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Experimental studies on the adsorption of diclofenac onto sandstone mineral clay

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GENERAL INTRODUCTION

General Introduction

One of the major environmental pollution is wastewater. These polluted waters come from the domestic, agriculture and industries establishments since the increasing of population and industrial expansion, especially from the developed countries. These contaminants are become a great concern to the environment and public health (Y. Binti Che Ani, 2004).

The priority of the water contaminants has turned recently to emerging micro-pollutants from different origins such as heavy metals, aromatics polycyclic hydrocarbon, dyes, pigments, radioactivities and pharmaceutical products which are more and more frequently found in various aquatic compartments (T.de Oliveira and all, 2017). The extensive use of pharmaceuticals in human and veterinary medicine has become a major environmental concern because pharmaceuticals are designed to be highly active or toxic to biological systems. Even though individual pharmaceuticals have been detected in low concentrations (ng- μ g/l) the occurrence of numerous pharmaceuticals with similar mechanisms of action may have significant effects on aquatic and terrestrial wildlife through additive exposures (Daughton and Ternes, 1999; A.C Mehinto, 2009)

Among pharmaceutical products that are non-biodegradable and recalcitrance to conventional wastewater treatments, diclofenac, a non-steroidal anti-inflammatory drug, is one of the few compounds that shows harmless actions on both aquatic and terrestrial ecosystems (P. Verlicchi and E. Zambello, 2014; M. Coquery and all, 2009; A. Sadezky and all, 2008; C. Miege and all, 2009). The occurrence of diclofenac in surface, groundwater and drinking water, as well as in wastewater, results to its high consumption in modern countries that stands to 200-2300 μ g day⁻¹ habitant⁻¹ (J. Schwaiger and all, 2004; B. Kasprzyk-Hordern and all, 2009) which leads thus to discharge with concentration up to 1000 ng L⁻¹ in wastewater plants influents (C. Miege and all, 2009; T.de Oliveira and all, 2017).

Up to now, many methods have been used to trap or degrade pharmaceutical contaminants from water, such as biological degradation (Burgos, W.D; and all, 2000) ozonation (Zhu, H.Cand all, 2014), photocatalytic degradation (Gcina, M.and all, 2015), etc. however, Their application is challenged by poor treatment efficiency, difficulty in generating microbial consortia, expensive analysis, and the generation of secondary pollutants (Ou, H.X and all, 2015; Wang, L, 2012).therefore, alternative methods are sought, among them adsorption, as it has been found to be potentially an effective and attractive process for the wastewater

treatment because of low operational cost and high efficiency in the preconcentration processes using natural adsorbents such as humic substances (Richter et al., 2009), organic materials (Kahle and Stamm, 2007a), soils (Kurwadkar et al., 2007; Sanders et al., 2008; Braschi et al., 2010) and clay minerals (Thiele-Bruhn et al., 2004; Gao et al., 2005; Kahle and Stamm, 2007b; X. Yang and all, 2017).

Recently, clay minerals have been attracted much attention by many researchers and industrialists in different fields of application, in addition of their easy availability and low-cost, clay minerals has remarkable physical and chemical properties such as thermal stability, elasticity, high absorption capacity, specific surface area, catalytic properties...etc, and an abundance and capacity to retain pollutants, which make them the scientists objective for several studies and applications in the industrial, petrochemical fields and waste water treatment (M.M Mhidi and K.K Amazigh, 2017). This work investigated the feasibility of diclofenac adsorption by raw, thermal and chemical modified sandstone. Surface properties of sandstone before and after modification were characterized by means of Fourier-transform infrared (FT-IR) spectra. Several key experimental parameters were investigated, including water temperature, adsorbent mass, as well as contact time. The experimental data were analyzed through isotherm adsorption models. The kinetic adsorption results have been analyzed using pseudo-first-order and pseudo-second-order reactions. The adsorption mechanism was also carried out according to thermodynamics and kinetics principles (X. Yang and all, 2017). Our master thesis is subdivided in two chapters:

- Chapter I which is a literature review about clays essentially the sandstone (composition, structure and classification) and we have summarized some essential information on anti-inflammatories.
- Chapter II is an experimental adsorption study of :
 - ✓ Various reaction parameters influences (adsorbent mass, contact time and temperature... etc).
 - ✓ Kinetic models.
 - ✓ Isotherms
 - ✓ Thermodynamic study

Finally, a general conclusion is done to summarize the results obtained and the perspectives.

Chapter I: litterature review

I-1- Introduction:

The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals, generally plastic at appropriate water contents and will harden when dried or fired. Clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired. Associated phases in clay may include materials that not impart plasticity and organic matter. The term "clay mineral" refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing, and they predominate the clay-sized ($<2 \mu\text{m}$) fraction of soils. Clay minerals are layer silicates that are formed usually as products of chemical weathering of other silicate minerals at the earth's surface (Dr. T. Al-Ani and Dr. O. Sarapää, 2008). These minerals are similar in chemical and structural composition to the primary minerals that originate from the Earth's crust; however, transformations in the geometric arrangement of atoms and ions within their structures occur due to weathering. Primary minerals form at elevated temperatures and pressures, and are usually derived from igneous or metamorphic rocks. Inside the Earth these minerals are relatively stable, but transformations may occur once exposed to the ambient conditions of the Earth's surface. Although some of the most resistant primary minerals (quartz, micas, and some feldspar) may persist in soils, other less resistant minerals (pyroxenes, amphiboles, and a host of accessory minerals) are prone to breakdown and weathering, thus forming secondary minerals. The resultant secondary minerals are the culmination of either alteration of the primary mineral structure (incongruent reaction) or neoformation through precipitation or recrystallization of dissolved constituents into a more stable structure (congruent reaction) (CD.Barton and A.D. Karathanasis, 2002).

Clay minerals act as "chemical sponges" which hold water and dissolved plant nutrients weathered from other minerals. This results from the presence of unbalanced electrical charges on the surface of clay grains, in which some surfaces are positively charged (and thus attract negatively charged ions), while other surfaces are negatively charged (attract positively charged ions). Clay minerals also have the ability to attract water molecules. Because this attraction is a surface phenomenon, it is called adsorption (Dr. T. Al-Ani and Dr. O. Sarapää, 2008). These secondary minerals are often referred to as phyllosilicates. Because, as the name implies (Greek: phyllon, leaf), they exhibit a platy or flaky habit, while one of their fundamental structural units is an extended sheet of SiO_4 tetrahedra (CD. Barton and A.D. Karathanasis, 2002).

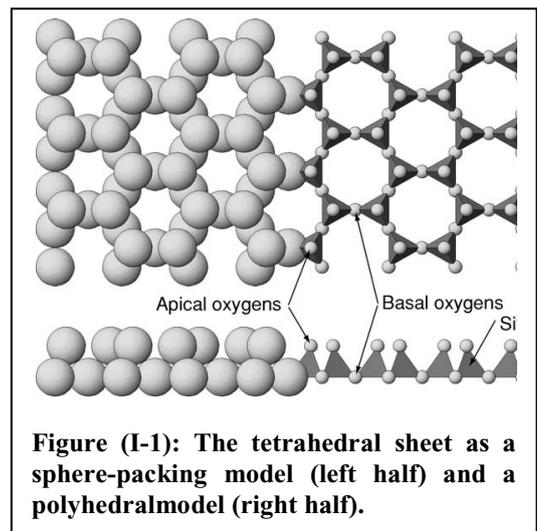
I-2- Major Element Composition of Clay Minerals

Most of the mass and volume of the Earth's crust is made up by only a few chemical elements. Oxygen and Silicium alone account for almost 75% of the mass, with most of the remainder, in order of decreasing abundance, consisting of Al, Fe, Ca, Na, K, Mg, Ti, H, P, and Mn. On a volume basis, oxygen alone accounts for more than 90% of the total volume. O, as O^{2-} , is the only abundant anion, while the other abundant elements are all cations. Most of these cations have only one stable oxidation state at the Earth's surface (Al^{3+} , Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Ti^{4+} , H^+ , P^{5+}); Fe (Fe^{2+} , Fe^{3+}) and Mn (Mn^{2+} , Mn^{3+} , Mn^{4+}) are the exceptions. The O^{2-} anions are much larger than most of the positively charged cations. The Earth's crust, therefore, can be characterized as large O atoms in an approximately close-packed arrangement held together by attraction to smaller cations located in the interstitial space. Most of the elements in the crust and in soils occur in minerals, and the elements listed above are major constituents of the most abundant minerals, including clay minerals. Building on the concept of packing O atoms in space, we will consider atoms as rigid spheres, realizing that this is an oversimplified but convenient model for developing the key structural concepts (D.G. Schulze, 2005)

I-3- Basic Structural Concepts

Two distinct structural features occur within the crystal structures of soil clay minerals as a consequence of packing the large O^{2-} ions together in space (D. G. Schulze, 2005)

I-3-1- The tetrahedron: is one of the solid geometric forms used to represent the arrangement of atoms in clay mineral crystal structures (Dr. T. Al-Ani and Dr. O. Sarapää, 2008). It is formed by connecting the centres of the four oxygen anions packed closely together, and can be described as three O^{2-} ions arranged in a triangle with the fourth O^{2-} occupying the dimple formed by the other three (figure I-1). The centers of the four O^{2-} ions form the apices of a regular tetrahedron, and the small space in the center is called a 'tetrahedral site.' Cations located in tetrahedral sites are in fourfold or tetrahedral



coordination, because they are surrounded by and bonded to four O^{2-} ions (D. G. Schulze, 2005). In the clay minerals the predominant central cation of the tetrahedron is silicon. A

limited number of tetrahedral are occupied by aluminium and occasionally ferric iron or other elements (Dr. T. Al-Ani and Dr. O. Sarapää, 2008).

I-3-1-1- Tetrahedral Sheet: The tetrahedral sheet consists of SiO_4 tetrahedra arranged such that three of the four O^{2-} ions of each tetrahedron are shared with three nearest-neighbour tetrahedra. These shared O^{2-} ions are all in the same plane and are referred to as basal oxygens. Note that adjacent tetrahedra share only one O^{2-} between them (the tetrahedra share apices or corners). The fourth O^{2-} ions of each tetrahedron are not shared with another SiO_4 tetrahedron and are free to bond to other polyhedral elements. These unshared O^{2-} ions are referred to as apical oxygens. Since each basal oxygen contributes a charge of -1 to each Si^{4+} ion, the addition of H^+ ions to the apical oxygens to form hydroxyls should result in an electrically neutral tetrahedral sheet. Such individual tetrahedral sheets do not form stable mineral structures by themselves and only occur in combination with octahedral sheets, all of the apical oxygens pointing in the same direction, namely, out of the plane of the paper toward the reader. This is the most common arrangement, but structures also occur in which the apical oxygens point alternately in opposite directions (D. G. Schulze, 2005).

