UNIVERSITÀ DEGLI STUDI DI PADOVA

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Master Thesis
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REMEDIATION OF CONTAMINATED SOIL BY NANO-TO-MICRO CLAY PARTICLES. CASE STUDY WITH DICLOFENAC

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1 INTRODUCTION AND DEFINITION OF THE TASK

A widespread recognition of the need to develop technologies for pollution control and environmental remediation has arisen only in relatively recent times, as a result of increased awareness of the effects of pollution on the health and longevity of both human beings and the earth's fragile ecosystems (Yuan et al, 2013).

Thus, new approaches with sustainable techniques and materials must be considered in order to face emerging environmental protection issues.

According to Bergaya and Lagaly (2013) clays and clay minerals will be recognized as the material of the 21st century: they are abundant, inexpensive, environment friendly and they have properties which make them suitable for various applications, not only industrial.

Only quite recently environmental uses of clay have been developed at great extent. In fact clay is a non-polluting and can be used also as a de-polluting agent, like in water and wastewater treatment, or as a pollution control agent, in waste liners and storage (Yuan et al, 2013).

The driving force of the present thesis is to assess the suitability of clay as sorbent for remediation of contaminated soil and thereby groundwater. In fact methods targeting soil pollution indirectly affect the quality of groundwater, and vice versa (Mueller and Nowack, 2010).

Since clay soil can naturally attenuate contamination plumes, it is already known as source for removal of pollutants, but its impervious property makes it difficult to be properly managed as a remediation technique.

For all of these reasons this thesis work focuses on the injection of suspension of nano-to-micro clay particles as a new approach for remediation of polluted soils.

Concerning this topic, no specific studies were conducted and the only available literature is mostly about the injection of nano and micro Zero Valent Iron particles for the removal of organic halogenated pollutants from groundwater.

In this work diclofenac, a non-steroidal anti-inflammatory drug, was chosen as the target pollutant for testing the efficiency of remediation. This compound is classified among emerging contaminants which are defined as chemical recently discovered in natural streams as a result of human and industrial activities (Grassi et al, 2012).

In Germany, up to 250 tons of this chemical have been sold in 1999 (Scheytt, 2002). As diclofenac is one of the most used drugs, it was also one of the first pharmaceutically active compounds that could be detected in the environment (Buser et al, 1998).

The main objective of the present thesis is to do a preliminary study in order to assess the feasibility of injection of clay particle suspensions into the soil as a new remediation technique approach.

In order to achieve this objective a specific experimental method, consisting in two main parts, was developed and different kind of materials were investigated:

- The first part deals with the evaluation of the infiltration properties of different types of clay materials (Bentonite, Kaolin and a secondary clay material product) suspensions into sandy porous media.

  This objective was investigated empirically by performing various small-scale column tests with injection of different nano-to-micro clay particles concentrations.

- Basing on the infiltration tests evidences the second part consists in the assessment of the sorption rate of diclofenac onto selected clay particles.

  In order to achieve this purpose two kind of tests were performed:
    - Batch tests to provide a set of data useful for develop sorption isotherms.
    - Column tests to simulate the injection of clay particle suspensions into a contaminated soil and to evaluate the remediation of the pollutant by sorption on different clay materials.

The present thesis was developed in collaboration with the Univeristy of Trier. All the experiments were performed in the Departments of Geology and Hydrology of the same University.

2 THEORETICAL BACKGROUND

2.1 Remediation of contaminated soil

2.1.1 State of the art

In recent times the cases of polluted soils have constantly increased since pollutants can enter directly the environment as a results of many factors: accidents, spills during transportation, leakage from waste disposal or storage sites, or from industrial facilities (Riser-Roberts, 1992). In order to face this growing need to address environmental contamination, many remediation technologies have been developed to treat soil and other media contaminated by various pollutants (Riser-Roberts, 1998) and many others are being assessed for future utilizations.

Khan et al (2004) described the main available technologies for contaminated soil remediation; their characteristics are summarized and reported in Table 2-1.

Table 2-1 Main technologies developed for remediation of soils and their basic features (Khan et al, 2004).

TECHNOLOGY	DESCRIPTION	TARGET CONTAMINANTS
Soil washing	Liquids (normally water combined with specific solvents) and mechanical processes are used to scrub soils and separate smaller particles where polluting compounds are supposed to be attached.	Semi-volatile organic compounds (SVOCs), petroleum and fuel residuals, heavy metals, PCBs, PAHs, and pesticides.
Soil vapour extraction	Vacuums are applied through the wells near the source of contamination to evaporate the volatile constituents of the contaminated mass which are subsequently removed through an extraction well.	VOCs and SVOCs.
Landfarming	Excavated contaminated soils are spread in a thin layer on the ground surface of a treatment site and aerobic microbial activity is stimulated within the soils through aeration and/or the addition of nutrients, minerals, and water.	Petroleum hydrocarbons.
Soil flushing	An extraction fluid is injected or infiltrated through in-place soils in order to move the contaminants to an area where they can be removed.	Inorganics and radioactive compounds.

Solidification-stabilization	Stabilization generally refers to the process of converting a contaminant into a less soluble, immobile, and less toxic form. Solidification refers to the process that encapsulates the waste materials in a monolithic solid of high structural integrity (Suthersan, 1997; Anderson and Mitchell, 2003).	Heavy metals and inorganic compounds.
Thermal desorption	Soils are heated to temperatures of 100–600 °C so that those contaminants with boiling points in this range will vaporize and separate from the soil.	Hydrocarbons and organic compounds.
Biopiles	This treatment involves the piling of petroleum-contaminated soils into piles or heaps and then aerobic microbial activity is simulated by aeration and the addition of minerals, nutrients and moisture (USEPA, 1998; Filler et al., 2001).	petroleum products, non-halogenated VOCs, halogenated VOCs, SVOCs and pesticides.
Phytoremediation	This treatment consists in using the property of plants to take up, accumulate, and/or degrade constituents that are present in soil and water environments (GWRTAC, 1996).	Heavy metals, radionuclides, chlorinated solvents, petroleum hydrocarbons, PCBs, PAHs, organophosphate insecticides, explosives, and surfactants (Nedunuri et al., 2000).
Bioslurry systems	The excavated soil is treated in a controlled bioreactor where the slurry is mixed to keep the solids suspended and the microorganisms in contact with the contaminants, in order to break them down.	Non halogenated SVOCs and VOCs.
Encapsulation	In this technique, the contaminated soils are physically isolated by low permeability caps, slurry walls, grout curtains, or cut off walls.	All kind of contaminants.
Aeration	This technology evaporates the volatile components of petroleum from the soil into the air increasing the area of contact between the water and the air.	SVOCs, pesticides, and fuels.
Bioventing	It involves the injection of air into the contaminated media at a rate designed to maximize in situ biodegradation and minimize or eliminate the off-gassing of volatilized contaminants to the atmosphere.	Aerobic degradable substances.

2.1.2 Remediation by fluid injection techniques

Concerning the topic of the present thesis, the remediation by fluid injection is the most interesting technique to investigate. In fact, no background knowledge about the infiltration of clay particles suspensions into the subsurface and no preliminary studies dealing with its feasibility as a remediation technology were conducted.
For this reason assessing the available techniques and their features can result in a better understanding of the issues involving the present study.

One of these techniques is **soil flushing**, which was already mentioned in Table 2-1. Its main aim is to mobilize the contaminants present in the soil, on the basis of their partition coefficients and solubility, by the injection of specific solvents. It doesn’t involve any adsorption or chemical reaction and the pollutants are then extracted from the soil in liquid phase.

Chemical reactions are present in the **ISCO** (In Situ Chemical Oxidation) technology. It involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming groundwater or soil contaminants into less harmful chemical species (Huling and Pivetz, 2006).
In particular this technology is used to reduce contaminant mass and concentrations in soil and groundwater, contaminant mass flux from source areas to downgradient pump-and-treat systems, and to reduce anticipated clean up times required for other remedial options (Huling and Pivetz, 2006).
The literature is mainly focused on permanganate and Fenton’s reagent, two of the most commonly used forms of injected oxidants.

Another very similar technology is the ISCR (In Situ Chemical Reduction). Particular interest in this field is given to the use of injectable micro- and nano-scale metallic, especially **Zero Valent Iron,** particles for the treatment of soil contamination. This is a recently developed but the most widely technology used for the remediation of soil and groundwater contamination with chlorinated solvents.
Due to their greater surface area per unit mass, nanomaterials can be much more reactive than larger particles (Rickerby and Morrison, 2007). According to Li et al. (2006) their reaction rates

may be up to 25-30 times higher compared to granular (in the range micrometer to millimetre range) iron and so it is for their sorption capacity.

In aqueous solutions, all nano ZVI particles react with water and oxygen to form an outer iron (hydr)oxide layer, resulting in a final core-shell structure (O'Carroll et al, 2013). In Figure 2-1 the main mechanisms for removal of pollutants are illustrated. The oxide layer allows electron transfer from the metal through different processes, in this way sustaining the capacity of the particles for reduction of halogenated compounds (Li et al, 2006). Moreover the same layer may also act as an efficient adsorbent for metals (O'Carroll et al, 2013).

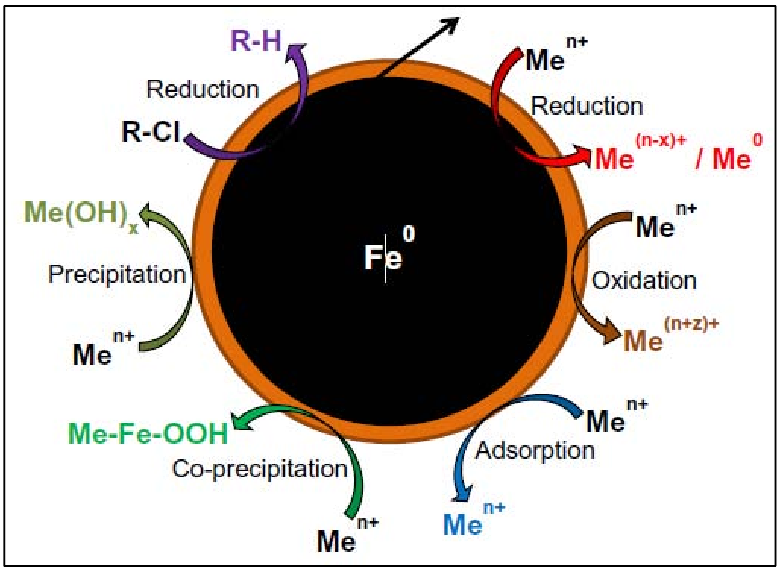

Figure 2-1 Iron (Hydr)oxide core-shell structure of nZVI representing various mechanisms for the removal of metals and chlorinated compounds (O'Carroll et al, 2013).

The nano ZVI- and micro ZVI-particles can be readily injected into the soil matrix, thus allowing for active treatment of source and plume areas (City Chlor, 2013).

The techniques that allow these particles to be effective in site remediation are summarized in Figure 2-2. They deals with the injection of ZVI particles in the subsurface in order to form a reactive barrier or a plume. Another possibility is to incorporate this material in the topsoil to remediate contaminants present in the ground surface.

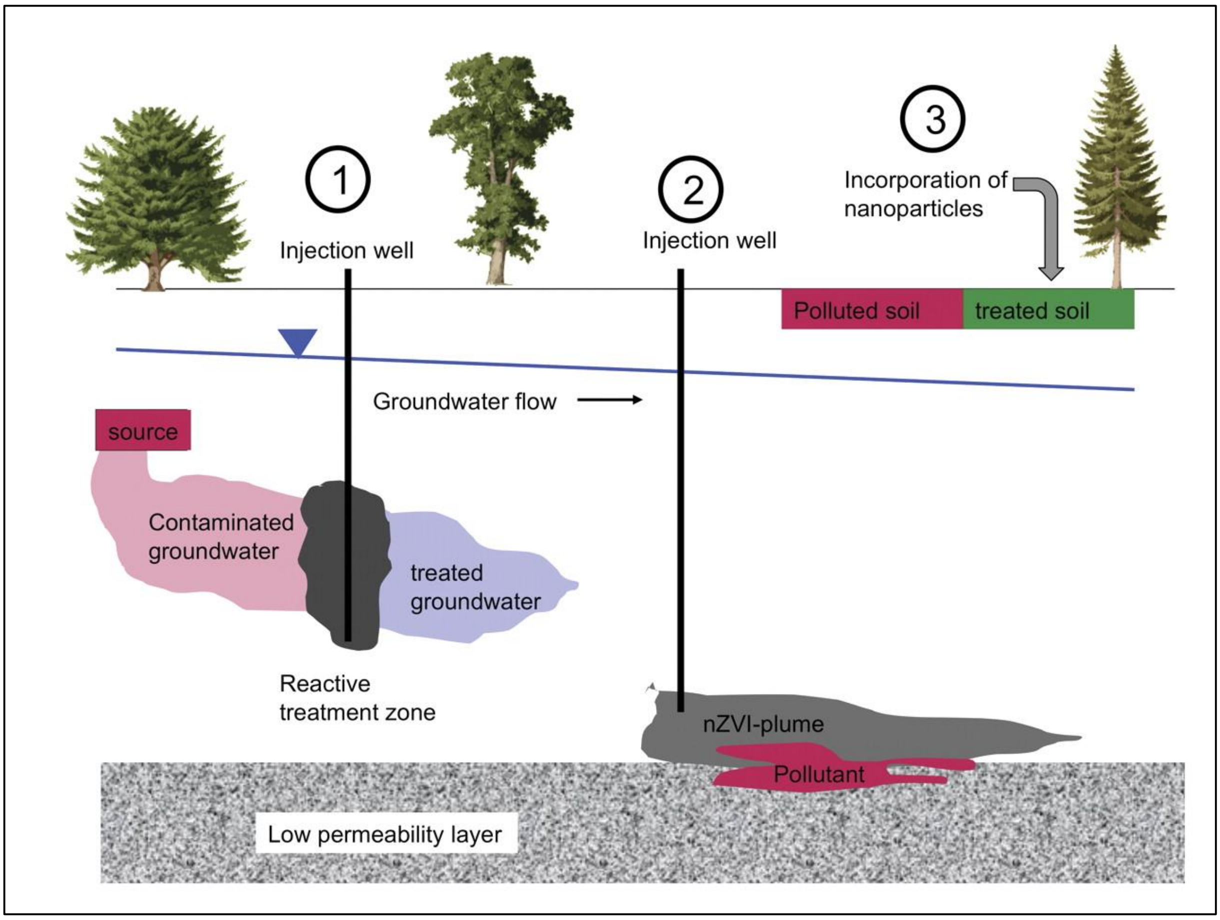

Figure 2-2 In situ technologies used to treat polluted groundwater and soils: 1) injection of nZVI to form a reactive barrier; 2) injection of mobile nZVI to form an nZVI plume; 3) incorporation of NP into topsoil to adsorb or degrade pollutants (Mueller and Nowack, 2010).

