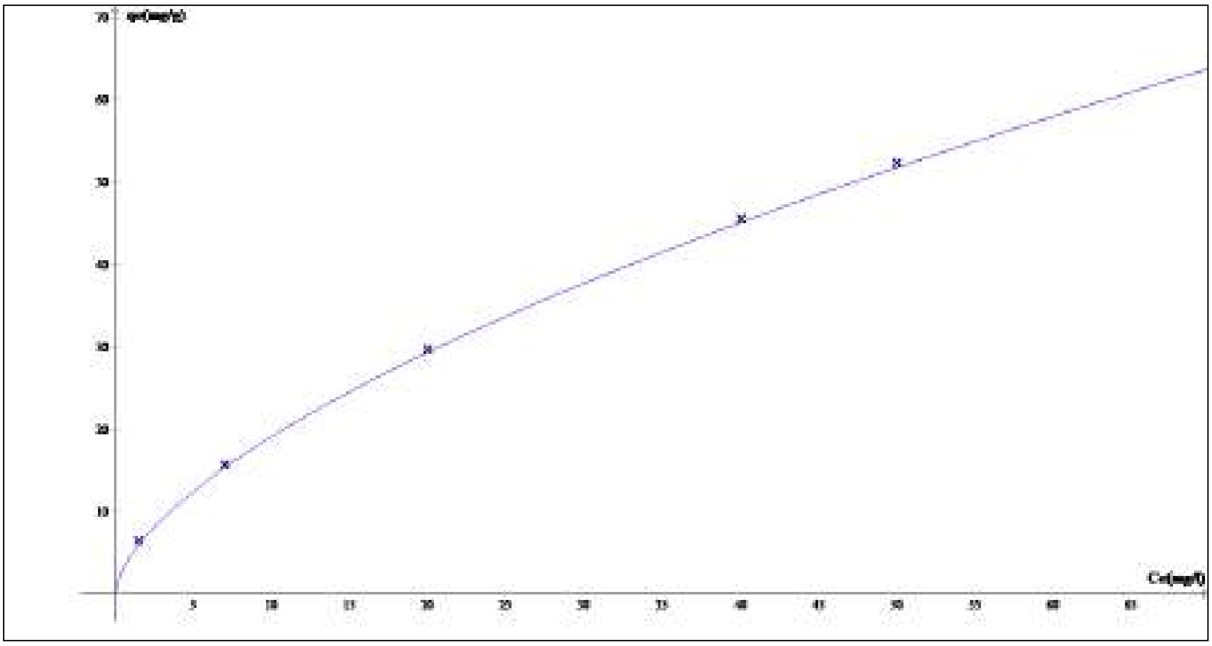


Figure22:isothermal adsorption Freundlich model of RS on clay with theexperimental points

II.2.3. Comparison of the two adsorption isotherm models

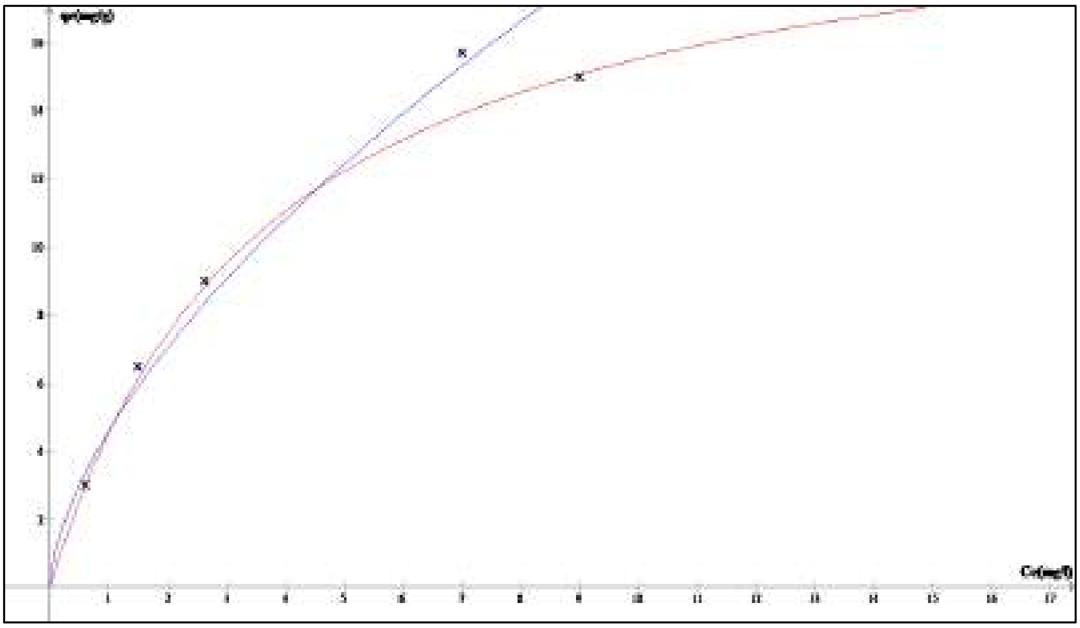


Figure 23:Comparison of the two RS adsorption isotherm models on clay with the experimental points.

The results for the clay shows that the isotherm is class L, which corresponds to the classification of Gilles. The isothermal class L has presented, at low concentrations of solution, a concavity facing downwards which reflects a decrease in free sites as the adsorption progresses.

The Langmuir model indicates a flats adsorption of bi-functional molecules. The ratio of the concentration in the aqueous and adsorbed solution decreases as the concentration of the solute increases. Thus describing a concave curve, this curve suggesting a gradual saturation of the adsorbent.

CONCLUSION

In our modern world we issued a lot of pollution in many different ways and some of them are crucial to our well-being and in our topic we issued water pollution by industrial dyes. And many researchers each one in his field trying to solve this pollution problem, and in chemistry there is many substances chemically and physically, synthetic and natural, can remove pollution we find clays and charcoal….ext.

In our study we spot light on RED sandocryl dye as polluted with different concentrations (10, 20, 30, 40, 50ppm) and different concentrations of montmorillonite (0.05 , 0.1, 0.2, 0.25, 0.3, 0.35; 0.4, 0.45, 0.5 g) as adsorbent.
We obtained the optimal dose for the adsorbent almost for all the concentrations is 0.2g.

Than we have focused our work on the optimal dose for clay in the adsorbate by measuring adsorption by UV-Vis spectrophotometer, and after all the results of our work we conclude;

A best dose for the adsorbent in low concentration of the adsorbate is 0.2g of montmorillonite, after using the optimal dose of adsorbent in low concentration 10, 20, 30, 40, 50 PPM

That montmorillonite is good adsorbent when it comes to low concentration of RED sandocryl.

Uses and recommendation

- ✓ Develop a batter uses for montmorillonite clay especially as natural and low cost substance
- ✓ Better activation and developing clay characteristics for the montmorillonite clay.

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