I-3-2- The Octahedron: structural feature consists of six closely packed Oxygen ions. Three of them are arranged in a triangle in one plane, and the other three, also in a triangle but rotated 60° relative to the first three, are in a second plane so that the two triangular groups intermesh (Figure I-2). The centers of the six O^{2-} ions form the apices of a regular octahedron, and the small space in the center is called an 'octahedral site.' Cations located in the octahedral site are said to be in sixfold or octahedral coordination because they are surrounded by and bonded to six Oxygen ions (D. G. Schulze, 2005). The cations are usually aluminium (Al), iron (Fe), and magnesium (Mg) atoms (Dr. T. Al-Ani and Dr. O. Sarapää, 2008).

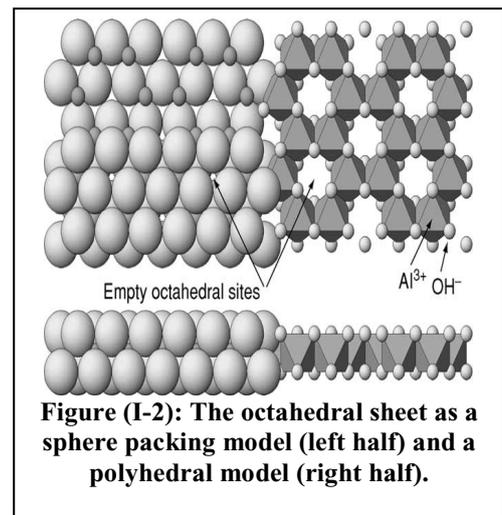


Figure (I-2): The octahedral sheet as a sphere packing model (left half) and a polyhedral model (right half).

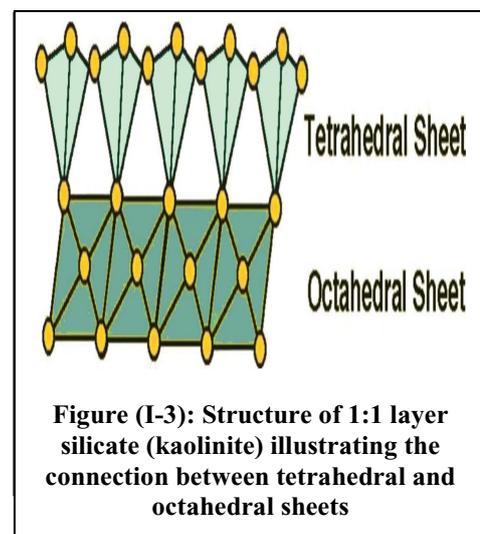
I-3-2-1- Octahedral sheet: Analogous to the tetrahedral sheet, we can consider the octahedral sheet as an assemblage of octahedra in which adjacent octahedra share two oxygens with one another. In other words, adjacent octahedra share edges. For the arrangement of octahedra, the octahedral sites are occupied by trivalent cations, typically Al^{3+} , and for charge balance, a

proton (H^+) must be associated with each O^{2-} . (The H^+ takes up very little space, and the HO^- ion can be considered a sphere of roughly the same size as an O^{2-} ion.) Each HO^- contributes one-half a negative charge to each cation because each HO^- is shared between two octahedra. Each Al^{3+} cation is therefore effectively surrounded by $6 \times 0.5 = 3$ negative charges and the sheet is electrically neutral. Note the pattern of empty and filled octahedral sites. Two of every three possible octahedral sites are filled when trivalent cations are present in the octahedral sites. This arrangement is called dioctahedral and is the most common in soil clay minerals. If the octahedral sites are filled with divalent cations such as Mg^{2+} then every possible octahedral site must be occupied to produce an electrically neutral structure. This arrangement is called trioctahedral. Octahedral sheets, stacked one on top of the other and held together by hydrogen bonds, make up the structure of gibbsite, $Al(OH)_3$, an aluminium hydroxide mineral that occurs in intensively leached soils. The structure of gibbsite is the simplest in a series of structures containing octahedral sheets (D. G. Schulze, 2005).

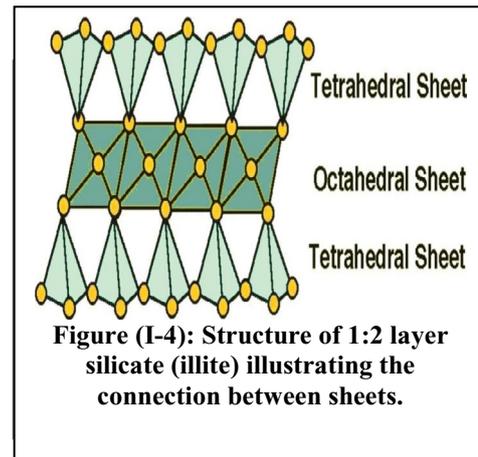
- **Tetrahedral and octahedral sites** differ in another important way. The space that can be occupied by a cation in a tetrahedral site is smaller than the space that can be occupied in an octahedral site. Since cations vary in size, smaller cations tend to occur in tetrahedral sites, somewhat larger cations tend to occur in octahedral sites, and the largest cations must fit into spaces that are even larger than octahedral sites. Cations with sizes intermediate between the optimum for two sites can occur in either site. The Al^{3+} ion, for example, can occur in either octahedral or tetrahedral sites (D. G. Schulze, 2005).

I-3-3- Layer types:

These basic building blocks are linked in clay minerals to form sheets of silica tetrahedral and aluminium or magnesium octahedral. The silica tetrahedral sheet (T) and the octahedral sheet (O) are joined in two possible ways: (1) The 1:1 layer silicate structure, 1(T) + 1(O) sheet so that the apical oxygen of the tetrahedral sheet replaces one hydroxyl of the octahedral sheet to form what is termed the 1:1 clay mineral layer as kaolinite (Figure I-3). The second way the 2:1 layer silicate



structure, 1(O) +2(T) sheets so that 2/3 of hydroxyls in the octahedral sheet between 2 tetrahedral sheets are replaced by apical oxygens of the tetrahedral sheet to form 2:1 clay mineral layer (Figure I-4). (Dr. T. Al-Ani and Dr. O. Sarapää, 2008).



I-4- Clay minerals Classification

The important structural and chemical differences among the clay minerals are the basis for the individual mineral species names and the arrangement of the species in groups. Planar hydrous phyllosilicates, the common clay minerals, are classified according to the layer type (1:1- and 2:1-type minerals), the magnitude of the net layer charge, and the type of interlayer material, the character of the octahedral sheet, and the composition or structure of individual species (Dr. T. Al-Ani and Dr. O. Sarapää, 2008).

I-4-1- Type Minerals 1:1

- Kaolinite:** Within the kaolin group minerals, kaolinite is the most abundant and has received most attention in terms of its structure, properties and industrial applications (Dr. T. Al-Ani and Dr. O. Sarapää, 2008). The structure of kaolinite consists of 1:1 layers stacked one above the other. Kaolinite contains Al^{3+} in the octahedral sites and Si^{4+} in the tetrahedral sites (Figure I-5). The 1:1 layer is electrically neutral and adjacent layers are held together by hydrogen bonding between the basal oxygens of the tetrahedral sheet and the hydroxyls of the exterior plane of the adjacent octahedral sheet. Kaolinite is a common mineral in soils and is the most common member of this subgroup. It tends to be particularly abundant in more weathered soils such as Ultisols and Oxisols. Kaolinites have very little isomorphous substitution in either the tetrahedral or octahedral sheets and most kaolinites are close to the ideal formula $Al_2Si_2O_5(OH)_4$. The 1:1 layer has little or no permanent charge because of the low amount of substitution. Consequently, cation exchange capacities and surface areas are typically low. Soils high in kaolinite are generally less fertile than soils in which 2:1 clay minerals dominate. Kaolinite can form in soils from Al and Si released by the weathering of primary and other secondary minerals. For example, feldspars often weather to kaolinite in soils formed from igneous rocks. Kaolinite can also be inherited from clayey, sedimentary soil parent materials.

- Halloysite:** Halloysite has a 1:1 layer structure similar to kaolinite except that the 1:1 layers are separated by a layer of H₂O molecules when fully hydrated (Figure I-5). This water is probably present as hydration shells around a small number of interlayer cations (cations that reside between two adjacent 1:1 or 2:1 layers), although the presence of interlayer cations and the existence of layer charge to attract them has been difficult to confirm. Most clay silicates occur as thin plates, but halloysite often occurs as tubular or spherical particles. Halloysite is usually found in soils formed from volcanic deposits, particularly volcanic ash and glass. It is a common clay mineral in the Andisol soil order. Halloysite forms early in the weathering process but it is generally less stable than kaolinite and gives way to kaolinite with time.