Despite of their useful remediation properties, some issues about their suitability are still a source of uncertainty.

Tratnyek and Johnson (2006) stated that high reactivity tends to correlate with low selectivity. Hence, the nZVI particles may react with non-target substances, including sulphate, oxygen, nitrate and water affecting the efficiency of the remediation and the stability of the ecosystem contaminants.

Another problem is their poor subsurface mobility. Due to strong attractive interparticle forces, primarily magnetic, nZVI tends to agglomerate to micron size particles, which have limited mobility in porous media (O’Carroll et al, 2013). Although many studies have simulated nZVI transport in controlled laboratory experiments, there are currently no published modelling studies of nZVI transport at the field scale (O’Carroll et al, 2013).

The only available information are about empirical results coming from laboratory and field scale tests. According to Tratnyek and Johnson (2006) the size of the ZVI utilized in real-world site remediation are larger than 100 nanometer and their mobility, under almost all relevant conditions, is thereby less than few meters.

As regards nZVI concentration in field, Saleh et al (2007) suggest to operate with at least 3 g/l for successful degradation. Henn and Waddill (2006), Phenrat et al (2009) found out that 10 g/l is the average concentration of injected slurries at typical field site, although concentrations are dependent on many site factors such as: geochemistry, application method, permeability of the aquifer, particle size (City Chlor, 2013).

To overcome the problem of mobility the use of special coatings has been developed. They can increase the surface load in order to achieve electrostatic stabilisation of the colloidal mixture (City Chlor, 2013).

Anyway there is still a need to operate more field applications with detailed characterization before and after nZVI injection to assess nZVI mobility and the extent of contaminant destruction (O'Carroll et al, 2013).

So far nZVI is the only application of nanomaterials in soil and groundwater remediation which has been successfully commercialized (Mueller and Nowack, 2010) but other technologies are promising for future development such as the utilization for sites remediation of **bimetallic nanoparticles (BNP)**, **nano oxides** and **emulsified ZVI (eZVI)**. Their implementation is reported in Figure 2-3, representing the proportion of remediation techniques by injection of nanoparticles used in 44 sites in 13 different countries.

Among these new technologies, nanoscale iron oxides have showed a strong adsorption capacity. Adding them to soils will immobilize soil metals and also successful preliminary studies were conducted for phosphate and arsenic removal (Mueller and Nowack, 2010; Rickerby and Morrison, 2007).

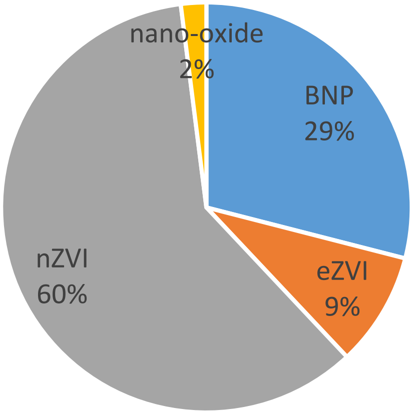

Figure 2-3 Types of nanomaterials tested in 44 selected remediation sites. (Karn et al, 2009)

Nanoscale calcium peroxide has also recently been used for the clean-up of oil spills (Karn et al, 2009).

However, these techniques are mostly used for groundwater remediation in porous soil, as Figure 2-4 points out (the percentages are related to the same sites of Figure 2-3).

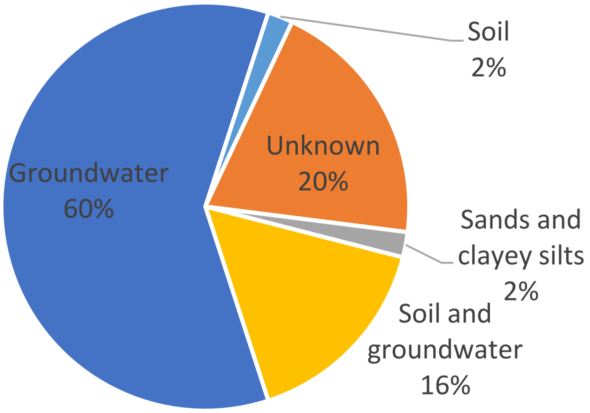

Figure 2-4 Types of media treated with nanoscale particles in 44 selected remediation sites (Karn et al, 2009)

Nonetheless remediation of contaminated soil is also strongly related to groundwater pollution since it can prevent pollutants to be mobilized and transferred to water sources.

2.2 *Properties of clays for pollution control.*

According to Kühnel (2006) clays have two main features which make them interesting:

1) Their common availability.
2) Their extraordinary properties.

The same author stated also that “*no other group of inorganic materials have so many species, show such a wide range of reactivity and propensity for modification, or enjoy such a diversity of practical applications as clay minerals. In addition to their conventional uses, as in ceramics and paper coating, clays have found many novel applications. Clay minerals are naturally occurring nanomaterials, abundant, inexpensive, and environmental friendly.*

The optimization of adsorption properties, swelling behaviour, colloidal and rheological properties, and the design of new types of organoclays also open prospects of using clay minerals for pollution control and environmental protection”.

Table 2-2 Applications of clays for pollution control and environmental protection (Yuan et al, 2013).

Contaminants for control	**Status (actual or potential use)**	**Relevant clay minerals properties**
Heavy metal cations and simple cations	Actual, mainly passive, use (e.g. in soils, liners).	Charge, Specific Surface Area , reactive surface groups.
Organic and biological cations	Potential for water and wastewater treatment, pesticide control.	Charge, Specific Surface Area, interlayer.
Non-ionic organic molecules	Actual, for water and wastewater treatment; potential, for pesticide control, waste liners.	Charge, Specific Surface Area, interlayer.
Anions	Actual, for water and wastewater treatment; potential for pesticide and nutrient leaching control.	Charge, reactive surface groups.
Turbidity and residual treatment chemicals	Actual, for treatment of potable water and some wastewaters and sewage.	Colloidal, from size and charge; charge, Specific Surface Area.
Leachates	Actual, for waste liners and radioactive waste storage.	Swelling, charge, Specific Surface Area, reactive surface groups.

In this context, the present thesis work has the purpose to investigate the possibility to use natural clays as low cost sorbents for soil remediation. This approach involves the study of different clays and clay minerals (especially montmorillonite and kaolinite) in suspension and in particular the infiltration and the sorption properties.

2.2.1 Clays and clay minerals

The joint nomenclature committees (JNC) have defined "**clay**" as "a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with dried or fired" (Guggenheim and Martin, 1995). The limit for the maximum particles size is commonly set at 4 micrometers in geology, 2 micrometers in pedology and 1 micrometer in colloid science.

Sometimes "clay" is used also to define "clay minerals" which are, according to JNC "phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing" (Bergaya and Lagaly, 2013).

A phyllosilicate is a sheet silicate formed by parallel and ideally continuous tethraedal sheets. Each tetrahedron consists of a cation, T, coordinated to four oxygen atoms, and linked to adjacent tetrahedra by sharing three corners (the basal oxygen atoms, Ox_b) to form an infinite two-dimensional 'hexagonal' mesh pattern along the a, b crystallographic directions as reported in Figure 2-5 (Brigatti et al, 2013).

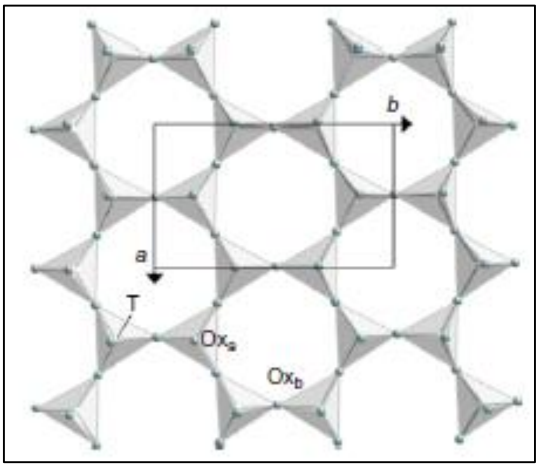

Figure 2-5 The tetrahedral sheet where T, tetrahedral cations; Ox_a, apical oxygen atoms; Ox_b, basal oxygen atoms. a and b refer to unit cell parameters (Brigatti et al, 2013).

Common tetrahedral cations are Si^{4+}, Al^{3+} and Fe^{3+}.

The tetrahedral can be distributed in the space forming an octahedral sheet consisting of a cation, O, coordinated by six oxygen atoms and linked to neighbouring octahedra by sharing edges in cis-oriented or trans-oriented position depending on the common edges (Figure 2-6).

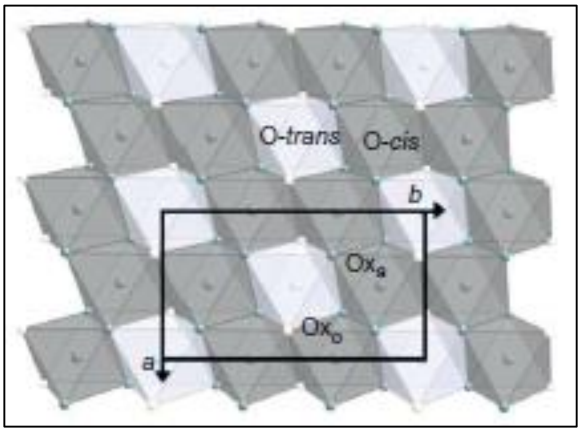

Figure 2-6 The octahedral sheet. O-trans, trans-oriented octahedra; O-cis, cis-oriented octahedra; Ox_a*, apical oxygen atoms;* a *and* b *refer to unit cell parameters (Brigatti et al, 2013).*

Octahedral cations are usually Al^{3+}, Fe^{3+}, Mg^{2+}, or Fe^{2+}.

These kind of sheets may interact and form different layer structures which identify the main phyllosilicate categories:

- The 1:1 group [T-O] formed by the repetition of one tetrahedral T and one octahedral O sheets.
- The 2:1 group [T-O-T] where an octahedral sheet O is interposed between two tetrahedral T sheets.

Since some phyllosilicates have the property to hold other ions or structures between two layers, the 2:1 group can be subdivided into other categories which are summarized by Brigatti et al (2013) in Figure 2-7. In the same Figure the composition of the different sheets are reported along with the different thickness of the unit structures.
Hence, 2:1 clay minerals can be also divided into the following groups:

- 2:1 (e.g. talc);
- 2:1 with anhydrous interlayer cations (micas group);
- 2:1 with hydrated interlayer cations (smectite group);
- 2:1 with octahedral interlayer sheet (chlorite group).

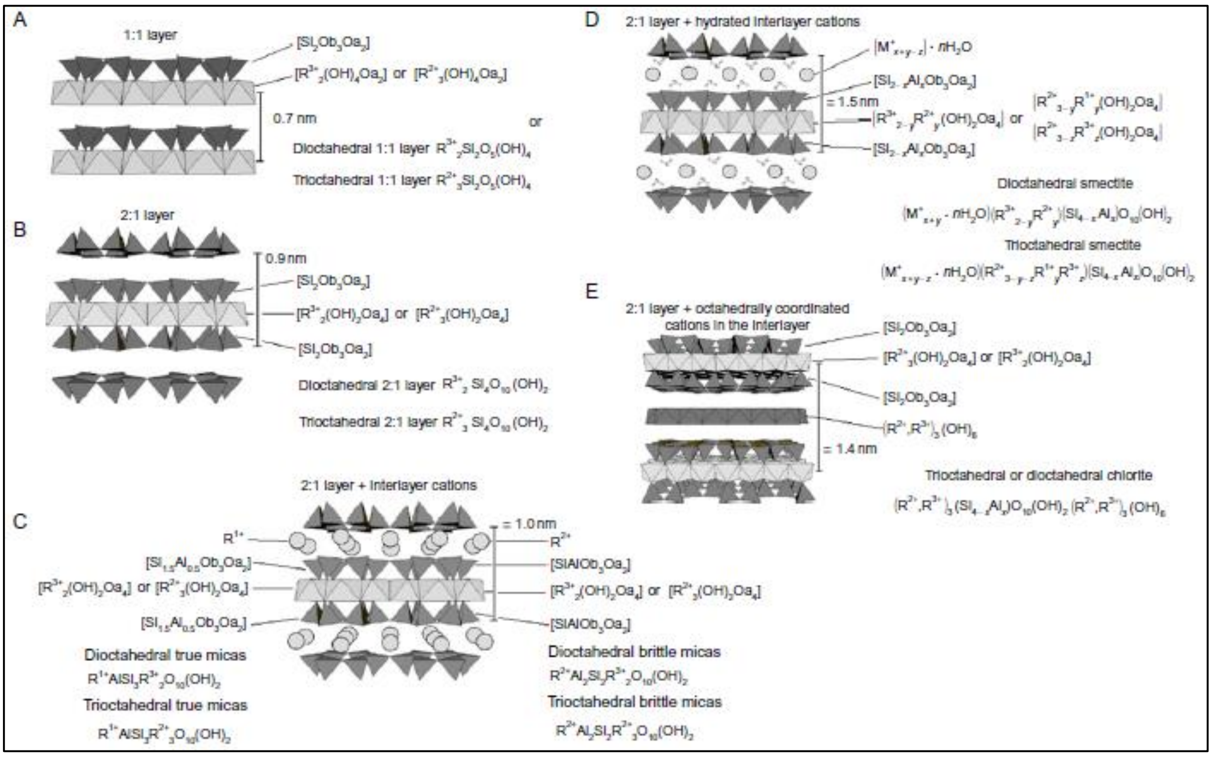

Figure 2-7 The different layer structures. (A) The 1:1 layer; (B) the 2:1 layer; (C) the 2:1 layer with anhydrous interlayer cations;(D) the 2:1 layer with hydrated interlayer cations; (E) the 2:1 layer with octahedral interlayer sheet (Brigatti et al,2013).

2.2.1.1 Clay minerals for environmental applications.

As regards environmental applications all the clay minerals are important but only few occurs in relatively monomineralic deposits (Murray, 1993). Among these minerals, in this thesis the main properties of kaolins and smectites (in particular montmorillonite) will be discussed.

Kaolinite has a 1:1 layer structure, with the basic unit consisting of a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{3+} as the octahedral cation (Bhattacharyya and Sen Gupta, 2008). Its formula is $Al_2Si_2O_5(OH)_4$ and its theoretical composition is: SiO_2 46.54%, Al_2O_3 39.50%, H_2O 13.96% expressed in terms of the oxides (Bhattacharyya et Sen Gupta, 2008).
Kaolinite has a very limited atomic substitution property in this two sheets structure: only exceptions are iron for aluminium in the octahedral sheet and some aluminium for silicon in the tetrahedral sheet (Murray, 1993). Thus, the net layer charge of kaolinite is 0, but normally in nature, kaolinite shows a small net negative change arising from broken bonds on the clay crystals (Bhattacharyya et Sen Gupta, 2008). As a result the surface of kaolinite is not completely inert.

The size of kaolinite particles varies from about 0.1 to 20 micrometer (Jepson, 1984).

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Montmorillonite belongs to the smectites group, which are 2:1 phyllosilicates with exchangeable cations in the interlayer and with a total layer charge between -0.2 and -0.6 per half unit cell (Brigatti et al, 2013). This mineral is a hydrated sodium, calcium, magnesium, iron, aluminium silicate where a central octahedral sheet shares oxygens and hydroxyls with a tetrahedral sheet on each side (Murray, 1993). Its general formula can be formulated as $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$ and the theoretical composition without the interlayer material is SiO_2 66.7%, Al_2O_3 28.3%, H_2O 5% (Bhattacharyya et Sen Gupta, 2008).

According to Murray (1993) in the octahedral sheet there is a considerable substitution of magnesium and iron for aluminium and in the two outer tetrahedral sheets some substitutions of silicon by aluminium. The same author pointed out that these substitutions of divalent ions for trivalent ions and trivalent ions for tetravalent ions cause a charge imbalance on the unit structure, so the surface charge is relatively high.

Smectite group particles size varies in a range between 0,1 to 2 micrometer, with average sizes of about 0.5 micrometer (Grim and Güven, 1978; Odom, 1984). The morphology of individual particles ranges from platy to lath-shape; some are even fibrous but mostly the particles are of irregular shape (Lagaly and Dékàny, 2013).

The main properties of kaolinite and montmorillonite are summarized in Table 2-3.

Table 2-3 List of properties specific to kaolinite and montmorillonite (Murray, 1993).

KAOLINITE	MONTMORILLONITE
1:1 layer	2:1 layer
Little or no substitutions	Octahedral and some tetrahedral substitutions
Very slightly charged	High charge
Very low base exchange	High base exchange
Low surface area	High surface area
Low sorptivity	High sorptivity
Low viscosity	High viscosity
Non-expanding	Expanding
Hydrophilic	Hydrophilic

Another significant clay mineral is also **illite**: a dioctahedral 2:1 phyllosilicate which commonly occurs in soils and sedimentary rocks. Generally the term “illite” is used for 2:1 clay minerals with a non-expandable layer and a wide variety of chemical compositions (Brigatti et al, 2013).

2.2.2 Infiltration of suspensions

The movement of clay suspensions into a porous media can be described by the filtration theory of colloids in porous media. In fact most of the clays can be considered as colloids since they have particles with effective diameters less than 10 micrometers (McCarthy and Zachara, 1989). This theory can be efficiently represented by the basic model for water filtration which was developed by Yao et al (1971). It is described by the general formula, reported as described in the reference book by Howe et al (2012) for filter beds in water treatment:

$$C = C_0 \exp\left[\frac{-3(1-\varepsilon)\eta \propto L}{2d_c}\right]$$

Where: C = particle concentration [mg/L] at a specific depth L [m]
C_0 = particle concentration in input [mg/L]
ε = porosity of the porous media [-]
η = transport efficiency [-]
α = attachment efficiency [-]
d_c = porous media average diameter [m]

On this model many assumptions were done and only the main particle filtration dependences are involved. In fact some influences on the porous media (e.g. grain shape) and on the suspension (e.g. turbidity, particle size distribution, particle density, water viscosity, temperature) have been neglected.

The suspensions transport mechanisms which occurs in a porous media are different and they are illustrated in Figure 2-8. Due to these processes the particles can come in contact with the porous media.

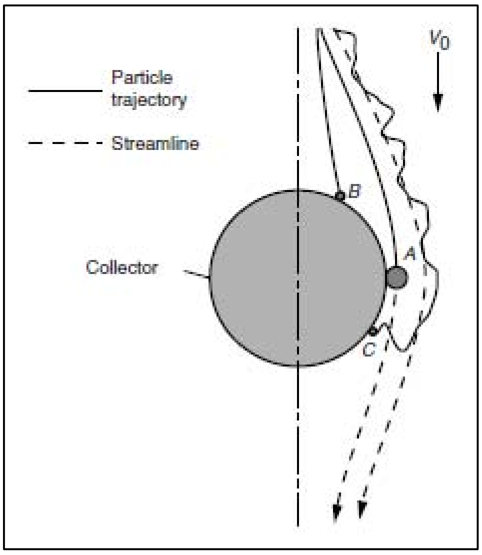

Figure 2-8 Particle transport mechanisms in fundamental filtration theory: (a) interception, particle A follows streamline but collides with the collector because of the proximity between the streamline and the collector; (b) sedimentation, particle B deviates from the streamline and collides with the collector because of gravitational forces; and (c) diffusion, particle C collides with collector due to random Brownian motion (Howe et al, 2012).

This model takes into account three kinds of mechanism of particle transport (Howe et al, 2012):

- Diffusion: it is the responsible for Brownian motion of particles and for their deviation from the fluid streamlines.
- Sedimentation: particles with a density significantly greater than water tend to deviate from fluid streamlines due to gravitational forces.
- Interception: Particles remaining centered on fluid streamlines that pass the media surface by a distance of half the particle diameter or less will be intercepted.

According to Bradford et al (2002) smaller particles are predicted to be removed more efficiently by diffusive transport, and larger particles by sedimentation and interception.

The attachment efficiency is affected by London–van der Waals forces, surface chemical interactions, electrostatic forces, hydration, hydrophobic interactions, or steric interactions between particles and porous media (Tobiason and O’Melia, 1988).

However experimental observations of colloid transport don’t always agree with colloid attachment theory. For example, researchers have reported enhanced colloid retention at the soil surface and that the spatial distribution of retained colloids does not follow a simple exponential decrease with depth (Bolster et al., 1999; Redman et al.,2001).

According to Bradford et al (2002) some of the discrepancies between colloid transport data and attachment theory may also be due to the fact that colloid attachment theory does not account for straining.

McDowell-Boyer et al (1986) defined “straining” as the trapping of colloid particles in the downgradient pore throats that are too small to allow particle passage.

In their study conducted on “Physical factors affecting the transport and fate of colloids in saturated porous media”, Bradford et al (2002) came to the conclusion that straining may also be influenced by other physical (water velocity, **colloid concentration**, **colloid and soil grain size distribution characteristics**, heterogeneity, and dimensionality) and chemical (**surface charge**) factors of both porous media and colloids. The experimental data, from the same study by Bradford et al (2002), strongly suggest that straining is an important mechanism of colloid retention for colloids with particle size up to 3.2 micrometer.

It can also happen that colloid particles are physically excluded from entering all of the soil pores. In this case a complete straining (mechanical filtration) occurs (McDowell- Boyer et al, 1986) and a filter cake or surface layer of colloids forms to the surface of the porous medium. This filter cake may significantly reduce the permeability of the porous medium-filter cake system (Willis and Tosun, 1980).

Incomplete straining can also happen when colloids are retained in small pores decreasing the effective pore size and it may therefore increase subsequent particle retention in this pores.

Sakthivadivel (1966, 1969) elaborated also geometrical relation for mass removal by straining reporting that straining was significant when the colloid diameter was greater than 5% of the median grain diameter of the porous medium.

In the present thesis, and in particular in Chapter 5, both physical and chemical factors were taken into account in order to assess the infiltration of clay suspensions.

As regards clays, and generally colloids, the main factor which affects straining is the destabilization of particles, or **coagulation**, induced by the elimination of the repulsive forces. The mechanism that is involved in the coagulation depends on the characteristics of the colloid particle itself.

As mentioned in paragraph 2.2.1.1 clay particles show a negative surface charge due to isomorphous replacement or to structural imperfections. Due to this characteristic a layer of cations is bound tightly to the surface to form a fixed adsorption layer (*Helmholtz* or *Stern layer*). Beyond the Helmholtz layer, a net negative charge and electric field is present that attracts an excess of cations (over the bulk solution concentration) and repels anions (Howe et al, 2012).

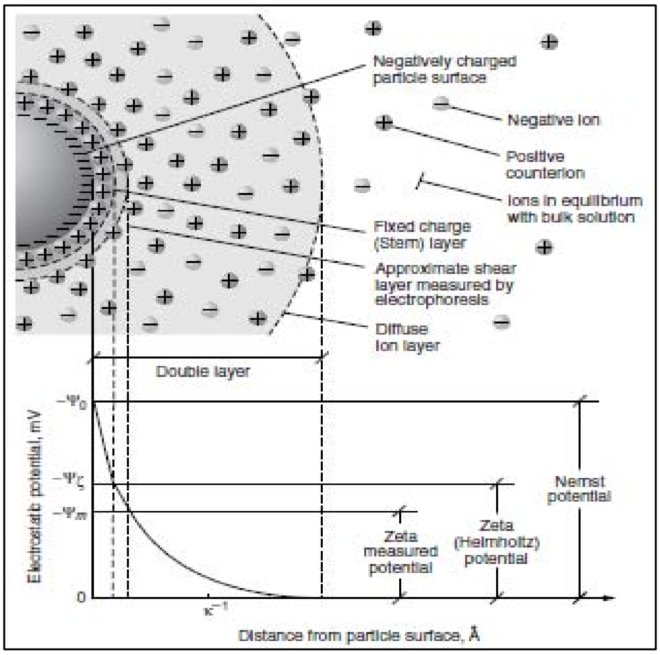

Figure 2-9 Structure of the electrical double layer. The zeta potential is measured at the shear plane and it is due to the particle movement in an electrical field (Howe et al,2012)

The layer that extends from the Helmholtz layer to the bulk solution where the charge is zero and electroneutrality is satisfied is called diffuse layer. Taken together the adsorbed (Helmholtz) and diffuse layer are known as the *electric double layer* (Howe et al, 2012) and it is shown in Figure 2-9.

The stability of a particle depends on the balance between this electrostatic repulsion and the van der Waals attractive forces. Due to the presence of the extension into the solution repulsion forces are predominant. When the electrical double layers are expanded and when the net particle charge does not equal zero the colloids are stabilized (Ouyang et al., 1996).

In Figure 2-10 the extent of these forces are given in function of the distance between two particles represented by flat plates with similar charge (Howe et al, 2012).

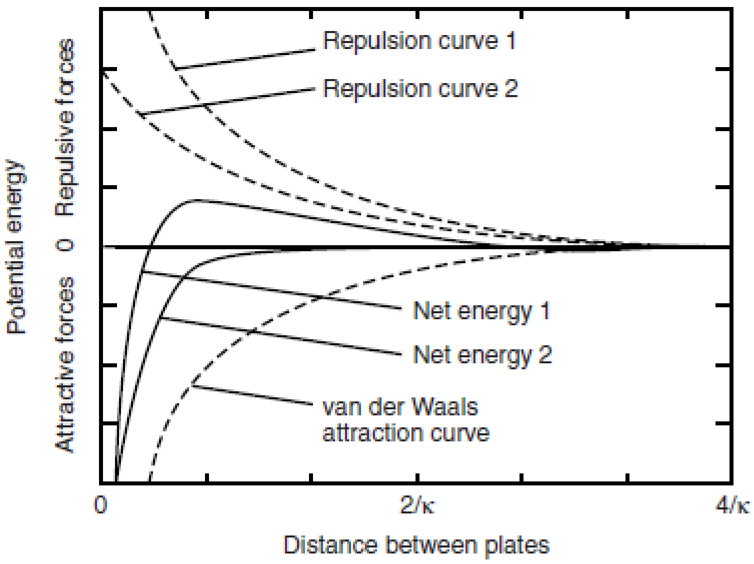

Figure 2-10 Attractive and repulsive potential energy that result when two particles are brought together (Howe et al, 2012)

In case 2) in Figure 2-10 the particles are destabilized without any additional energy since the attractive forces are higher than the repulsive ones.

The main methods to destabilize and thus coagulating colloid particles, and especially clays, are (Howe et al, 2012):

- Compression of the electrical double layer (increasing **electrolytes concentrations** and thus ionic strength in the solution). The more extended is the double layer the higher salt concentration is needed.

  Unlike other colloidal dispersions, well-dispersed clay minerals (kaolinites, smectites, illites, palygorskite) in the sodium form may be coagulated by very low concentrations of inorganic salts: this critical coagulation concentration, C_k, of sodium chloride varies between 3 and 20 mmol/L (Lagaly and Dékàny, 2013). A typical reagent that can raise up the C_k value is Sodium Diphosphate. In a sodium Montmorillonite dispersion even an addition of 0.1 mmol/L $Na_4P_2O_7$ increased the C_k of NaCl from 5 to 195 mmol/L (Permien and Lagaly, 1994).
- Neutralization of the charge (lowering **pH** in the solution: it affects colloid and solid **surface charge** by changing pH dependent surface charge sites (Bradford et al, 2002)). The more is a particle charged the lower should be the pH.

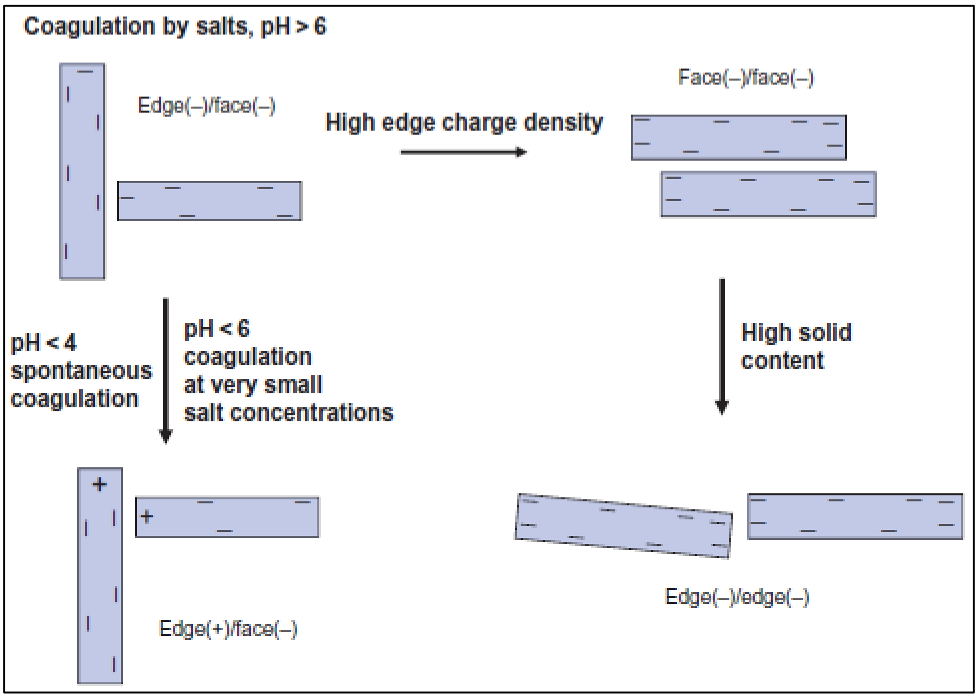

Figure 2-11 The different modes of coagulation of clay mineral particles (Lagaly and Ziesmer, 2003).