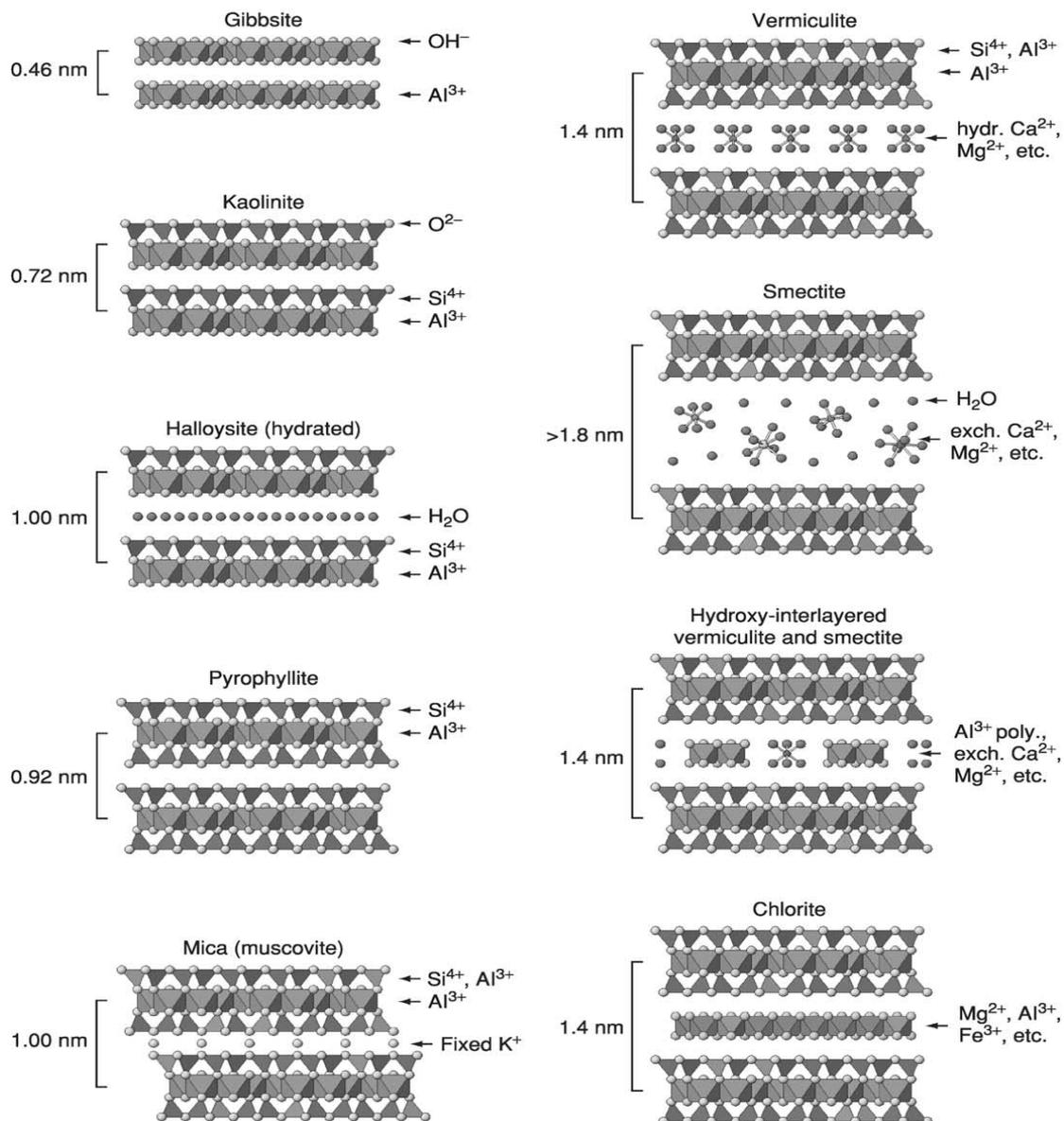


Figure (I-5): Structural scheme of soil minerals based on tetrahedral and octahedral sheets.

I-4-2- Type Minerals 2:1

In contrast to the 1:1 minerals, which are represented in soils by only two major minerals, the 2:1 minerals are structurally more diverse and are represented by several mineral species.

- **Pyrophyllite:** The simple structure of pyrophyllite is a good starting point for discussing 2:1 structures. Pyrophyllite consists of 2:1 layers stacked one above the other. The tetrahedral sheets contain only Si^{4+} and the octahedral sheet contains only Al^{3+} , resulting in the ideal formula $\text{Al}_2(\text{Si}_4)\text{O}_{10}(\text{OH})_2$. The charge is balanced completely within the 2:1 layer, making the layer electrically neutral, and adjacent 2:1 layers are held together only by weak van der Waals forces. Pyrophyllite occurs only rarely in soils, usually only when it is inherited from low-grade metamorphic rocks.
- **Micas:** Mica minerals have the 2:1 layer structure described for pyrophyllite but with two important differences. First, instead of having only Si^{4+} in the tetrahedral sites, one-quarter of the tetrahedral sites are occupied by Al^{3+} . Because of this substitution, there is an excess of one negative charge per formula unit in the 2:1 layer. Second, this excess negative charge is balanced by monovalent cations, commonly, that occupy interlayer sites between two 2:1 layers (Figure I-5). This gives an ideal formula of $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ for a mica mineral with Al in the octahedral sites.
- **Vermiculites:** Vermiculite has a 2:1 layer structure as described for mica, but, instead of having a layer charge of 1 per formula unit and K^+ in interlayer positions, vermiculite has a layer charge of 0.9–0.6 per formula unit and contains hydrated exchangeable cations, primarily Ca and Mg, in the interlayer (Figure I-5). A typical formula for an idealized vermiculite weathered from muscovite is: $\text{M}^{+}_{0.75}\text{Al}_2(\text{Si}_{3.25}\text{Al}_{0.75})\text{O}_{10}(\text{OH})_2$, where M^{+} represents exchangeable cations. The high charge per formula unit gives vermiculite a high cation exchange capacity and causes vermiculite to have a high affinity for weakly hydrated cations such as K^+ , NH_4^+ , and Cs^+ . Fixation of K^+ by vermiculite can be significant in soils that are high in vermiculite and that have not received large amounts of chemical fertilizers. Vermiculites in soils are believed to form almost exclusively from the weathering of micas and chlorites. The weathering of micas to vermiculite (or smectite) is believed to occur by replacement of K^+ in the interlayer sites with hydrated exchangeable cations. The integrity of the 2:1 layer is preserved, but there is a reduction in the layer charge. Vermiculite does not swell as extensively as smectite and this is shown in

Figure I-5 by the presence of only two planes of water molecules surrounding the hydrated cations in the interlayer space.

- **Smectites:** The smectite group consists of minerals with the 2:1 structure already discussed for mica and vermiculite, but with a still lower charge per formula weight, namely 0.6–0.2. As in vermiculite, the interlayer contains exchangeable cations (Figure I-5). An idealized formula for a common soil smectite, the mineral beidellite, is: $M^{+}_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$, where M^{+} represents exchangeable cations, typically Ca^{2+} and Mg^{2+} . The most common smectite minerals range in composition between three end-members: montmorillonite, beidellite, and nontronite. All are dioctahedral, but they differ in the composition of the tetrahedral and octahedral sheets. Smectites do not fix K^{+} as readily as do vermiculites because smectites have a lower layer charge, but smectites swell more extensively than vermiculite. This is illustrated in Figure I-5 by the larger spacing between the 2:1 layers. Smectites are important minerals in temperate region soils. Many plant nutrients are held in an available form on the cation exchange sites of soil smectites. Soils rich in smectite tend to be very effective at attenuating many organic and inorganic pollutants because of the high surface area and adsorptive properties of the smectites. Smectites shrink upon drying and swell upon wetting. This shrink–swell behavior is most pronounced in the Vertisol order and in vertic subgroups of other soil orders. The shrink–swell properties lead to cracking and shifting problems when houses, roads, and other structures are built on smectitic soils.
- **Chlorites:** Like mica, chlorite minerals have a 2:1 layer structure with an excess of negative charge. In contrast to mica, however, the excess charge is balanced by a positively charged interlayer hydroxide sheet (Figure I-5), rather than. The interlayer hydroxide sheet is an octahedral sheet as shown in Figure I-3 and can be either di- or trioctahedral. Instead of being electrically neutral as in gibbsite, the hydroxide sheet has a positive charge caused by substitution of higher-valence cations for lower-valence ones, for example, $Mg_2Al(OH)_6^{+}$. Either octahedral sheet the one that is part of the 2:1 layer or the interlayer hydroxide sheet – can be di- or trioctahedral, and can contain Mg^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Al^{3+} , Fe^{3+} , and Cr^{3+} , giving a large number of different mineral species (D. G. Schulze, 2005).
- **Illite:** Illite is clay mineral mica, which was named by Grim et al. (1937). The structure is a 2:1 layer in which the interlayer cation is potassium. The size, charge, and coordination number of K is such that it fits snugly in hexagonal ring of oxygens

of the adjacent silica tetrahedral sheets. This gives the structure a strong interlocking ionic bond which holds the individual layers together and prevents water molecules from occupying the interlayer position as it does in the smectite. Simply it might say that illite is a potassium smectite (Dr. T. Al-Ani and Dr. O. Sarapää, 2008).

I-5- The sandstone clay

Sandstone is a type of rock made from sediment — a sedimentary rock. The sediment particles are clasts, or pieces, of minerals and fragments of rock, thus sandstone is a clastic sedimentary rock. It is composed mostly of sand particles, which are of a medium size; therefore, sandstone is a medium-grained clastic sedimentary rock. More precisely, sand is between 1/16 mm and 2 mm in size (silt is finer and gravel is coarser). The sand grains that make up sandstone are aptly referred to as framework grains. Sandstone may include finer and coarser material and still be called sandstone, but if it includes more than 30 percent grains of gravel, cobble or boulder size it's classified instead as conglomerate or breccia (together these are called rudites). Sandstone has two different kinds of material in it besides the sediment particles: matrix and cement. Matrix is the fine-grained stuff (silt and clay size) that was in the sediment along with the sand, that occupy the spaces between the sand grains, whereas cement is the mineral matter, introduced later, that binds the sediment into rock. Sandstone is formally defined strictly by particle size, but rocks made of carbonate minerals don't qualify as sandstone. Carbonate rocks are called limestone and given a whole separate classification, so sandstone really signifies a silicate-rich rock. (A medium-grained clastic carbonate rock, or "limestone sandstone," is called calcarenite.) This division makes sense because limestone is made in clean ocean water, whereas silicate rocks are made from sediment eroded off the continents.

I-5-1: Constituents of Sandstones

- **framework grains:**
 - quartz (usually dominant)
 - feldspar
 - rock fragments
 - heavy minerals
 - micas
 - clastic carbonates
 - glauconite (local, sometimes abundant in quartz-rich ss)

- **void filler:**
 - quartz (as secondary over growths)
 - quartz (as recrystallized amorphous silica)
 - chert (amorphous silica)
 - calcite (dolomite less common)
 - Hematite (primary, secondary)
 - exotica (anhydrite, gypsum, barite, halite, siderite, etc.)
- **matrix (fine material, not authigenic):**
 - fine detrital nonphyllosilicates (quartz, feldspar, carbonates)
 - fine detrital phyllosilicates (starts as clay-mineral mud, gets recrystallized to "sericite", "white mica", chlorite)
 - reorganized phyllosilicate-rich coarse rock fragments (M.Ferraz)
- The cement in sandstone is usually one of three materials: silica (chemically the same as quartz), calcium carbonate or iron oxide. These may infiltrate the matrix and bind it together, or they may fill the spaces where there is no matrix.
- Depending on the mix of matrix and cement, sandstone may have a wide range of color from nearly white to nearly black, with gray, brown, red, pink and buff in between.

I-5-2- The properties of sandstone:

- **fundamental:**
 - "component" composition (minerals, rock fragments, fossils, organic matter)
 - texture (grain size, grain shape, grain arrangement)
 - sedimentary structures
- **derived:**
 - chemical composition
 - bulk density
 - color
 - strength (tensile, compressive, shear)
 - porosity and permeability
 - elastic wave velocity
 - electrical properties
 - heat capacity
 - Thermal conductivity. (M.Ferraz)

I-6- The anti-inflammatories

Inflammation or inflammatory reaction is caused by release of chemicals from tissues and migrating cells (R. Botting and all, 1987). The anti-inflammatory are widely used for the treatment of minor pain and for the management of edema and tissue damage resulting from inflammatory joint disease (arthritis). A number of these drugs possess antipyretic activity in addition to having analgesic and anti-inflammatory actions, and thus have utility in the treatment of fever (J. DeRuiter, 2002).