In Figure 2-11 clay particles as charged plates and their coagulation modes (depending on pH, salt concentration, and solid content) are represented.

2.2.2.1 Clay minerals rheology

The effect of salt addition on the aggregation of clay mineral particles in dilute (<2%) dispersions and the resulting rheological properties are schematically shown in Figure 2-12 (Lagaly and Dékàny, 2013). Both the yield value and the viscosity are low when salt is absent. They decrease even further after the addition of modest amounts of salt (Permien and Lagaly, 1995), and then increase steeply. High salt concentrations can low down viscosity and yield value again (Lagaly and Dékàny, 2013).

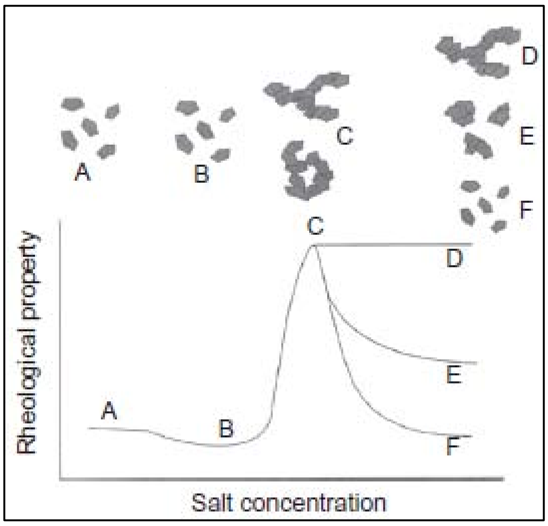

Figure 2-12 Influence of electrolytes on the flow behaviour of diluted clay dispersions. (A, B) isolated particles, (B) minimum of rheological properties (viscosity, yield value), (C, D) aggregation in the form of networks, and (E, F) fragmentation of the networks at high salt concentrations (Lagaly and Dékàny, 2013).

As regards rheological properties, **montmorillonite** suspensions is strongly dependent on pH and salt concentration (Brandenburg and Lagaly, 1987). In fact due to the small particle size (submicron), the high surface charge, the thin flake-shaped particles and the expansion of the structure, montmorillonite (especially the sodium one) has a very high viscosity also at a solids concentration of 10% wt/wt (Murray, 1993). The dependence of the shear stress on the pH is illustrated in Figure 2-13 for two kinds of montmorillonite.

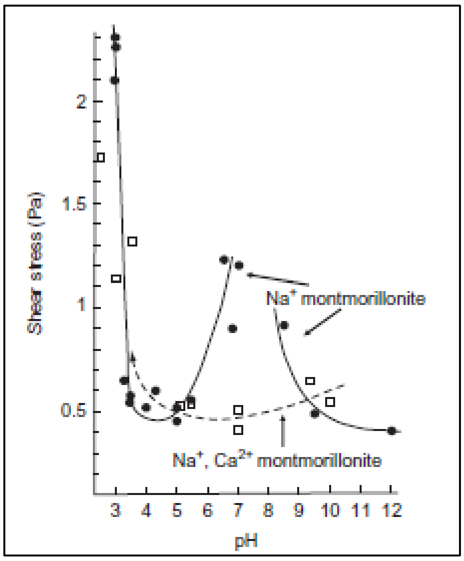

Figure 2-13 Dependence of the shear stress (at a rate of shear of 94.5 s^{-1}*) on the pH value for the dispersion of Na-Montmorillonite and of the parent (Na*$^{+}$*, Ca*$^{2+}$*)-bentonite (Lagaly and Dékàny, 2013).*

Adding calcium ions has a strong effect on the kind of aggregation. Small additions can strongly increase the yield value of Na$^+$ -Montmorillonite dispersions, but high amounts of Ca^{2+} ions reduce this value considerably (Permien and Lagaly, 1994b). At pH 7 the maximum of the shear stress disappears in the presence of even small amounts of calcium ions. (Permien and Lagaly, 1995; Benna et al, 1999). The behaviour of montmorillonite and thus bentonite suspension is therefore complex and depends on the **Na$^+$/Ca^{2+}** ratio.

For colloids in general McCarthy and Zachara (1989) reported that monodispersed particles may be produced through disaggregation if the ion balance is shifted from one dominated by divalent Ca^{2+} to one dominated by monovalent Na$^+$.

An example is given by the activation of Calcium Bentonite by soda. **Bentonite** is the name for an impure clay which contains smectites and in particular montmorillonite as main component. Calcium bentonite can adsorb between 150% and 200% water related to its own weight (Koch, 2008). With the addition of Na_2CO_3, Na^+ ions are entering the interlayer space: since the electrical interaction between the monovalent Na^+ ions and the negatively charged platelets is much weaker compared to the Ca^{2+} ions with two positive charges, water molecules can enter the interlayer area, surrounding the Na^+ ions with a larger hydration shell (Koch, 2008). This behaviour is schematically illustrated in Figure 2-14.

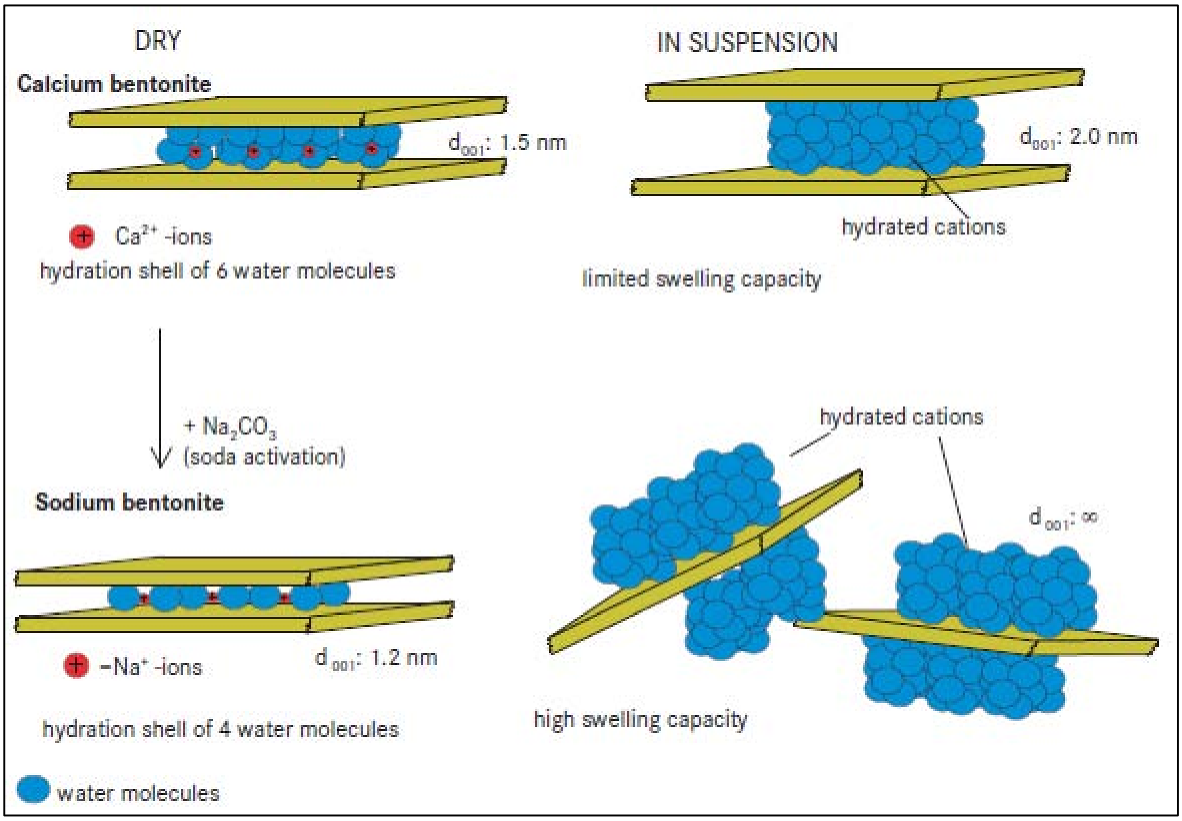

Figure 2-14 Cation-exchange and swelling behaviour of Ca- and Na- Montmorillonite (Koch,2008).

Montmorillonite is a **swelling** mineral and in its sodium form, it can be easily dispersed in suspension in a “card house” configuration. For this reason it also shows relevant rheological properties like thixotropy (Koch, 2008).

Due to its low surface charge, low surface area, and the crystalline morphology of the particles, **kaolinite** show excellent rheology at high solids concentrations (up to 70 %) (Murray, 1993). In fact this mineral is hydrophilic and can be dispersed easily in water.

In Figure 2-15 the results of the tests performed by Alves et al (2008) are reported. The viscosity of a kaolin suspension with 50 % wt/wt of solids is decreasing with the shear rate. This behaviour is typical of a thixotropic flow.

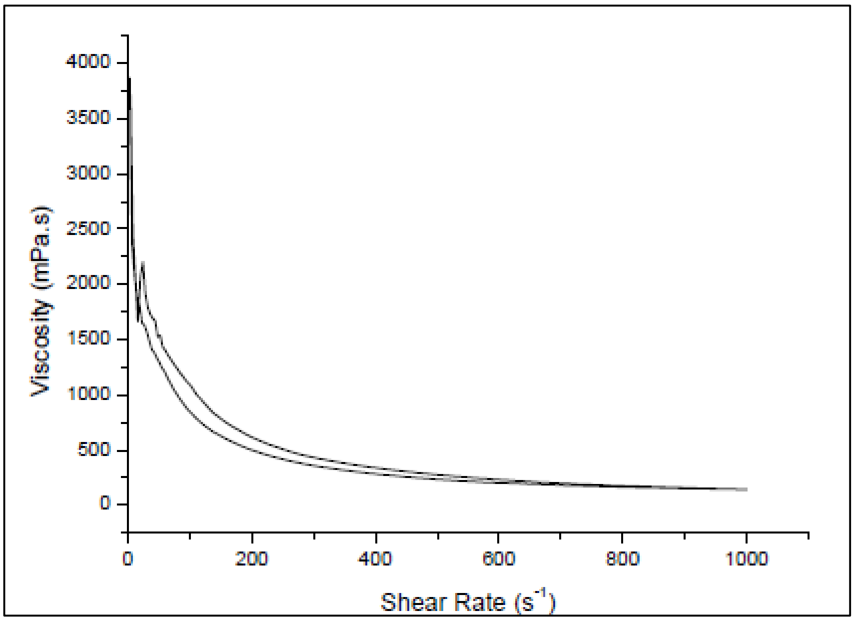

Figure 2-15 Viscosity versus shear rate of kaolin slurry with 50% of solids and without deflocculant (Alves et al,2008).

Alves et al (2008) found out that increasing the solid content up to 70 % corresponds to an increase of 10 times on viscosity.

Hence the authors stated that the in order to obtain low viscosity of kaolin pulp is necessary: low solid concentration (50%), high pH (10) and high deflocculant concentration (8 kg/t).

2.2.3 *Sorption properties*

Sorption is a general term for all fixation and retardation processes of substances (Wagner, 1992). In particular, clays can remove pollutants through adsorption.

Adsorption is a superficial mechanism involving molecular attraction which occurs when two phases come in contact: a solid one (adsorbent) and a liquid or gaseous phase (adsorbate).

Two factors determine this process (Grassi, 2010):

- Low affinity between solute and solvent.
- High affinity between solid and solute.

In order to determine the first factor solubility is the most significant parameter: when dissolved in water a compound may have hydrophobic or hydrophilic properties. Hydrophobic substances, with low solubility, are preferred for sorption.

Concerning the second factor, different kinds of attraction forces must be considered (Grassi, 2010):

- Electrostatic forces; ionic bonds between compound ions and surface charges are created.
- Van der Waals forces; this is the case of physical adsorption. It occurs at low temperature and it deals with weak intermolecular forces. The process is considered reversible.
- Chemical forces; this is the case of chemisorption. It occurs at high temperature and the adsorbate molecules are chemically bound to the adsorbent surface sites, thus they are not free to move.

Most of sorption phenomena are due to all three mechanisms and therefore it is not possible to distinguish between chemical and physical adsorption.

According to Grassi et al (2012) the factors affecting the adsorption process are:

- surface area;
- nature and initial concentration of adsorbate;
- solution pH;
- temperature;
- interfering substances;
- nature and dose of adsorbent;

In this thesis work these parameters were taken into account in order to assess the adsorption extent of clay suspensions in laboratory scale tests.

Because of their **low cost**, **high surface area**, high porosity, chemical and mechanical stability, **high cation exchange capacity** and abundance in most continents, clays are excellent adsorbent materials (Grassi et al, 2012; Srinivasan, 2011). Natural clay can be assumed as a “low cost" sorbent since it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Bailey et al, 1998). The price of clay is about \$0.005–0.46/kg, and the price of montmorillonite is about \$0.04–0.12/kg, which is about 20 times cheaper than activated carbon (Babel and Kurniawan, 2003; Virta, 2006).

Industrial wastes such as sludge, fly ash, and red mud can also be classified as low-cost materials and if they are locally available, they can be used as adsorbents for removal of pollutant from aqueous solution (Grassi et al, 2012). One of these materials was also tested as sorbent in the present thesis.

The compounds accumulate on clay surface and they are immobilized through the processes of ion exchange, coordination, or ion-dipole interactions (Srinivasan, 2011).
Moreover natural clay minerals contain inorganic cations which, in aqueous medium, are strongly hydrated, and confer their surface a hydrophilic character (Sanchez-Martìn et al, 2006). Hence, they are good adsorbents of **ionic or polar compounds** but not of non-ionic or hydrophobic organic compounds (Sànchez-Camazano et al, 1994; Cox et al, 1997). In fact, these last compounds are more favourably adsorbed by the organic matter, when it is present, than by the clay minerals (Arienzo et al, 1994; Sànchez- Martìn et al, 2000).
Sometimes the pollutants can be held through H-bonding, van der Waals interactions, or hydrophobic bonding (Srinivasan, 2011).