Anti-inflammatory are routinely administered to humans and animals for the treatment of infections and are subject to prophylactic use in bioterrorism threats, animal feeding and aquaculture (Rooklidge SJ, 2004). Although anti-inflammatories are metabolized within the body, as much as 90% of orally administered doses may be excreted unmetabolized (Kumar K and all, 2005). Therefore, it is not surprising that they are frequently detected at sub-inhibitory concentrations in surface water and ground water (J Kolpin D and all, 2002; Boxall ABA and all, 2003; Giger W and all, 2003). The major concern is that widespread use of anti-inflammatories may lead to the emergence of new strains of bacteria that are resistant to these drugs and, in turn, resulted in untreatable livestock diseases (Solomons I, 1978). A potentially more dangerous scenario is the possible transmission of such strains to humans, resulting in untreatable human diseases (Kumar K and all, 2005; Y. Lu and all, 2014).

Diclofenac is an acidic pharmaceutical which belongs to the non-steroidal anti-inflammatory drugs family. This drug is widely used in the relief of pain and inflammation, the prevention of intra-operative miosis during cataract extraction, the treatment of inflammation after surgery and laser eye treatment, and the relief of ocular signs and allergic conjunctivitis. Therefore, Diclofenac is one of the top 10 compounds most commonly found in aquatic environments, due to its high level of consumption and for that the removal percentage in conventional wastewater treatment plants can be even less than 20%. It has been detected in rivers, estuaries, surface water, ground water and even drinking water in many countries at 1 g-ng L^{-1} concentration levels (T.A. Ternes, 1998; J.L. Sotelo and all, 2014)

The main challenge for the removal of anti-inflammatories from water is their high polarity, persistent and solubility in water. Because of these characteristics, complete removal is impossible in conventional water treatment plants (E.N. Evgenidou and all, 2015; D. Zhang and all, 2014; I. Villaescusa and all, 2011; J.R.Domínguez and all, 2011). However, methods

for the efficient removal of such organic pharmaceuticals from wastewater are being developed gradually.

To date, a variety of methods such as photodegradation, coagulation–flocculation, biodegradation, chlorination, ozonation, and other advanced oxidation processes (AOPs) have been used to remove diclofenac analogs. Despite this, although some of these degradation methods efficiency (e.g., AOP or ozonation), they have several drawbacks, i.e., the production of residual toxic by-products (S. Esplugas and all, 2007; M. Klavarioti and all, 2009). Consequently, adsorption of contaminants has become a popular method for the removal of organic contaminants from water, as it is simple, reliable, and cost effective (J.L. Sotelo and all, 2014; B.N. Bhadra and all, 2016).

Chapter II: The Experimental Part

II-1- Introduction:

As a result of the high and widespread consumption of the pharmaceutical products in modern countries, they became within the emerging micropollutants that present the priority of the water contaminants. Pharmaceutical products are one of the most severe environmental problems due to their non-biodegradability, recalcitrant to conventional wastewater treatments and severe toxicity and adverse effects on the environments. In particular diclofenac, widely used and also frequently reported in wastewater effluents, and drinking water sources (A.C Mehinto, 2009), it is become one of top priority contaminants among anti-inflammatories analogues. However, the removal of diclofenac cannot be readily accomplished in the natural environment or in biological water treatment plants. Therefore, the efficient elimination of diclofenac from the environment is of interest (X. Yang and all, 2017).

Adsorption represents an effective and simple technique to remove micropollutants. In addition of that, clays have attracted much attention in the different disciplines of chemistry because of their chemical and physical properties and their uses in various fields. therefore; it is being used in drinking water treatment (M.M Mhidi & K.K Amazigh, 2017).

Indeed, it turns out that the adsorption process is mainly controlled and monitored according to physic-chemical factors such as the contact time, the temperature and the mass of the adsorbate, and trying to determine the optimal elimination conditions of this clay, we tested the influences of these principal parameters on the elimination of diclofenac during an adsorption process, as well as we applied the different models of kinetic and isotherms adsorption.

in this part we present the experimental aspect. we have given the description of all the experiments carried out, as well as the methods of analysis used, and finally we discussed the results.

II-2- Materials and methodes

Our work was based on the elimination of a medical pollutant (diclofenac sodium) from aqueous solutions with one type of natural clays called sandstone, no material was synthesized during this work, and all the materials were pure commercial products.

II-2-1- Adsorbent:

The adsorbent used is sandstone obtained from deposit clay mineral, this clay mineral which collected in the region of mostaganem-algeria (littoral) was used in this study as a starting material. The sandstone was fractionned to 45 – 100 μm and was modified by temperature at 600,750 and 900 °C and by impregnation in NaOH solution 2.5 N,#. Probably, it turns out that it contains the irons oxid material since we realized the appearance of the orange rust at high temperatures.

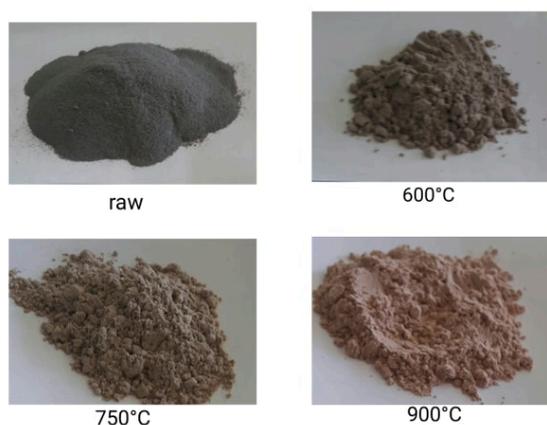


Figure (II-1): the raw and thermal modified sandstones

II-2-2- Diclofenac sodium:

Diclofenac sodium (2-[(2,6-Dichlorophenyl)amino] benzeneacetic acid monosodium salt of which $\text{pK}_a = 4.2$), molecular weight = 318.1 g/mol, was purchased from SAIDAL - Algeria, and assumed to have a purity > 98 %. (M. Adeyeye, 1990).

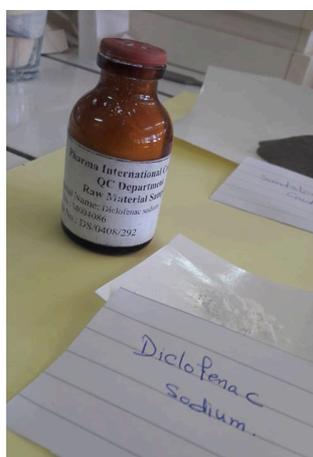


Figure (II-2): diclofenac sodium

II-2-3- Experimental techniques:

During our work, the following techniques were used:

- Spectroscopy UV-Visible.
- Fourier-transform infrared spectroscopy (FTIR).

II-2-3-1-Spectroscopy UV-Visible:

Analysts have developed large number of instrumental techniques and these techniques are extremely sensitive and can yield results rapidly to a high degree of accuracy. Among these instrumental analytical techniques, spectrophotometric technique occupies a unique position, because of its simplicity, sensitivity, accuracy and rapidity. Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength (P. Dehahay, 1967). While relatively simple in concept, determining the reflectance or transmittance involves careful consideration of the geometrical and spectral conditions of the measurement. The national scales for reflectance and transmittance in the ultraviolet, visible and nearinfrared spectral regions (250 nm to 2500 nm). The availability of spectrophotometer made this technique indispensable to the modern analytical chemists.

Spectrophotometric method is the most important for determining metals in alloys, minerals and complexes, owing to its selectivity. In comparison with similar techniques, it offers the advantage of having calibration graphs that are linear over a wider range. A very extensive range of concentration of substances (10^{-2} - 10^{-8} M) may be covered.

Previsioly, the first recognition that color intensity can be the indicator of concentration was probably the earliest application of employing molecular absorption spectroscopy for quantitative estimation. Using the human eye as the detector and undispersed sunlight or artificial light as the light source made the first measurements, later it was found that the accuracy and the precision could be improved by isolating specific frequencies of light using optical filters.

Absorption spectrophotometries in the ultra-violet and visible regions are considered to be one of the valued techniques for the quantitative analysis.

The basis of spectrophotometric methods is the simple relationship between the color of a substance and its electronic structure. A molecule or an ion exhibits absorption in the visible or ultra-violet region when the radiation causes an electronic transition in molecules containing one or more chromophoric groups. The color of a molecule may be intensified by

substituents called auxochromic groups, which displace the absorption maxima towards longer wavelength (bathochromic shift). The color determining factors in many molecules is the introduction of conjugated double bonds by means of electron donor or electron acceptor groups (W. J. Blaedel and V. M. Meloche, 1964). The quantitative applicability of the absorption method is based on the fact that the number of photons absorbed is directly proportional to the number or concentration of atoms, ions or molecules. The sequence of events in a spectrophotometer is as follows:

- i) The light source shines through the sample.
- ii) The sample absorbs light.
- iii) The detector detects how much light the sample has absorbed.
- iv) The detector then converts how much light the sample absorbed into a number.
- v) The numbers are either plotted straight away or are transmitted to a computer to be further manipulated (e.g. curve smoothing, baseline correction).

The scanning was done for the studied sample using the spectrophotometer Uv-Visible (from 200 to 800 nm) and that's to indicate the absorbance at a specific wavelength to this sample. therefore, the concentration will be determined from the calibration curve, which follow's the Beer's law: $A(\lambda) = \log(I_0/I) = \mu.l.C$

With:

$A(\lambda)$: absorbance

μ : the extinction coefficient ($\text{mol.L}^{-1}.\text{cm}^{-1}$)

l : the length of the cuvette in which the sample is contained (cm).

C : is the concentration of the compound in solution (mol L^{-1})

I : the transmitted light intensity

I_0 : the initial light intensity.

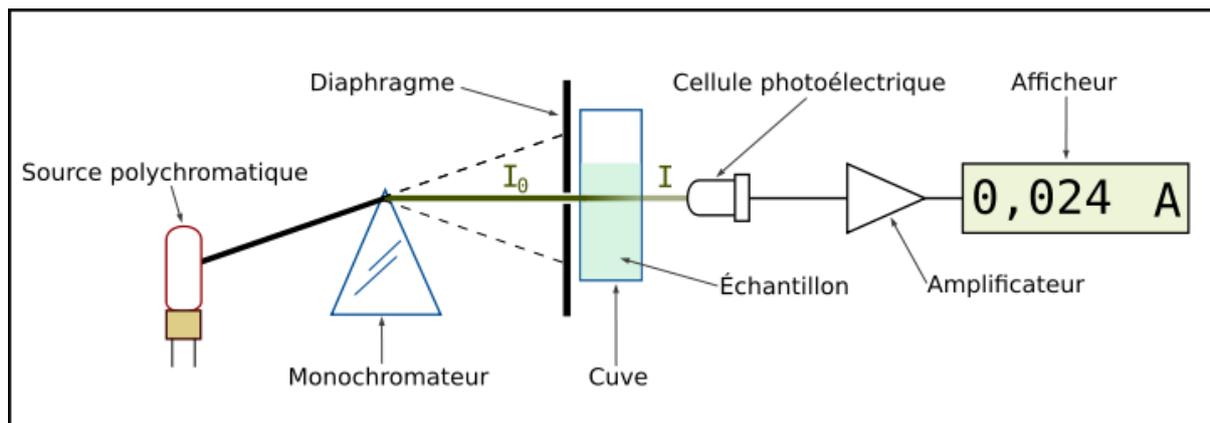


Figure (II-3): Principe of spectrophotometer UV-Vis

As a part of this work the completed analysis was quantitative in the field of UV (200 to 400 nm) with a JASCO V-730 UV-Visible spectrophotometer.