The influence of pH on the sorption process is a known phenomena. For example, according to Mitchell (1993) though **kaolinite** is the least reactive clay (Suraj et al,1998), its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment. Kaolinite has a very low base exchange capacity, which is generally less than 2 cmol/kg (Murray, 1991) and a low surface area in 8-15 m^2/g range (Murray,1993).
As regards polar and ionic compounds, their maximum adsorption by the **montmorillonite** clay occurs when the solution pH is closed to compounds pK_a value (Weber, 1970; Weber et al, 1965) At pH values higher than pK_a the compound is present primarily in the molecular form and is adsorbed by H bonding or through polar adsorption forces (Delle Site, 2001).
Sodium montmorillonites from Wyoming have a base exchange capacity of 90-120 cmol/kg (Elzea and Murray, 1990) and calcium montmorillonites from Texas 70-80 cmol/kg (Van Olphen and Fripiat, 1979).

2.2.3.1 *Sorption mathematical models*

In order to provide a mathematical and quantitative analysis of the sorption process, **sorption isotherms** are used. They describe the sorption capacity, at constant temperature, correlating the amount of sorbed compound per sorbent unit (q_e) and the compound concentration in solution (C_e) at equilibrium (Grassi, 2010). This capacity can be calculated with the following relation:

$$q_e = \frac{(C - C_e)\, V}{M}$$

Where: q_e = amount of solute sorbed per unit of sorbent [MM^{-1}]
C = initial concentration of solute in solution [ML^{-1}]
C_e = concentration of solute in solution at equilibrium [ML^{-1}]
V = volume of the sorption reactor [L]
M = mass of the sorbent [M]

Different mathematical models were developed in order to express this correlation. The most used ones are reported in this thesis.

The simplest model describes a **linear sorption correlation** with concentration-independent distribution equilibrium (K_d = constant) between fluid and solid phase (Jürgensohn, 2012). The related equation is:

$$q_e = K_d \cdot C_e$$

Where K_d [L/M] is the partition coefficient.

Another kind of correlation is proposed by the **Langmuir isotherm.** It is based on the following assumptions (Howe et al, 2012):

- The adsorbent surface has individual fixed sites where molecules of adsorbate may be bound.
- Adsorption to every adsorption site has the same free-energy change.
- Each site is capable of binding only one molecule of adsorbate: monolayer accumulation is occurring.

It is a non-linear sorption model that enables the calculation of a maximum charge of the adsorbent (Jürgensohn, 2012).

Its formulation is reported in the following formula:

$$q_e = \frac{a \cdot b \cdot C_e}{1 + (b \cdot C_e)}$$

Where: a = maximum adsorption capacity [mg/g].

b = Langmuir adsorption constant [L/mg]

Figure 2-16 illustrates its graphical schematic pathway.

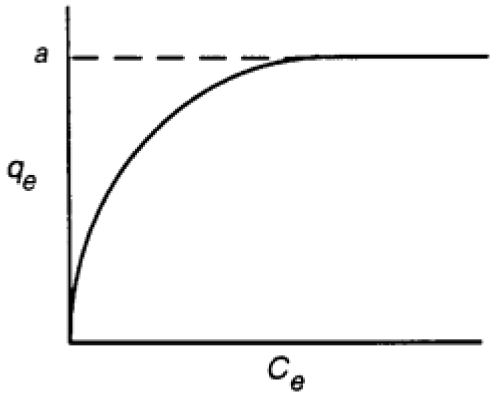

Figure 2-16 Schematic pathway of Langmuir isotherm. C_e = compound concentration in the solution at equilibrium; q_e = adsorbed amount of the compound (Grassi, 2010).

The most used model in contaminant adsorption cases is the **Freundlich isotherm**. In fact the requirements for constant site energy and monolayer coverage are not satisfied for many sorbents (Howe et al, 2012). This isotherm is used to describe the equilibrium for sorbents having adsorption sites with different energies and its formulation is:

$$q_e = K_f \cdot C_e{}^{1/n}$$

Where: K_f = Freundlich adsorption capacity parameter [(mg/g) (L/mg)$^{1/n}$]

1/n = Freundlich adsorption intensity parameter [-]

Its schematic graphical representation is reported in Fig. 2-17:

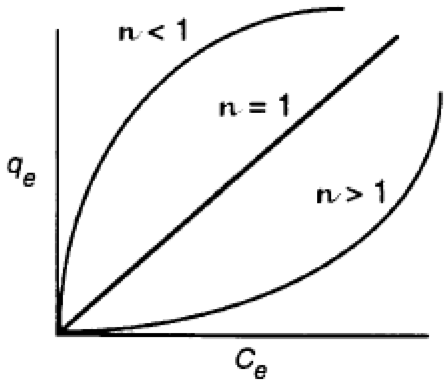

Figure 2-17 Schematic pathway of the Freundlich isotherm according to different values of the adsorption intensity parameter 1/n (Grassi, 2010).

It should be noticed that when n=1 then $K_f = K_d$.

The constants in the Freundlich isotherm can be determined by plotting log q_e versus log C_e.

2.3 Diclofenac in the environment

Diclofenac is a non-steroidal anti-inflammatory drug used in human medical care as analgesic, antiarthritic and antirheumatic compound (Morant & Ruppauer, 1994). Its molecular structure is reported in Figure 2-18.

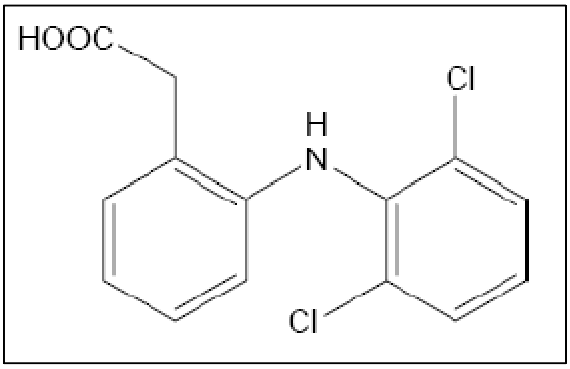

Figure 2-18 Molecular structure of diclofenac (Jiskra 2008).

Diclofenac is a broadly used medicament: only in Germany up to 250 t have been sold in 1999 (Scheytt, 2002). For this reason it was also one of the first Pharmaceutically Active Compounds (PhACs) that could be detected in the aquatic environment (Buser et al, 1998).

Concerning pollutants classification, it is considered among the emerging contaminants which are chemicals recently discovered in natural streams as a result of human and industrial activities (Grassi et al, 2012). Most of them have still no regulatory standard and can potentially cause deleterious effects in aquatic life at environmentally relevant concentrations (Grassi et al, 2012). Though no limit values for diclofenac in the environment have been assessed yet, its toxicity is evident in literature. Findings show that veterinary use of diclofenac is likely to have been the major cause of the rapid vulture population declines in South-East Asia (Swan et al, 2006; Taggart et al, 2007) and its presence in water has been shown to cause gill alteration and renal lesions in rainbow trout (Schwaiger et al, 2004).

2.3.1 Fate of diclofenac

The fate of diclofenac in environment is similar to most of pharmaceuticals. As illustrated in Figure 2-19 they enter the environment through many routes, including human or animal excreta, wastewater effluent, treated sewage sludge, industrial waste, medical waste from health-care and veterinary facilities, landfill leachate and biosolids (World Health Organization, 2011).

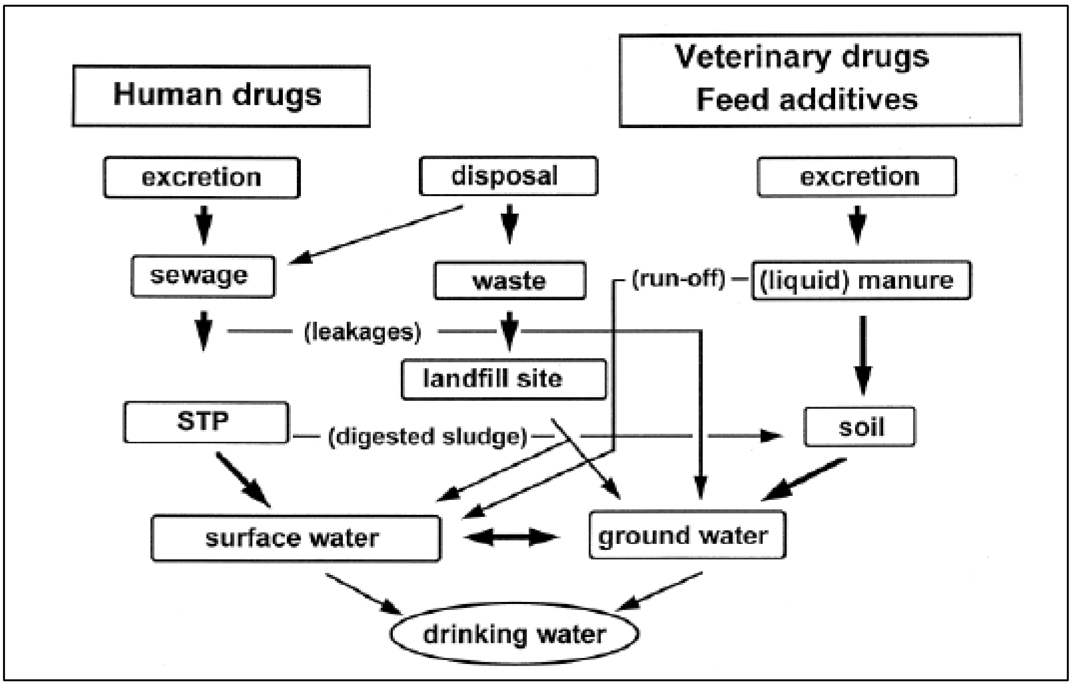

Figure 2-19 Fate of pharmaceuticals in the environment (Ternes, 1998)

Thus most of the diclofenac is excreted and can be found in **aquatic environments**. Since it occurs in trace concentrations, removal efficiency is not defined and concentrations from 0.1 to over 5 µg/l diclofenac in the effluents of a sewage treatment plants can be expected in Europe (Jiskra, 2008).

The diclofenac fate in aquatic ecosystem is related to its chemical properties. Diclofenac is a carboxylic acid (pK_a = 4,16) and occurs in the aquatic environment as an anion, what explains a high solubility and very low volatilisation (Jiskra, 2008). Moreover it isn't sensitive to hydrolysis (Andreozzi et al, 2003), chemical reactions, sedimentation and photodegradation was found to be the main degradation process in lakes (Buser et al, 1998).

Diclofenac traces were detected also in **soil and groundwater aquifers** (Heberer et al, 2004). In fact, since human drugs enter the environment via sewage treatment plants effluents, the use of sludges in agriculture, or leachates from waste disposal sites, veterinary pharmaceuticals may contaminate the environment through manure or directly due to aquacultural use (Henschel et al, 1997). Moreover municipal treated waste water can be reused for agricultural irrigation purpose. Due to this application pharmaceuticals can probably accumulate in the soils if long-term irrigation occurs, which may result in environmental problems such as the contamination risk to groundwater (Xu et al, 2009).

Thus **sorption** in soil is a fundamental process to understand the fate of diclofenac as it can act as a retardation factor. Studies on different kind of soil were performed by Xu et al (2009) and on sand sediments by Scheytt et al (2005).

Xu et al (2009) performed diclofenac adsorption batch tests for four kinds of agricultural soils with the characteristics reported in Table 2-4.

Table 2-4 Textural and chemical properties of the four soils tested (Xu et al, 2009).

Soil	**Clay (%)**	**Sand (%)**	**Silt (%)**	**OM (%)**	**pH**
HLS	3.6	95.6	0.8	0.58	7.54
ASL	12.5	70.9	16.6	1.93	7.06
ISC	42.5	10.8	46.7	2.46	7.48
PSL	18.1	32.2	49.7	5.45	7.14

The tests leaded to the construction of adsorption isotherms (parameters are listed in Table 2-5) which consists in significant sorption properties, especially where organic matter is present. Other studies have shown that soils with high amounts of organic matter also have the highest amount of sorption of organic compounds (Das et al, 2004; Sangsupan et al, 2006). When organic is not present sorption to mineral surfaces and ion exchange are important components influencing the mobility and transport of contaminants (Wilcox 2007).

Table 2-5 Adsorption coefficients of diclofenac in four agricultural soils. K_f and n are Freundlich affinity coefficient and Freundlich linearity index respectively (Xu et al, 2009).

Soil	**K_f [$mg^{1/n}$ L^n kg^{-1}]**	**1/n**
HLS	1.03 ± 0.47	1.10 ± 0.27
ASL	3.18 ± 0.26	0.90 ± 0.06
ISC	11.04 ± 0.26	0.74 ± 0.04
PSL	2.66 ± 0.38	0.83 ± 0.10

Scheytt et al (2005) conducted the same kind of experiments using two different sediments: one from Lieper Bucht (LP), medium sand with fine-grained sand and little fines and an organic carbon content of 0.2%, the other from Stopler Heide (ST), fine grained sand with medium sand and little fines and an organic carbon content of 0.13%.

Table 2-6 Freundlich constant (Kf) and linearity parameters (1/n) for diclofenac with direct measurement of two different sediments: LP (medium grained) and ST (fine grained) (Scheytt et al., 2005).

Sediment	**K_f [$\mu g^{(1-1/n)}$ $L^{1/n}$ kg^{-1}]**	**1/n**
Lieper Bucht (LP)	0.81	1.18
Stopler Heide (ST)	7.31	0.57

The results are reported in Table 2-6 proved that sorption even in sandy sediment is a relevant process and therefore diclofenac is less mobile in groundwater dynamics (Jiskra, 2008).

3 INSTRUMENTAL METHOD

3.1 Vibrating screen machine

The vibrating screening machine was used in order to characterize the grain size distribution of a granulated material sample. It consists in a vibrating deck which contains the screening drive and holds the sieves column in place.

The sample was placed at the top of the column where the sieve with the bigger openings was placed. The vibration of the machine induced particles smaller than the openings to pass through the sieves. The material retained on each sieve was weighted in order to provide a grain size distribution by weight fractions. The sieves utilized belongs to the ASTM E11 Standard series:

- 4 mm – No. 5
- 2 mm – No. 10
- 1 mm – No. 18
- 0,5 mm – No. 35
- 0,25 mm – No. 60
- 0,125 mm – No. 120
- 0,063 mm – No. 230

Figure 3-1 Vibrating screen machine for granulometric analysis.

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3.2 X-ray diffraction device

The X-ray diffraction (XRD) is a non-destructive technique used for the qualitative and quantitative analysis of crystalline materials in solid state. Using this analytical technique it is possible to record the X-rays diffracted by crystalline materials. Each material produces a diffraction spectrum that forms a fingerprint making possible the identification of an unknown material for comparison with a library of spectra of known substances. Basically the X-ray diffraction is obtained as a reflection of a beam of X-rays from a family of atomic planes parallel and equidistant, following Bragg's law.

$$2d \text{ sen } \theta = n\lambda$$

$$d = \lambda / 2\text{sen } \theta$$

Where d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam.

When a beam of monochromatic X-rays with a wavelength (wavelength of the radiation that is produced by an X-ray tube) is incident on a lattice plane with an angle θ there is a diffraction if the path of the rays reflected by successive planes (with a distance d) and a multiple of the wavelength. The study of the intensity of diffraction at various angles (setting by the device) allows to identify the symmetry of the crystal and the size of its unit cell.

The device utilized is the Siemens XRD Diffractometer D5000, illustrated in Figure 3-2.

Figure 3-2 Siemens XRD Diffractometer D5000.

The clay samples (< 2µm grain size) in this thesis were measured between 2-35° 2θ with a step size of 0.02° 2θ/s. The measurements were carried out using Co-K-α radiation (40 kV, 30 mA). Oriented samples of the clay fraction were prepared, after which the diffraction patterns were measured air-dried, after ethylene glycol and after heating to 550 °C. Presence of the kaolinite was determined by the analysis with DMSO treatment after Franco and Ruiz Cruz (2002).

3.3 Atomic absorption spectrometer

Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements of a sample using the absorption of optical radiation (light) by free gaseous atoms.

In order to atomize a sample, this is sprayed with a pneumatic atomizer into the flame. The flame is lined up in a beam of light of the appropriate wavelength. The energy of the flame causes the atom to undergo a transition from the ground state to the first excited state. When the atoms make their transition, they absorb some of the light from the beam. This results in a constant, time-independent signal which is proportional to the concentration of the element of interest. There are various flame types that are suitable for different elements, or matrices. In fact any atom has its own distinct pattern of wavelengths at which it will absorb energy, due to the unique configuration of electrons in its outer shell.

Since in this technique only liquids can be sprayed into the flame, they must be dissolved using a suitable digestion process in the presence of solid samples. This process was done by dissolve samples in a 0,5 N hydrochloric acid, lithium tetraborate, lithium carbonate and lanthanum oxide mixture. This acid mixture was then melted to a glass bead and can then be dissolved in 1 N hydrochloric acid solution again.

The device used in this thesis is the Varian SpectrAA 220, reported in Figure 3-3.

Figure 3-3 Varian SpectrAA 220 used for atomic absorbtion spectrometry for samples chemical analysis.

3.4 Rotavapor

Rotavapor is a device used for the removal of solvents from samples by evaporation. The main components of a rotary evaporator are:

- an evaporation flask containing the solution to be evaporated;
- a thermostatic bath, in which plunges the evaporation flask to keep the solution to a suitable temperature;
- a vacuum system, to substantially reduce the pressure within the evaporator system;
- a motorized mechanism, able to put in rotation the evaporation flask;
- an inclined condenser that provides to knock down the vapours which developed;
- a condensate-collecting flask at the bottom of the condenser, to catch the distilling solvent after it re-condenses.

The flasks, the capacitor and connecting elements between these are made of glass, and the entire system mounted must guarantee a perfect vacuum seal.

The device used for the research was a Rotavapor BÜCHI 461 Waterbath, reported in Figure 3-4.

Figure 3-4 Rotavapor BÜCHI 461 Waterbath.

3.5 Solid phase extraction

Extraction is a separation process consisting in the separation of a substance from a matrix. The solid phase extraction is a physical process between a solid phase and a liquid phase in which the solid phase has a greater affinity for the compound to be isolated with respect to the solvent in which the same compound is dissolved. When the sample passes through the solid phase analytes are concentrated on the surface of the adsorbent material while the other compounds present in the sample elute without interacting. The result is the purification and concentration of the substances isolated from the adsorbent material. This can be achieved through specific interactions between the functional groups of the compounds and the substrate of the solid phase.

The utilized solid phase was contained in Oasis HLB 3cc VAC 60 mg cartridges. A vacuum manifold was used to control the pressure during the extraction.

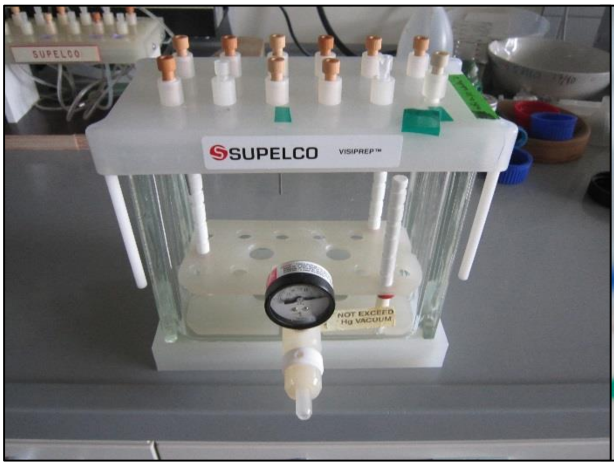

Figure 3-5 Vacuum manifold for solid phase extraction.

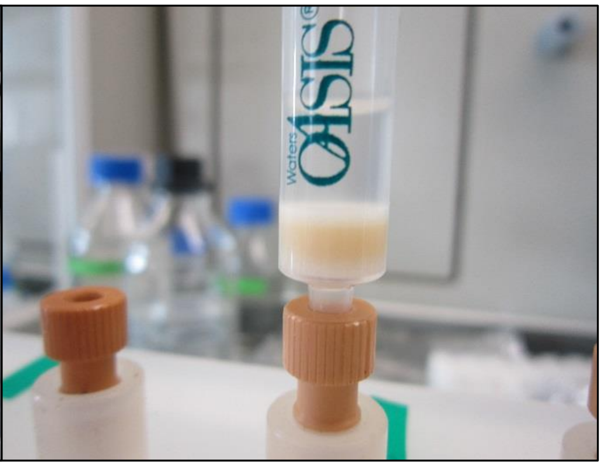

Figure 3-6 Oasis cartridges for solid phase extraction.

3.6 High-performance liquid chromatography

HPLC is utilized to separate the components in a mixture, to identify each component, and to quantify each component. In this process a sample is guided in a fluid mobile phase (eluent) in a column under high pressure through a stationary phase. The mobile phase may consist of a solvent or a mixture. The difference in the chemical properties between different molecules in the mixture and their relative affinity for the stationary phase of the column will promote separation of the molecules as the sample travels the length of the column. The components of the sample passed with different velocities through the column and they are detected using a suitable UV detector.

It is possible to change, during the separation process, the mixing ratio of the eluent and / or the pressure of the flow.

The HPLC analysis were carried out with the following instruments (Figure 3-7):

- Column: Nucleodur C18 gravity EC 125/3 3µm (Macherey&Nagel);
- Detector: SPD-20A DAD (Shimadzu) 215-260nm;
- Pump: LC10AP VP (Shimadzu);
- Autosampler: SIL20AC HT (Shimadzu);
- Controller: CBM-20A.

Figure 3-7 HPLC equipment.

4 MATERIALS

The materials utilized for the purposes of this thesis are three different kind of clay and three types of porous media, available at the Department of Geology of the University of Trier.

4.1 Clays

The three kind of clay were bentonite, kaolin and a red clay. Samples of these raw materials are reported in Figure 4-1.

Figure 4-1 Samples of raw bentonite, kaolin and red clay.

Chemical analysis were performed by Varian SpectrAA 220 as Atomic Absorption Spectrometer and mineralogical analysis by Siemens XRD Diffractometer D5000 (Chapter 3) in the laboratory of Geology at the University of Trier.

The raw clay materials were crushed and filtered through a clean sieve with 63 µm openings (N. 230 from ASTM E11 series). In this way **nano-to-micro clay particles** were obtained. The resulting clay powder was collected in a plate and stored in a dry environment at room temperature for the entire experiment.

4.1.1 *Bentonite*

The tested bentonite was purchased from IBECO and it is called Bentonite HT-X. As can be seen from the chemical analysis reported in Table 4-1, it is a sodium activated bentonite.

Table 4-1. Chemical composition of bentonite. Results are reported in % oxides.

Si	**Ti**	**Al**	**Fe**	**Mn**	**Mg**	**Ca**	**Na**	**K**	**L.O.I 1050°**	**Sum %**
52,09	**0,77**	**14,66**	**5,74**	**0,07**	**3,39**	**4,54**	**1,47**	**0,44**	**16,6**	**99,77**

The mineralogical analysis are reported in Figure 4–2.

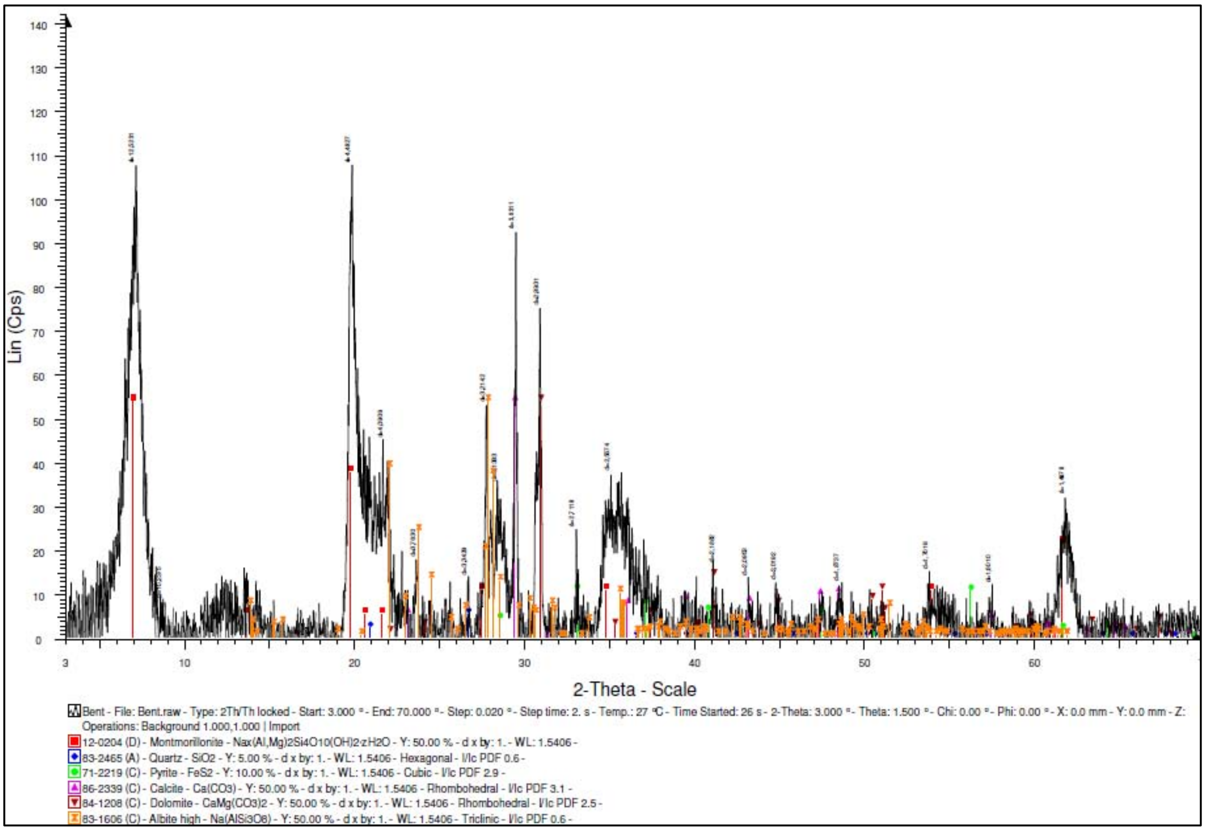

Figure 4-2 Bentonite mineralogical composition.

Typical minerals like montmorillonite, calcite, dolomite and albite were identified as well as some impurities like Pyrite and Quartz.

4.1.2 Kaolin

Tested kaolin was purchased from Amberger Kaolinwerke. Its chemical analysis is reported it Table 4-2, while its mineralogical composition is illustrated in Figure 4-3.

Table 4-2 Chemical composition of kaolin. Results are reported in % oxides.

Si	**Ti**	**Al**	**Fe**	**Mn**	**Mg**	**Ca**	**Na**	**K**	**L.O.I 1050°**	**Sum %**
50,05	**0,52**	**34,46**	**0,64**	**0,01**	**0,18**	**0,08**	**0,06**	**1,83**	**12,1**	**99,93**

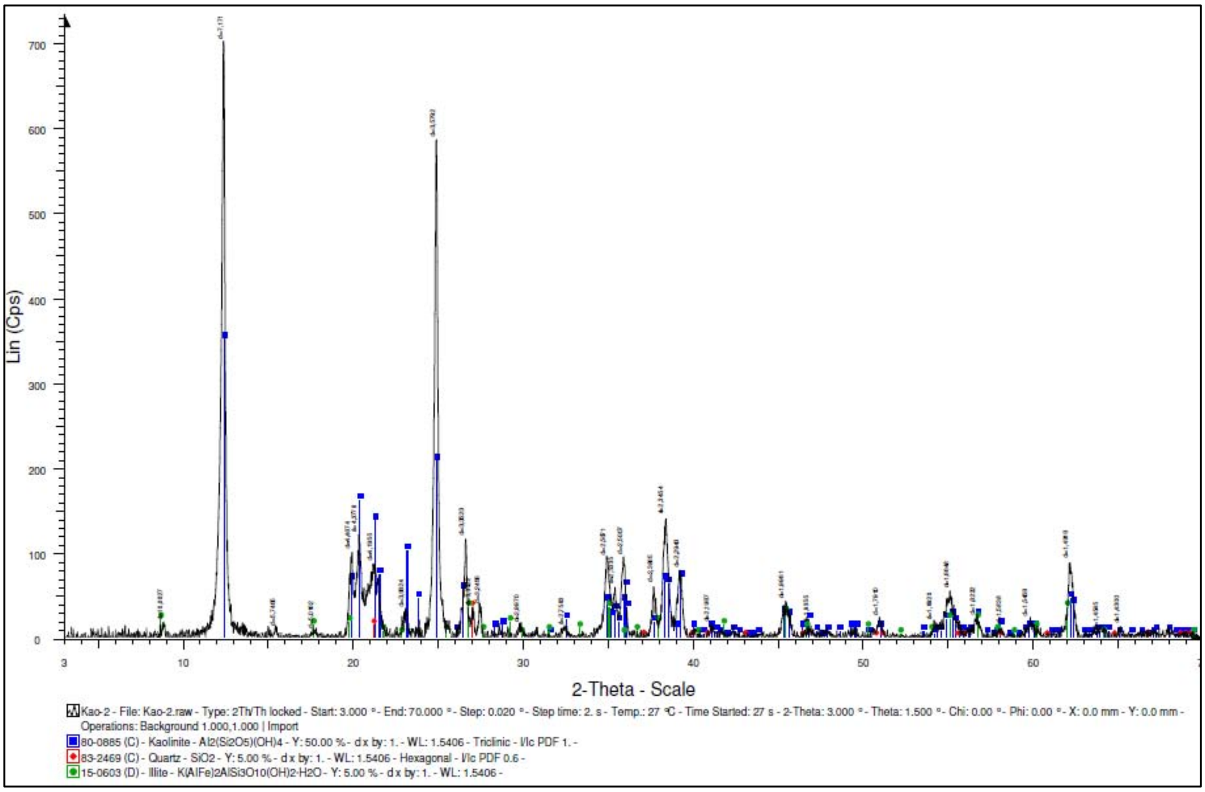

Figure 4-3 Mineralogical composition of kaolin.