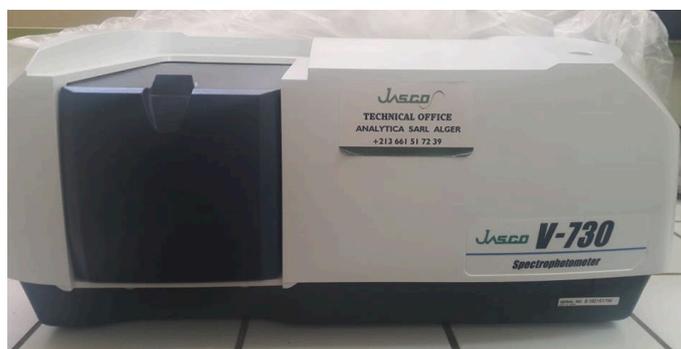


Figure (II-4): spectrophotometer UV-Vis

✓ The calibration curve:

The different solutions were prepared by specifying their mass concentrations (25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 150 mg/L, 200 mg/L) then the spectrophotometric analysis was performed to obtain the calibration curve $A = f(C)$.

II-2-3-2-Fourier-transform infrared spectroscopy (FTIR):

Infrared spectroscopy is the analysis technique of infrared light interacting with molecules. In particular, it is the measurement of the wavelength and intensity of the absorption of near-infrared light by a sample. Infrared spectroscopy is widely used by chemists to determine the functional groups in molecules. It's based on the electromagnetic radiation that interacts with a substance can be absorbed, transmitted, reflected, scattered, or have photoluminescence (PL), which provides significant information on the molecular structure and the energy level transition of that substance (Cui, H. and all, 2017; Bakar, N.A and all, 2016; A. Munajad and all, 2018). The absorption measurement was limited in the domain between $(400-4000\text{cm}^{-1})$.

In 1891, A. A. Michelson revolutionized the world of spectrometry by designing a two-beam interferometer. The interferometer is a main part of virtually all infrared spectrometers used today (FTIR spectrometers). The Michelson interferometer consists of two mirrors, one fixed and one movable, and a beam splitter. An infrared beam is created by a source and is guided by mirrors via the interferometer through the spectrometer onto the sample compartment and finally reaches the detector. The detected signal (also denoted interferogram) is subsequently Fourier Transformed to yield a spectrum. This calculation is the reason for the name given to this spectrometric technique (FTIR) (Griffiths, P. R and all, 2007; L. Ohlin, 2015)



Figure (II-5): a Fourier Transform Infrared Spectroscopy (FTIR)

In our study, the IR analysis were performed on a Fourier Transform Infrared Spectroscopy (FTIR) of the (PERKIN ELMER) brand controlled by a computer.

II-3- The operating mode:

The batch experiment was conducted to investigate the adsorption behavior of DCF onto sandstone. A solution of diclofenac sodium was prepared with a concentration of 200 mg/l by introducing a crushed quantity of diclofenac into one litre of distilled water and was shaken well to make sure that there's no apparent particules and obtaine a homogeneous solution.

The other solutions of 150 mg/l, 100 mg/l, 75 mg/l, 50 mg/l and 25 mg/l were prepared by dilution of the stock solution to obtain the calibration curve later with the spectrophotometer UV-Visible.

The solid to liquid ratio was kept constant, where 50 mg of sandstone were added to 50 mL of diclofenac aqueous solutions in flasks. Samples were shaken on a rotary shaker at 700 rpm during 2 h in order to reach the equilibrium final concentrations and the centrifugation was at rpm for 30 min. Both supernatants and sorbents after contact with the diclofenac were removed and analyzed through UV-Vis. The result of the amount of adsorbed diclofenac was

calculated by the difference between the initial and equilibrium final concentrations using the following formula:

$$Q_t = (C_0 - C_e) * \frac{v}{m} \quad (1)$$

With:

Q_t : the quantity adsorbed at the instant t (mg/g)

C_0 : the initial pollutant concentration (mg/l).

C_e : the pollutant concentration at instant t (mg/l)

v : the volume of the solution (ml).

m : the mass of the adsorbent in solution (g).

Or by determining the rate of the removal of the pharmaceutical pollutant, noted R and expressed in percentage (%) and defined by:

$$R (\%) = 100 * \frac{C_0 - C_e}{C_0} \quad (2)$$

C_0 : the initial concentration of pollutant (mg/l).

C_e : the pollutant concentration at instant t (mg/l).

II-3-1- The effects and parameters of the adsorption of diclofenac with sandstone:

II-3-1-1-The time effect:

To determine the equilibrium time of the adsorption of diclofenac on calyx we studied the evolution of the adsorption results according to the contact time between the adsorbate – adsorbent. In our work, the studied solutions were mixed from 5min to 2h.

II-3-1-2- the mass effect:

The mass effect is one of the parameters that should be considered to monitor the rate advancement in the adsorption of diclofenac. Thus, the mass used of sandstone is necessary to be specified and planned for the optimal adsorption process and rapid recovery of diclofenac. To reach this goal, we have two different methods. The first is to fix the volume of the samples and change the added masses; the second method which we used in our work is to fix the added masses and change the added volumes of the pollutant solution, with regard to have the same quantity of diclofenac in all the samples. In our work a series of experiences

were done in 10 different volumes from 25ml to 250ml of the diclofenac solution with 25ml difference between every sample, and in an ambient temperature.

II-3-1-3- The temperature effect:

the temperature effect was studied during our work since it is a principal parameter and have an important influence on the rate of the adsorption, generally, the influence is illustrated by the increase or decrease of the direct or indirect proportion between the adsorption rate and the temperature, and that's corresponding to the endothermic or exothermic nature of the adsorption reaction.

In our work we tested the adsorption in 3 different temperatures (15, 25, 45 °C) during a kinetic experiment for each temperature.

II-4- Results and discussions

II-4-1-Characterization of the adsorbent

Sandstone from Mostaganem (Western region of Algeria) was ground analysed by D8 Advanced A25 BRUKER X-ray diffractometer (XRD) and ALPHA BRUKER FTIR spectrophotometer at Center of Scientific and Technical Research in Physico-Chemical Analysis (CRAPC) Algiers.

The X-ray diffractogram of the sandstone is presented in figure (II-6):

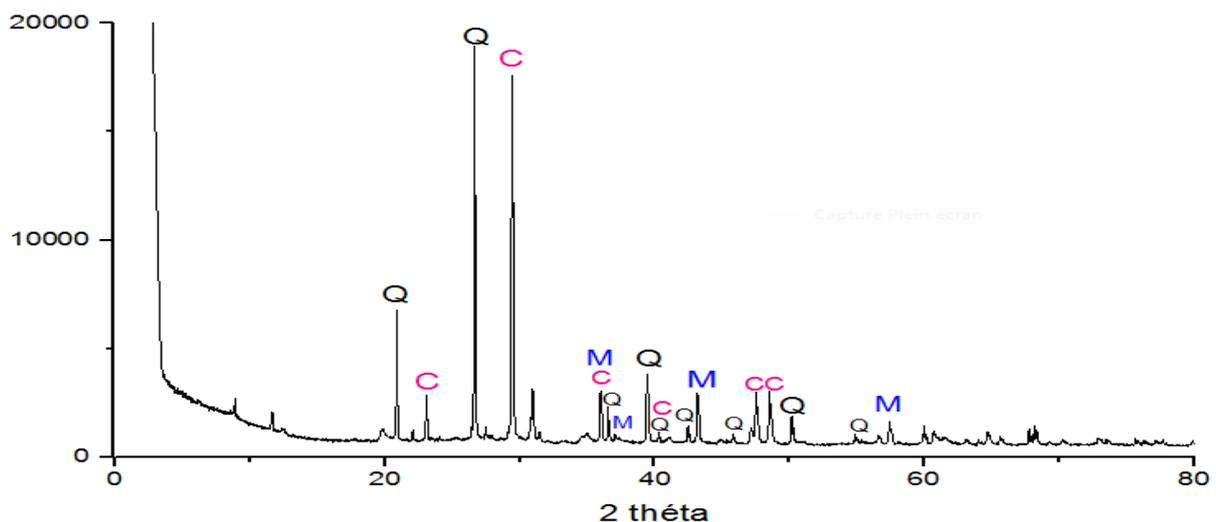


Figure (II-6): XRD patterns of raw sandstone

Figures (II-6) represent the XRD pattern of the sandstone clay specimens. The identified phases are quartz, calcite and probably magnetite. The main crystalline phases are quartz and calcite of almost same peak intensities. The XRD line of:

- Quartz (\pm -SiO₂) of 100 % relative intensity is positioned at $2\theta = 26.62^\circ$, whereas the second strongest line is positioned at $2\theta = 21.82^\circ$.
- Calcite CaCO₃ of 100 % relative intensity is positioned at $2\theta = 29.43^\circ$, whereas the second strongest line of 21.8 % is positioned at $2\theta = 21.82^\circ$.
- Magnetite Fe₂O₃ of 100 % relative intensity is positioned at $2\theta = 35.38^\circ$, whereas the second strongest line of 21.8 % is positioned at $2\theta = 62.88^\circ$.