Kaolinite is obviously present. Illite and quartz were also identified.

4.1.3 Red clay

The so-called “red clay” comes from a gravel quarry close to Folschette, a town situated in the North-East of Luxembourg. The extraction of the gravel is managed by Carrières Feidt SA company. The red clay is a secondary raw material derived from the washing of the gravel. It has a reddish-brown colour and it has a homogenous and plastic consistency.

According to Thomé (2008) its grain size distribution is approximately 25% of clay fraction (< 2µm) 70% silt (< 63 µm) and 5% fine sand. The presence of organic matter is negligible. A rheological study on this material was conducted by Herbst (2005) which stated that its low viscosity, compared to other clays, was due to the lower clay fraction content. The tendency to aggregate in suspension was weak even at higher solid content (200 g/L).

Its chemical composition is reported in Table 4-3.

Table 4-3. Chemical composition of red clay. Results are reported in % oxides.

Si	**Ti**	**Al**	**Fe**	**Mn**	**Mg**	**Ca**	**Na**	**K**	**L.O.I 1050°**	**Sum %**
56,07	**0,82**	**17,68**	**11,37**	**0,09**	**1,95**	**1,32**	**0,13**	**2,76**	**7,7**	**99,89**

As reported in Figure 4-4, the mineralogy composition consists in some quartz and mainly in the clay mineral illite which is also part of the silt fraction.

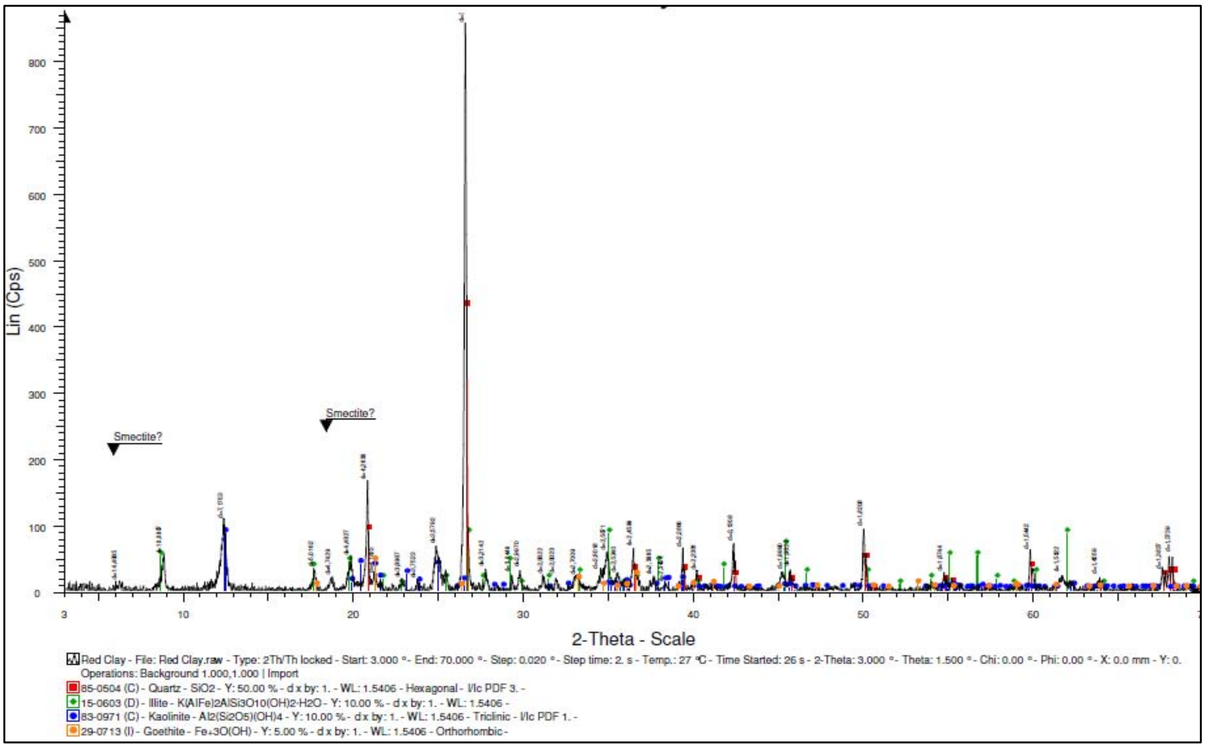

Figure 4-4 Mineralogical composition of red clay.

4.2 Porous media

The tested porous media were all sands with different granulometry, porosity and permeability. Their chemical and mineralogical analysis confirmed that they were composed entirely by quartz minerals. The sand material with the coarser average grain size was called “coarse sand”, while the other two “medium sand” and “fine sand”.

Their grain distribution size was assessed with the vibrating screen machine (Chapter 3). Dry analysis was done for the coarse and medium sands, while a wet one was performed for the fine sand.

3 Kg samples were used for each sand. These samples were the same utilized also for the successive tests. They were kept in a dry environment at room temperature for the entire experiment duration.

The results of the grain size distribution analysis are reported in table 4-4 in terms of percentages of weight of retained material on the sieves and graphically in Figure 4-5.

Table 4-4. Sands grain size distribution analysis. Percentages in weight of retained material on different sieves.

SIEVE OPENINGS	FINE SAND	MEDIUM SAND	COARSE SAND
2 mm	0,00	0,00	11,58
1 mm	3,16	0,01	65,93
0,5 mm	8,24	24,85	21,21
0,125 mm	61,62	73,95	1,16
0,063 mm	24,29	1,18	0,10
undersieve	2,69	0,02	0,03
Total	100,00	100,00	100,00

A 11,58% of the coarse sand was actually in the gravel grain size range.

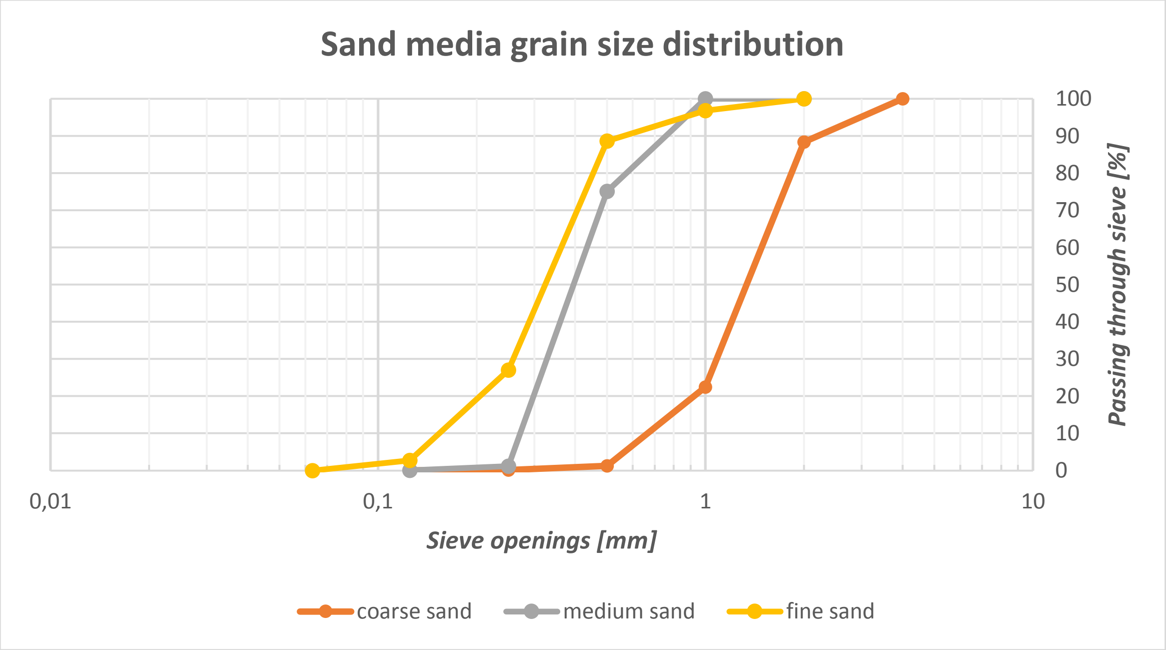

Figure 4-5 Grain size distribution of sands.

The uniform coefficients (C_u) were also calculated and reported in table 4-5. D_{10} and D_{60} are the particles sizes for which 10% and 60% respectively of the sample is finer.

Table 4-5. Sands uniformity coefficients C_u.

SAND MEDIA	D_{10}	D_{60}	$C_u = D_{60} / D_{10}$
FINE SAND	0,14	0,35	2,50
MEDIUM SAND	0,25	0,45	1,80
COARSE SAND	0,65	1,60	2,46

The porosity of the materials was empirically assessed by verifying the amount of water necessary to fill a 100 ml glass column filled with sand samples.

The estimated porosity were 0,40 for coarse sand, 0,36 for medium sand and 0,38 for fine sand.

The hydraulic conductivity was estimated with the empirical formula by Hazen (1930) for loose sands: $K = C_H \cdot D_{10}^2$.

Where K = Hydraulic conductivity [m/s]

C_H = Hazen empirical coefficient

D_{10} = particle size for which 10% of the soil is finer [mm]

The limitations on the application of this formula are: 0,1 mm < D_{10} < 3 mm and $C_u < 5$.

The Hazen coefficient is assumed from literature $C_H = 0{,}01$ (Aysen, 2002).

Therefore the estimated hydraulic conductivities are reported in Table 4-6.

Table 4-6 Estimated hydraulic conductivity for tested sands.

SAND MEDIA	K (cm/s)
FINE SAND	0,020
MEDIUM SAND	0,063
COARSE SAND	0,423

4.3 Diclofenac

Diclofenac was purchased from Sigma-Aldrich in the form of Diclofenac Sodium Salt. Its chemical structure is reported in Figure 4-6.

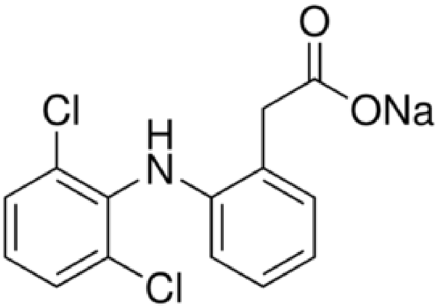

Figure 4-6 Chemical structure of Diclofenac Sodium Salt.

Its solubility in water at room temperature is 50 mg/ml.
The acidity behaviour is given by its $pK_a = 4$.
The partition coefficient is $\log K_{OW} = 13,4$.
A stock solution was prepared in advance at the concentration of 100 mg/L (Figure 4-7) and kept at -20°C. Before the use it was allowed to equilibrate for 1 hour at room temperature.

Figure 4-7 Diclofenac sodium salt stock solution and purchased powder.

5 EXPERIMENTAL PART

5.1 Experimental design

The main objective of the present thesis is to do a preliminary study on the feasibility of injection of clay particle suspensions into the soil as a new remediation technique approach.
Hence two clay properties had to be assessed: the infiltration of clay suspensions into a porous media and their contaminant sorption capacity.
In order to evaluate these properties, a specific experimental method was developed:

- In the first part (Chapter 5.2), **infiltration** tests were performed with the three clay materials (bentonite, kaolin and red clay) suspensions into the three sandy porous media. The materials with the more remarkable properties were then selected for a further percolation test and for the second part of the experiment. For these materials a suitable clay content in suspension was found.

- In the second part (Chapter 5.3) the **sorption** rate of diclofenac onto the selected clay particles was assessed using the clay content value found in the infiltration test. Two kind of tests were performed:
    - *Batch tests*, in order to provide a set of data useful for develop sorption isotherms of diclofenac on each clay.
    - *Column tests* with the selected porous media in order to simulate the injection of clay particles suspensions into a contaminated soil and to evaluate the remediation of the pollutant by the selected clay materials.

5.2 Infiltration tests

The first part of the experiment consisted in performing **small scale column tests** in order to assess the infiltration capacity of the bentonite, kaolin and red clay suspensions through three different kind of porous media.

The behaviour of clay particles dispersed in water is known in literature and it is described in detail in chapter 2. Coagulation, and thus destabilization of particles, was found to be one the limiting process affecting the mobility of a clay suspensions through a sand media. In fact, with aggregation of particles, the straining effect becomes evident. The main parameters influencing this process are pH, salt concentration and the solid content.

Since the main aim of this thesis was to test the feasibility of clay particles infiltration as a soil remediation technique, the purpose of this test was to find **limit concentration values** of solid content for each kind of clay. These values corresponded to the **maximum clay/water proportion** which can provide an easy infiltration of the suspension through different porous media, and they represented the amount of clay available for remediation of soil.

Due to the high viscosity of bentonite suspension, a different behaviour and lower limit concentration values were expected compared to the kaolin and red clay ones.

Moreover, since infiltration is affected also by the soil grain size characteristics, higher values were expected for coarser porous media.

5.2.1 Experimental method

Since scarce literature was known about the suspensions concentration values and no tests were conducted before with the available porous media, the first part of the experiment was carried on by trial-and-error approach.