The FTIR spectrum of the sandstone is presented in figure (II-7):

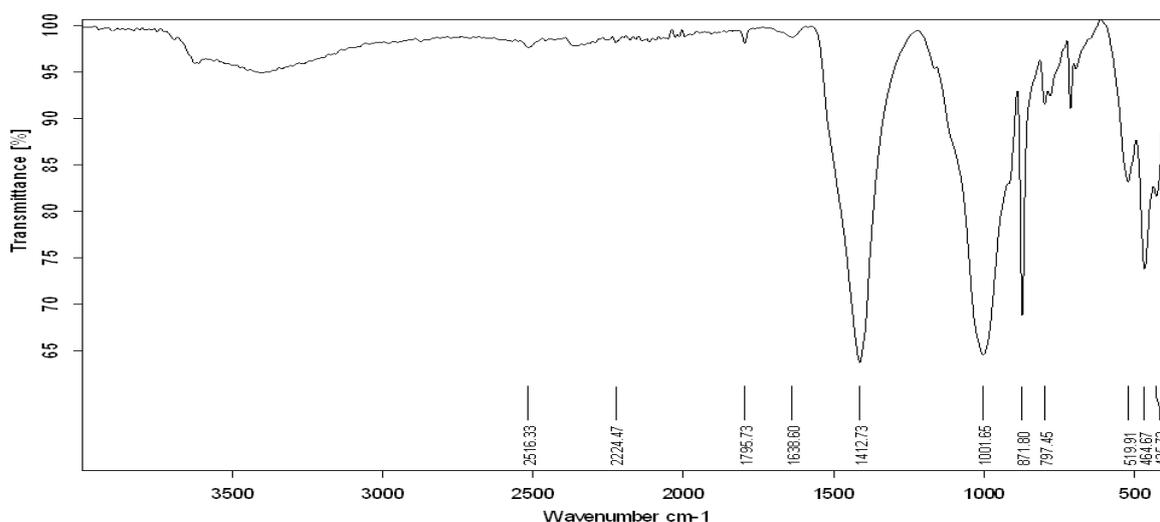


Figure (II-7): FTIR Spectrum of raw sandstone

IR spectra of clay minerals are usually characterized by three main areas: (i) the stretching and bending vibrations of the inner surface HO⁻ groups observed in the region of 3700 to 3600 cm⁻¹, (ii) the stretching and bending vibrations of the Si–O groups and (iii) the Si–O–M (with M=Al, Mg..) vibrations with (ii) and (iii) extending from 1200 to 400 cm⁻¹.

The spectrum of raw sandstone (figure II-7) presented a large band between 3200 and 3700 cm⁻¹ of with two optimum respectively at 3403 and 3630 cm⁻¹, The first HO⁻ stretching vibration band is associate at water and the second at 3630 cm⁻¹ corresponding to the calcium hydroxide Ca(OH)₂. The CO₃²⁻ stretching vibration band is located at 1413 cm⁻¹ where the CO₃²⁻ bending vibration is situated at 872cm⁻¹. These bands are typical fundamental bands for calcite.

For typical quartz spectrum, The major absorption features of quartz are the peaks in the range of 1200 to 900 cm⁻¹ assigned to the asymmetric stretching vibration of the Si–O groups with a peak maximum at 1080 cm⁻¹, the symmetric stretch at 800 and 780 cm⁻¹, and the symmetric and asymmetric Si–O bending mode at 695 cm⁻¹, 520 cm⁻¹, and 450⁻¹,

respectively. The spectrum of sandstone mineral is shown in figure(II-7) contains a percentage of quartz, and therefore, several signals are overlapping or may be assigned to typical vibrations of quartz.

II-4-2- Adsorption Kinetics of the fixation of diclofenac on sandstone

Adsorption is a process involving liquid/solid interaction and mass transfer from liquid phase to the solid surface. An equilibrium adsorption model is a mathematical equation which relates the equilibrium diclofenac adsorption at solid/liquid interface to equilibrium concentration of diclofenac in solution. Adsorption kinetic models are useful in prediction of adsorption rate and provide information about the mechanism of adsorption. In addition to equilibrium models many researches were reported on the modeling of experimental kinetic data by different kinetic models (A. Barati-Harooni and all, 2016).

Table (II-1): Kinetic adsorption models.

Kinetic model	Equation
Pseudo-first order	$\ln (q_e - q_t) = \ln (q_e) - K_1 t$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$

As we mentioned earlier, the adsorption process is governed by several parameters, in this part we will present a detailed analysis of the adsorption kinetics of Diclofenac on the sandstone. First, we will discuss the adsorption mechanism according to the required mass of sandstone to obtain the best efficiency. also; we will study the evolution of contact time, the temperature influence, and finally, the effect of the thermal and chemical modification on the sandstone.

II-4-2-1- The calibration curve:

The calibration curve is a method to obtain the concentration from % transmittance or absorbance derived from the display of their readout devices.

For our purposes, calibration curves are defined as graphs with absorption or %T plotted on the Y axis, and increasing concentrations of standard along the X axis. If Beer's Law is followed, the resulting line representing absorbance vs. concentration will be straight. A calibration curve is constructed after obtaining the %T/Abs readings from a number of solutions of known concentration (standards) used in a reaction or procedure (A. Alexander and all, 2011). Their absorbance is determined by the measurement at the optimum selected

wavelength λ . So it is advisable to carry out a range of different concentrations and to check in which field of concentration the Beert-Lambert law is verified.

The selected equilibrium concentrations of Diclofenac sodium were determined using of a JASCO V-730 UV / Vis spectrometer under the following experimental conditions:

Table (II-2): properties of diclofenac sodium

adsorbat	Chemical formula	The molar mass (g/mol)	λ theoretic (nm)	λ experimental (nm)
Diclofenac sodium	C ₁₄ H ₁₀ N NaO ₂	296,148	276	276

A typical calibration curve for diclofenac sodium at 276 nm was made with a good correlation of fitting of $R = 0.999$ presented in figure II.1 (M.M Mhidi & K.K Amazigh, 2017).

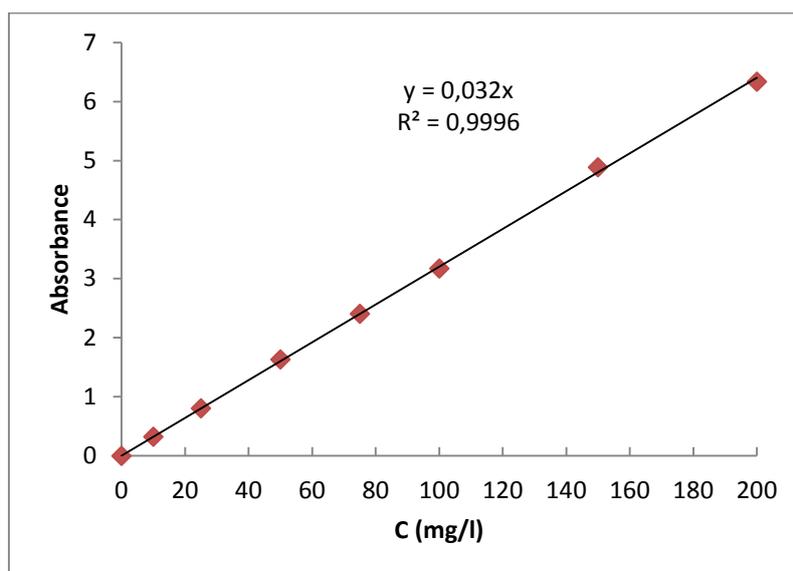


Figure (II-8): The calibration curve of diclofenac sodium

II-4-2-2- The mass effect:

In order to estimate the optimal amount of sandstone to add to the diclofenac solution for the optimum adsorption rate, we studied the mass effect of raw sandstone. The experiments were carried out using 1 L of the 150 mg/L diclofenac sodium solution. As we mentioned before, our work was investigated according to the second methode, which we change the samples volumes and fix the adsorbent mass. In this strategy, 50mg of sandstone were added to 10 different volumes from 25 ml to 250 ml of the diclofenac solution and shaken pending various

times from 5min to 2h during a kinetic experiment at constant conditions of shaking speed and ambient temperature.

The attained results are illustrated in Figure (II-9):

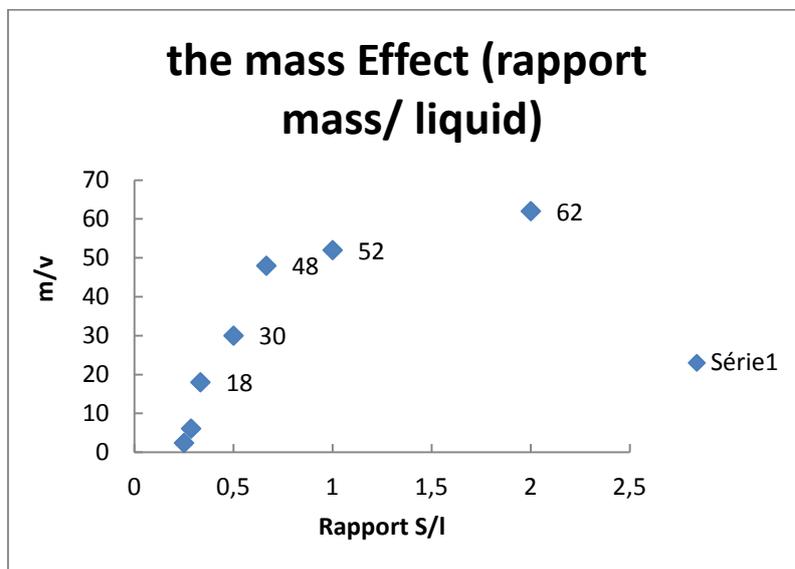


Figure (II-9): the mass Effect (rapport mass/ liquid)

From the figure (II-9), we noted that the optimal adsorption ratio is obtained at 2 g/l with 62% of diclofenac elimination. However, at 1 g/l the elimination amount was 52%, therefore for economic reasons, it is better to minimize the adsorbent quantity and choose the concentration of 1 g/l for the rest of our work.

II-4-2-3- The contact time effect:

In order to study the evolution of the diclofenac adsorption on sandstone according to the rotation time, a series of experiences were done for different concentrations of pollutant solution (25, 50, 75, 100, 150 and 200 mg/l). While 50 mg of sandstone was added to flasks contains a volume of 50 ml of the diclofenac sodium solutions. It has been shaken during a time interval from 5 min to 2 h. After 30 min of centrifugation, the analysis were done using UV-Vis spectrophotometer at 276 nm. The effect of the contact time on removal percentage of diclofenac is shown in the figure (II-10):

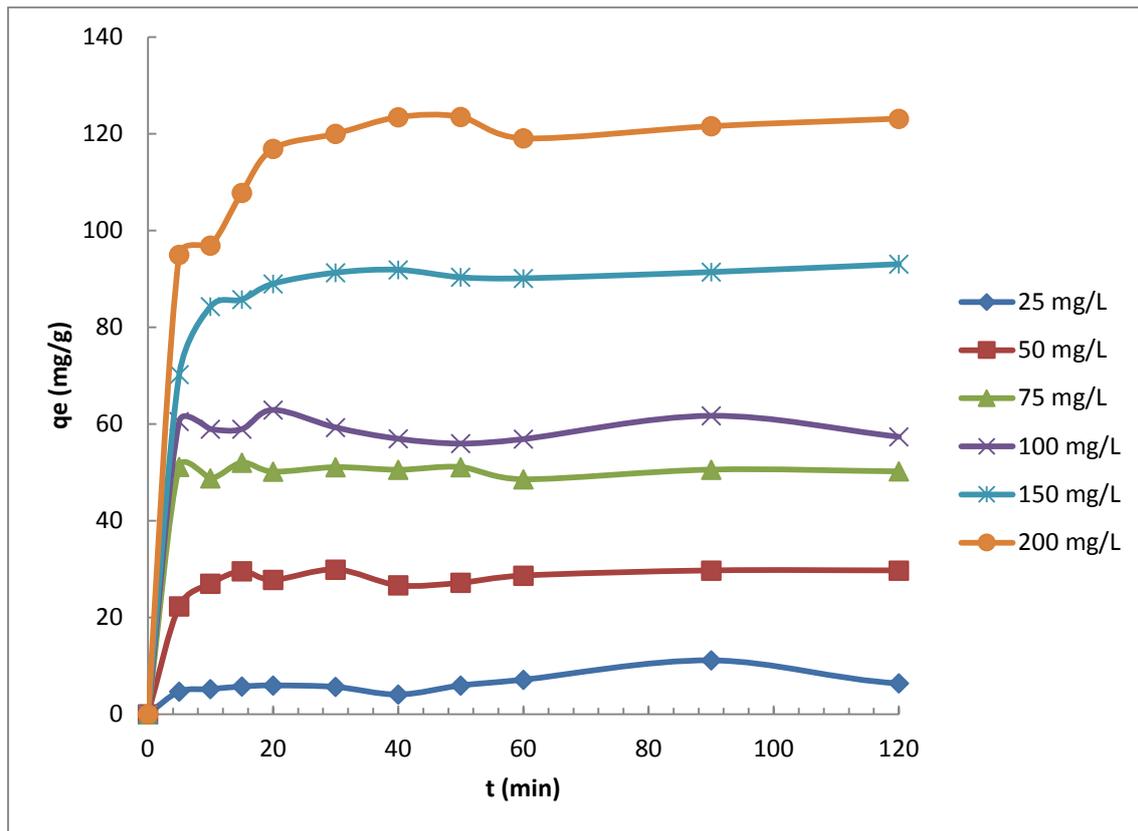


Figure (II-10): Kinetics adsorption of diclofenac on sandstone

As a result, we noticed that all the graphs have the same profile for all the different concentrations. The adsorbed amount of diclofenac onto sandstone increases with the increase of contact time and the concentration of diclofenac solution, as shown in Fig (II-10), the diclofenac adsorption reached equilibrium in about 20 min. Adsorption capacity for diclofenac showed a rapid increase in adsorbed amount during the first 20 min. This fast adsorption capacity at the initial stage by sandstone indicated higher driving force that made fast transfer of diclofenac to the surface of sandstone particles, this results indicated a significant effectiveness in using sandstone as an adsorbent .

To evaluate the kinetic adsorption mechanism, the pseudo first-order, pseudo second-order models were tested and drawn respectively according to the equations of table (II-1).the results were summarized in the table (II-3).

Table (II-3): adsorption kinetics models

C (mg/l)	Ce (mg/l)	Qe(mg/g)	R%	Pseudo first-order	pseudo second-order
25	13,9375	11,125	44,389	K=-0,003 R ² =0,508	K=0,137 R ² =0,992
50	21,25	29,71875	58,307	K=-0,034 R ² =0,552	K=0,033 R ² =0,998
75	23,91	51,09	68,13	K=-0,033 R ² =0,373	K=0,019 R ² =0,999
100	37,5	61,6875	62,193	K=-0,027 R ² =0,378	K=0,017 R ² =0,996
150	68,55	84,2578	55,138	K=-0,034 R ² =0,531	K=0,010 R ² =0,999
200	74,6875	123,4375	62,303	K=-0,036 R ² =0,686	K=0,008 R ² =0,999

From the table (II-3), we can conclude that all kinetics follows the pseudo second-order and only the pseudo second-order model provided the best match for all experimental data, with a different kinetics rates that decrease with the increase in the diclofenac initial concentration.

II-4-2-4-Thermal modification (600, 750, 900 °C)

Generally, the thermal modifications was performed as a suggested solution for it's significant influences on the adsorbent performance, for what its make of different structure

changes resulting from high temperatures, While the effect of thermal modification on some adsorbents structures is to increase or decrease their porosities volumes relatively with their adsorption capacity .Therefore, it's became a helpful methode to ameliorate the adsorbent efficiency and make it appropriat for each sampling situation.Thus ,the thermal modification was executed in order to test the effect of the modification on our adsorption material, also to verify the exsistance of the iron oxids that been obviously noticed in the raw sandstone in the form of rust.

In our work, the raw sandstone was modified at 600, 750 and 900 °C. The morphological structures of thermally modified sandstone became shortened, and have reduced the particle sizes and decreased the agglomeration. Moreover, it can be seen that the thermal modification on sandstone approuved the outside look expectations and detect the existence of iron oxid material which been clearly verified since we realized the appearance of the orange rust at high temperatures.

The adsorption experiments were performed for each modified sandstone using 1 L of 200 mg/l of diclofenac solution, in every experiment 50 mg of modified sandstone was added to 8 samples contains 50 ml of diclofenac solution and shaken from 5 min to 2 h during a kinetic experiment at an ambient temperature.

The results were shown in the following figure:

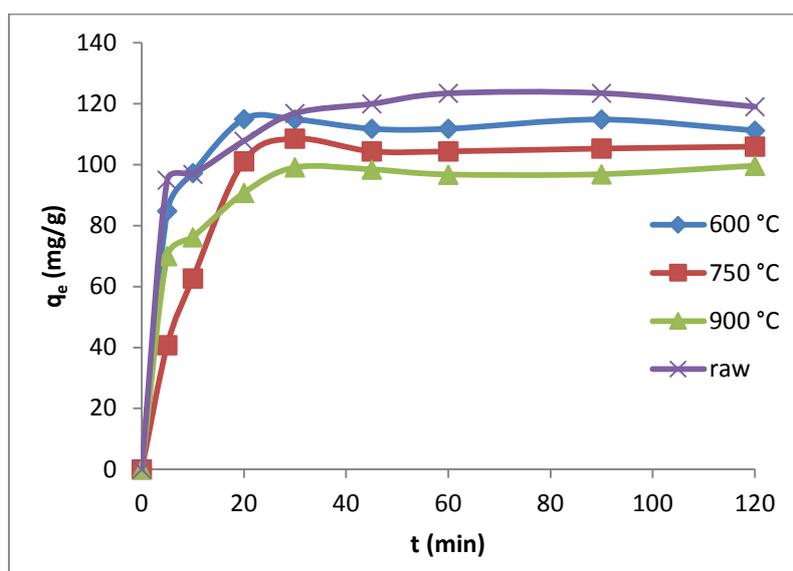


Figure (II-11): the kinetic adsorption experiments of the diclofenac on the thermal modified sandstone

From the figure (II-11) we noticed that the kinetics adsorption of the diclofenac on the raw and thermal modified sandstone has two evident stages, the first is fast and corresponds to the external mass transfer and that was obvious in the increase of the adsorbed amount of diclofenac with the increase of the contact time, the diclofenac adsorption was reached equilibrium in about 20 min for the 3 modified sandstone. While, the second stage is slow and that's related to the stabilization in the removal of diclofenac after 20 min of the contact time due to the saturation and the decrease in the number of the available active sites on the surface of the adsorbent material.

As a conclusion, it's been remarked that the thermal modification on sandstone has a negative influence on the internal adsorbent structure thereby the adsorption performance, as the adsorbed amount decreased gradually with the increased temperature from 115 to 90.78 mg/g, for this reason we will work with the raw sandstone for the rest of our work.

II-4-2-5-Chemical modification 2.5 and 5 N

Generally, the chemical modification of adsorbents has been used as a technique for improving physical and chemical properties as it's may introduce functional groups within the structure of the adsorbents or increase their porosity, with an increasing and enhancing in their adsorption capacity (A.C Mehinto, 2009). Also, to reduce their unwanted properties, and it provides more active sites, better ion- exchange, and significant adsorbate-adsorbent interaction (D. Schwantes and all, 2019; Y.x. Wanga and all, 2015; M.M. Amer and all, 2018).

Additionally, the modification with chemical reagents in low-cost solutions such as acids or bases, causing an increase in the proportion of active surfaces and an increase in the pollutant-removing capacity (A. J. Miola and all, 2014; D. Schwantes Jr and all, 2014) without increasing the cost of final product (G. F. Coelho and all, 2014; V. C. G. Dos Santos and all, 2011) and, thereby, their widespread use may not be impeded (D. Schwantes and all, 2016).

In our work the modification process has been investigated using the base of NaOH as well as it had the efficiency to increase the adsorption due to negatively charged hydroxyl anions. while, Hydroxyl ions charge adsorbent surfaces negatively and metal cations adsorbed on the surface (M.E. ARGUN and all, 2006).

The sandstone in our work was modified in 2.5 N of NaOH solution over 48h, filtered and repeatedly rinsed with distilled water until a neutral pH was attained. the adsorption experiments were carried out using 1 L of 200 mg/l of the diclofenac solution, in every

experiment 50mg of modified sandstone was added to 8 samples contains 50 ml of diclofenac solution and shaken from 5 min to 2 h during a kinetic experiment at constant conditions of shaking speed and ambient temperature.

To investigate the quality of the adsorbent after chemical modifications, the adsorption experiments was then analysed by spectrophotometer Uv-Vis to verify the improvement of the adsorption capacity, the results were exposed in the figure (II-12):

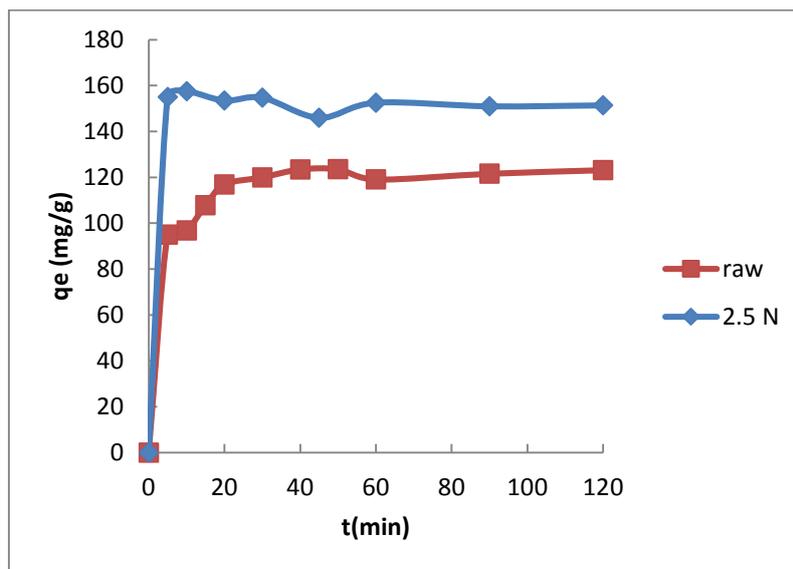


Figure (II-12): the kinetic adsorption experiments of the diclofenac on the chemical modified sandstone

From the figure (II-12) we noted the amelioration in the adsorbed quantity which passed from 123.5 to 157.5 mg/g respectively for raw and modified sandstone, this amelioration may signifies the modification of functional groups at sandstone surface or modification of the internal structure of adsorbent, both, favorise the interaction or retention of diclofenac.

II-4-3- the adsorption isotherm

The adsorption isotherm describes how the adsorption molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state. The analysis of the isotherm datas by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (Hameed B.H And Ahmad A.A, 2009). Table (II-4) shows the equations and parameters of different analysed isotherm models. In order to assess their ability to correlate with experimental results (N. Ertugay and E. Malkoc, 2019).

Table (II-4) Equilibrium and parameters equilibrium adsorption models

Isotherm model	Equation	Linearization	Model parameters
LANGMUIR	$q_e = \frac{q_m k_{ad} C_e}{1 + K_{ad} C_e}$	$\frac{C_e}{q_e} = \frac{1}{k_{ad} q_m} + \frac{C_e}{q_m}$	$q_m=333.33$ $K_{ad}=0.003$ $R^2=0.110$
FREUNDLICH	$q_e = K_f C_e^{n_f}$	$\log q_e = \log K_f + n_f \log C_e$	$K_f=0,2026$ $n_f=0,815$ $R^2=0,87$
TEMKIN	$q_e = \frac{RT}{b_T} \ln(A_T C_e)$	$q_e = B_T \ln A_T + B_T \ln C_e$	$A_T=1.5$ $b_T=16.97$ $R^2=0,96$
DUBININ–RADUSHKEVICH	$q_e = Q_m \exp(-K\varepsilon^2)$ $\varepsilon = RT \ln(1 + C_e^{-1})$	$\ln q_e = \ln Q_m - K\varepsilon^2$	$Q_m=107.55$ $\varepsilon=0.0000089$ $R^2=0.96$
JOVANOVIC	$q_e = q_m(1 - e^{K_j C_e})$	$\ln q_e = \ln q_{max} - K_j C_e$	$q_{max}=15.52$ $K_j=0.028$ $R^2=0.729$
HALSEY	$q_e = \left(\frac{K_{H_a}}{C_e}\right)^{1/n_{H_a}}$	$\ln q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_e$	$K_H=0.75$ $n_H=0.83$ $R^2=0.869$
ELOVICH	$\frac{q_e}{q_m} = K_E C_e \frac{q_e}{q_m}$	$\ln \frac{q_e}{C_e} = \ln(K_E \cdot q_m) - \frac{q_e}{q_m}$	$K_E=0.021$ $q_m=62.5$ $R^2=0.832$
Redlich-Peterson	$q_e = \frac{K_{RP}}{(1 + a_{RP} C_e^B)} C_e$	$\ln\left(\frac{K_{RP}}{q_e} - 1\right) = B \ln(C_e) + \ln(a_{RP})$	$B=1.647$ $a_{RP}=0.01$ $K_{RP}=1.732$ $R^2=0.968$
SIPS	$q_e = \frac{q_s C_e^{B_s}}{1 + a_s C_e^{B_s}}$	$B_s \ln q_e = -\ln\left(\frac{K_s}{q_{He}}\right) + \ln a_s - \frac{1}{n_H} \ln C_e$	$q_s=2.18$ $a_s=0.008$ $B_s=0.92$ $R^2=0.96$

Table (II-4) shows also the analysis of experimental equilibrium adsorption data and calculated parameters for different equilibrium models. According to Table (II-4), the TEMKIN, DUBININ–RADUSHKEVICH, REDLICH-PETERSON and SIPS models are more suitable to fit the experimental adsorption data.

Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of adsorption (H_{ads}) of all molecules in the layer decreases linearly as a result of increase surface coverage, the parameter b_T is Temkin constant which is related to the heat of sorption ($J \cdot mol^{-1}$) and K_T is Temkin isotherm constant ($L \cdot g^{-1}$).

The three-parameter model, R–P and Sips equations have been applied to evaluate the fit by isotherm for the adsorption of diclofenac. The higher R^2 values for the three-parameter isotherms suggest the applicability of these models to represent the equilibrium sorption of diclofenac by sandstone. It is believed that adsorption capacity obtained from the Sips equation could be more realistic than that from the Langmuir equation. By analogy between Redlich–Peterson and Langmuir equations, we might have expected that the ratio K_{RP}/a_{RP} , would be related to the adsorption monolayer capacity. It was reported that, b , is considered a measure of the adsorption affinity.

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms and can be derived using either equilibrium or thermodynamic approach. The Sips isotherm returns to the Langmuir isotherm and predicts homogeneous adsorption. On the other hand, deviation of B_S value from the unity indicates heterogeneous surface.

II-4-3-1- Effect of temperature:

The effect of temperature on the diclofenac adsorption onto sandstone was investigated at 15, 25, and 45 °C using a heater basin to maintain the temperature at the desired value and by using the thermometer to maintain the required temperature, the experiments were carried out under the constant conditions of operating parameters on the system such as contact time, mass of sandstone, initial diclofenac concentration, volume of diclofenac solution and shaking speed. The results are shown in Figure (II-13). The experimental results demonstrate that the magnitude of adsorption is proportional to the solution temperature. The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution for highly concentrated suspensions. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (DO AN M and all, 2009; N. Ertugay and E. Malkoc, 2014). As seen in Figure (II-13), the adsorption of diclofenac on sandstone increased from 102.4 mg/g to 127.9 mg/g when temperature was increased from 15 to 45 °C at an initial concentration of 200 mg/L.

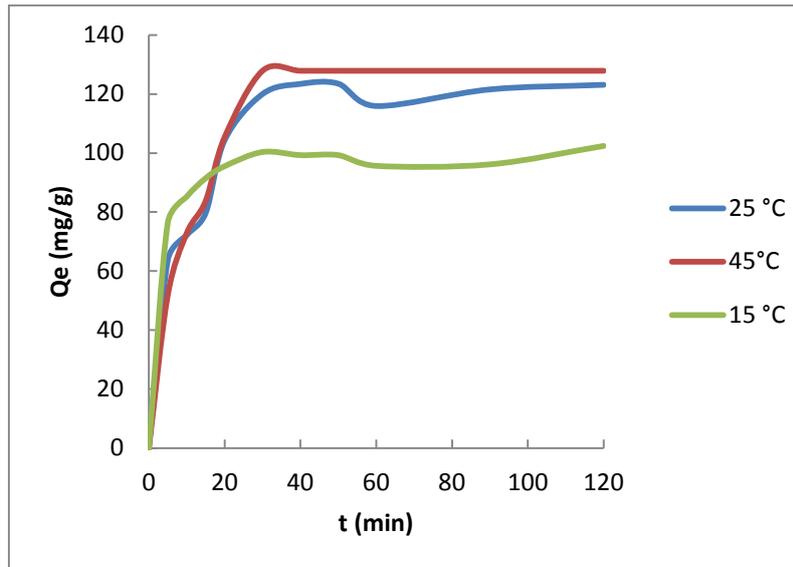


Figure (II-13): the effect of temperature on the adsorption of diclofenac on sandstone

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibbs free energy change, ΔG , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG is a negative value. The thermodynamic parameters of Gibbs free energy change, ΔG , enthalpy change, ΔH , and entropy change, ΔS , for the adsorption processes are calculated using the following equations:

$$\Delta G = -RT \ln K_d \quad (3)$$

And:

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

Where R is universal gas constant ($8,314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature in K . The apparent equilibrium constant (K_d) of the adsorption is defined as:

$$K_d = Q_e / C_e \quad (5)$$

The results were summarized in the table (II-5).

Table (II-5): Thermodynamic parameters for diclofenac adsorption onto sandstone.

" H (KJ/mol)	" S (J/mol)	" G (KJ/mol)		
		288 K	303 K	318 K
13,527849	47,932911	-0,27682937	-0,99582303	-1,7148167

As seen in table (II-5), the negative values of " G confirm the feasibility of the process and the spontaneous nature of adsorption with a high preference of diclofenac by sandstone. The decrease in the negative value of " G with the temperature increase indicates that the adsorption process of diclofenac on sandstone becomes more favorable at higher temperatures (Zaki, A.B and all, 2000; J.He and all, 2010). The positive value of " H° indicates the endothermic nature of the adsorption, which explains the increase of diclofenac adsorption efficiency as the temperature increased (A. Achmad and all, 2012). Entropy has been defined as the degree of chaos of a system. The positive value of " S° suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process (Gupta, V.K, 1998; J.He and all, 2010).

General conclusion

General Conclusion

The objective of our work is to study the adsorption efficiency of local mineral clay to eliminate an anti-inflammatory drug “diclofenac” from waste waters. This consists in studying the different adsorption parameters that control this process and the validation of different isothermal and adsorption kinetic models.

The XRD and FTIR characterization of clay proved that it returns to the sandstone clay family composed essentially from quartz and calcite with trace of iron oxide.

The study of adsorption parameters shows:

- A contact time of 20 minutes
- An optimum adsorbent/adsorbate ratio of 1g/l.
- A kinetic model of pseudo second order for different diclofenac solutions concentrations of 25 to 200 mg /l with a kinetic constant about 0.137 to 0.008 min.mg⁻¹.g.
- The thermal modification of sandstone at 600,750 and 900 °C reveals a decrease in the adsorption capacity while the chemical modification by NaOH solution demonstrates a significant increase in adsorption capacity about 20 mg/g.
- The TEMKIN, DUBININ–RADUSHKEVICH, REDLICH-PETERSON and SIPS isotherm models are more suitable to fit the experimental adsorption data.
- The thermodynamic study shows :
 - ✓ A negative value of ”G confirms the feasibility of the process and the spontaneous nature of adsorption with a high preference of diclofenac by sandstone.
 - ✓ A positive value of ”H indicates the endothermic nature of the adsorption.
 - ✓ A positive value of ”S suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface.

As a consequence from the results we suggest to:

- Complete the characterization of sandstone to explain the phenomena of adsorption
- As the chemical modification pointed out that testing the modification using other concentrations or other solutions like acid will ameliorate the sandstone adsorption efficiency, so it's recommended to be experimented.
- Study the sandstone capacity on the adsorption of other pharmaceutical products as it's could be a useful solution in water treatment plants.

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