The method consisted in running series of small scale column tests injecting each time a progressively increasing clay particles concentration in suspension. This procedure was followed for each clay material and for each porous media and the results were assessed empirically. Once selected the materials which gave the best results, percolation tests were carried out.

The used clay materials are taken from the uniform samples obtained as described in Chapter 4.

The porous media (fine, medium and coarse sands) samples used for the grain size distribution analysis (Chapter 4) were taken for this experiment and stored in a dry environment at room temperature.

The general experimental procedure consisted in the following steps:

- A specific clay concentration was decided. In most of the cases it was 10 g/l more than the previous one for each clay (Table 5-1).
- 10 ml of distilled water were poured into a 30 ml plastic container.
- The clay powder was weighted (through an electronic scale precise till the order of magnitude of milligrams) in order to reach the decided clay content. Then it was suspended in the 10 ml distilled water container (Figure 5-1).

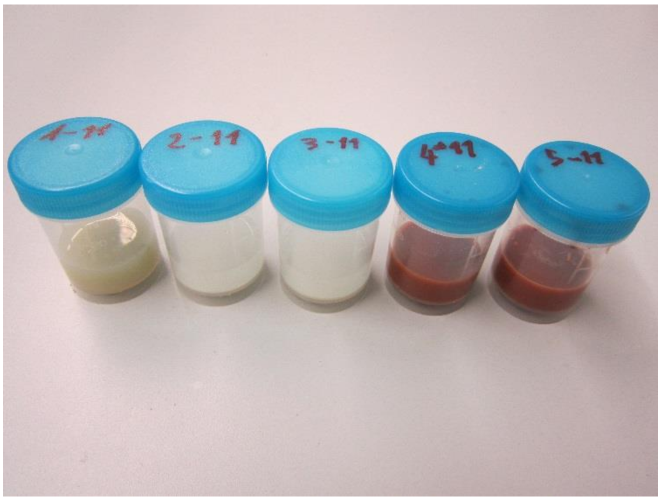

Figure 5-1 Example of clay particle suspensions preparation.

- Another 30 ml plastic container was adopted as a small column through cutting its bottom part. Once placed and fixed over a 63 µm openings sieve, it was filled with a volume of 20 ml of the selected sand media (Figure 5-2).

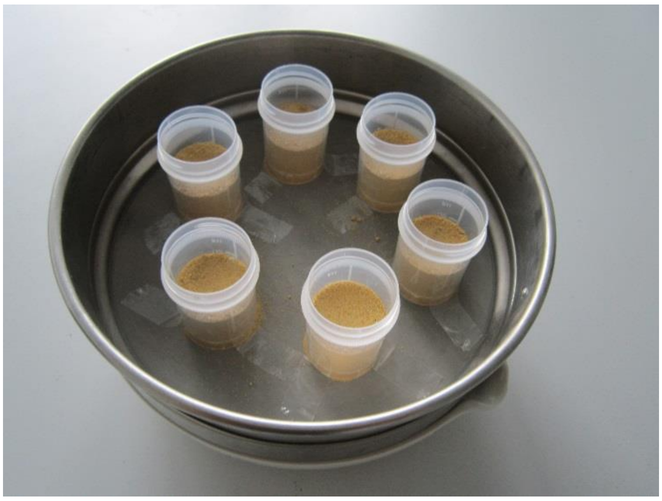

Figure 5-2 Example of test equipment: small columns fixed on 63 µm sieve and filled with sand.

- A collector container was then put under the sieve and the column. (Figure 5-3).

Figure 5-3 Example of test equipment: collectors put under columns.

- The clay suspension was then injected into the column filled with the porous media by the use of a Pasteur pipette, providing a slow injection rate, a uniform infiltration and no pressure head (Figure 5-4).

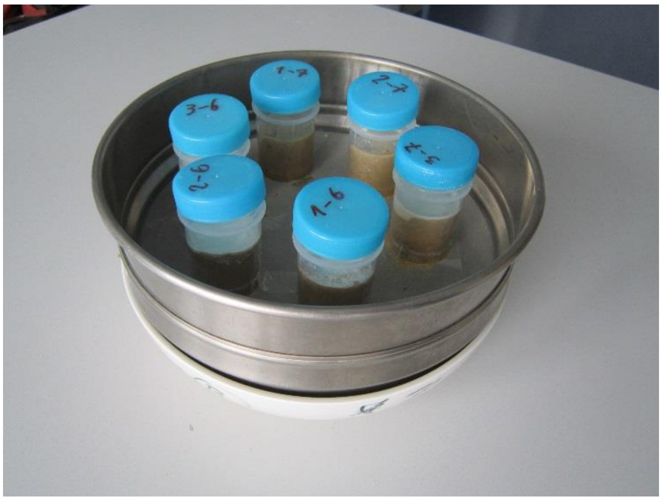

Figure 5-4 Example of small scale column test performing.

- The column test ran for 24 hours in order to provide enough time to the clay suspension to infiltrate through the sand and through the sieve and to accumulate in the collector (Figure 5-5) The sieve allowed only the particles with a size less than 63 µm to pass through. In this way, according to the sand granulometry, only clay particles in suspension could pass.

Figure 5-5 Example of small scale column tests results in collectors after 24 hours of infiltration time.

- The presence of clay particles in the collector was considered a positive result. Its presence was determined by letting the collected suspension dry for at least 24 hours (depending on the amount of water passed through the column) at room temperature. Measuring the clay content in the collector was not significant since too many factors, such as the column plastic walls and the sieve straining effect, were interfering.
- In case of positive result the test was run again with a higher clay content after the sieve was cleaned in an ultrasonic bath. For each kind of clay the tests performance ended when a negative result occurred and an approximation of 5 g/l on the maximum clay concentration was achieved.

For bentonite the same test procedure was applied using also 10 ml of sodium diphosphate solution instead of distilled water. This solution was prepared mixing in 1 litre flask 20 g of $Na_4P_2O_7 \cdot 10\ H_2O$ in 1 litre of distilled water.

Once every clay material was tested for every porous media, the results were assessed and discussed. A further **percolation test** was performed with the materials which gave the best results in terms of infiltration capacity.

This test consisted in performing again the selected column tests for 5 times with the same porous media sample and infiltrating each time the same clay content with the same metod described in this chapter.

5.2.2 *Results and discussion*

The results obtained for the first **screening** part of the test are summarized in Table 5-1.

Table 5-1 List of tested clay concentrations for each material during screening part of infiltration test. The values on the green cells represents the maximum clay content that can be infiltrated in suspension through a specific porous media with a positive result; DW = test performed with distilled water; $Na_4P_2O_7$ = test performed with sodium diphosphate solution as anticoagulant.

	CLAY CONTENT (g/L)			
	BENTONITE		**KAOLIN**	**RED CLAY**
	DW	$Na_4P_2O_7$	DW	DW
FINE SAND	10	20	20	30
	20	30	30	40
	25	40	35	50
	30	45	40	55
		50		60
MEDIUM SAND	20	40	30	50
	30	50	50	70
	40	60	70	90
	50	65	80	100
	55	70	85	105
	60		90	110
COARSE SAND	50	60	80	100
	70	80	100	150
	80	100	130	180
	85	105	150	200
	90	110	155	205
			160	210

This table provides with the list of all the tests which were performed for each material. An increasing clay content was applied till a negative result was obtained. The green coloured cells represent the maximum content of a specific clay in suspension which could infiltrate through a specific sand media giving a positive test result.

For the purpose of this thesis, the clays which gave the best results were the red clay and kaolin. Taking into consideration their low viscosity properties when dispersed into suspension these results were predictable. Bentonite maximum values, even in sodium diphosphate solution, were significantly lower, especially with coarse sand. Bentonite tendency to aggregate and coagulate in suspension was known from literature and it was confirmed by this experiment.

Actually also many of the results achieved with the fine sand, and some with the medium one, were not significant. In fact, even if a positive result occurred, an impermeable clay layer was observed at the top of the column (Figure 5-6). This phenomena was due to a complete straining effect, explained in Chapter 2, and it prevented other successive suspensions to infiltrate. The coarse sand was found to be the more suitable material for laboratory tests.

Figure 5-6 Examples of complete straining effect in fine sand media for bentonite (20 g/L), kaolin (30 g/L) and red clay (50 g/L) in column tests.

Therefore fine and medium sand along with bentonite were not considered for the percolation part of the test. In fact the first part of the experiment could be considered as a screening test: only suitable materials were chosen for further tests.

These results were useful in order to give an approximation of the clay content values which could provide suspensions with only partial infiltration. At maximum values many of the clay particles were still attached to the sand grains and their accumulation over time could have affected the infiltration capacity of other injected suspensions. This was the reason why a further percolation test was performed in order to define the maximum clay contents which showed the best infiltration capacity and which could be suitable for real soil application.

These values were found for kaolin and red clay suspensions infiltrating in coarse sand media and the results of the successful tests are reported in Figures 5-7 and 5-8.

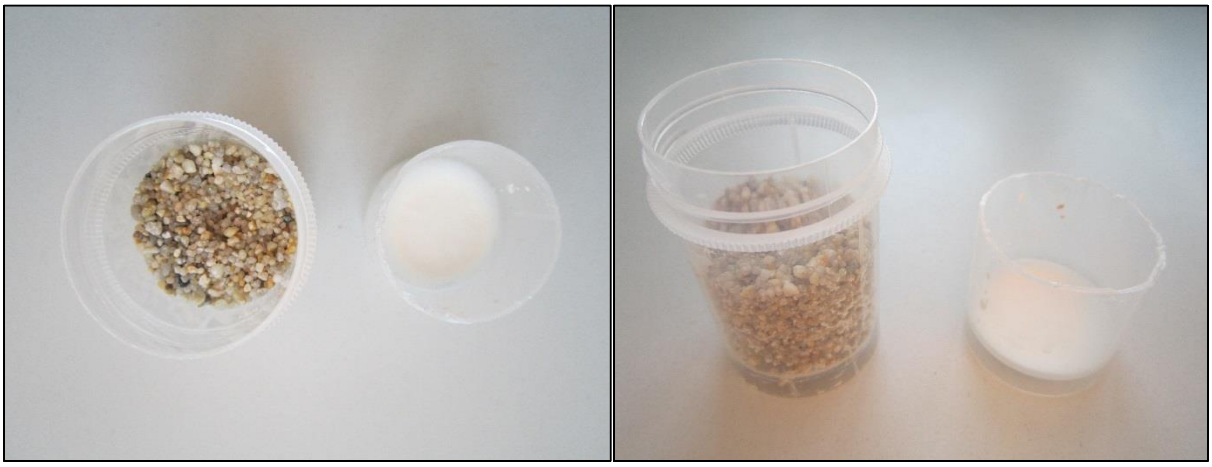

Figure 5-7 Percolation test: column and collector result after the fifth injection of 10 ml suspension at 80 g/L of kaolin.

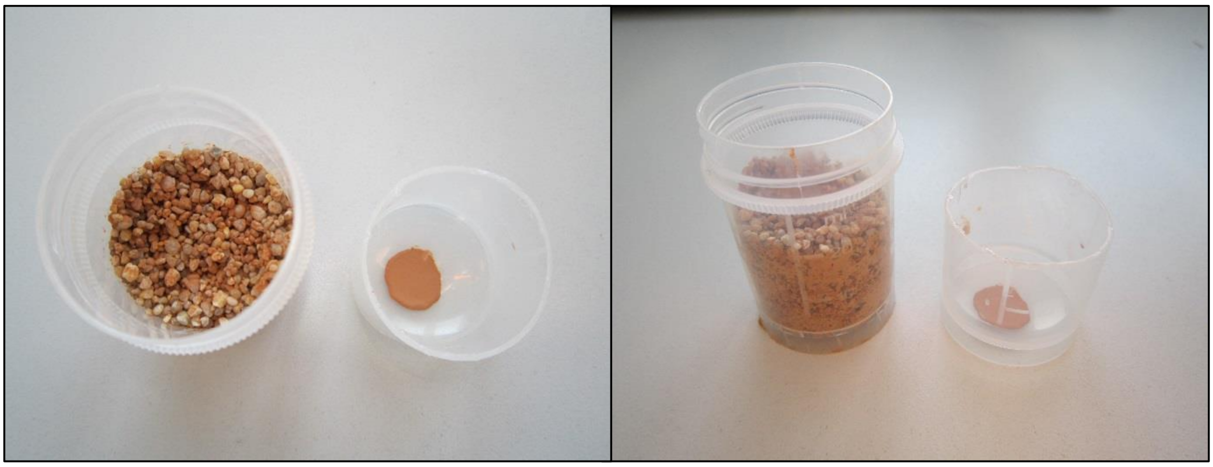

Figure 5-8 Percolation test: column and collector result after the fifth injection of 10 ml suspension at 100 g/L of red clay.

Tests were conducted for clay concentration lower than 150 g/L for kaolin and 200 g/l for red clay.

Experimental results showed that **80 g/L** of **kaolin** and **100 g/L** of **red clay** suspensions could be successfully infiltrated in a **coarse sand** porous media column. These amounts represented the available clay contents which could be used for assessing the capacity of remediation by sorption.

5.3 Sorption tests

This part of the experiment consisted in developing a method in order to assess the sorption, and thus the remediation capacity of the nano-to-micro clay particles taken into consideration.
The performance of infiltration tests resulted in the choice of kaolin and red clay as materials to be tested and coarse sand as soil to be remediated. In fact they were assessed as the more suitable materials in order to perform a significant sorption test.
The main assumption made was to maintain for all the tested suspensions the **same clay content** (or **soil/solution ratio**) in order to make the results significant and comparable. This value was chosen basing on the results of the infiltration tests and it was fixed at **80 g/L** (**soil/solution ratio = 1:12,5**). This clay content allowed both the kaolin and the red clay to infiltrate.
Since the red clay is a secondary material and it is not a pure clay, its sorption properties were expected to be lower than the kaolin ones. In both cases the presence of organic matter is consider irrelevant and sorption occurred on clay mineral surface.

5.3.1 Batch test

The batch test was aimed at estimating the sorption behaviour of diclofenac on the two different clay particles. The main purpose was to obtain a sorption value which could be used to estimate the maximum removal in real environmental conditions. In this case the results gave the possibility to construct sorption isotherms to predict remediation in conditions simulated by column tests.
According to OECD (2000) the batch test sorption represents the process of the binding of a chemical to surfaces of a material and it does not distinguish between different adsorption processes (physical and chemical adsorption) and such processes as surface catalysed degradation, bulk adsorption or chemical reaction. Therefore the kind of sorption could only be predicted but not verified. However from literature (chapter 2) it is known that clay minerals are suitable sorbents for ionic and polar compounds such as diclofenac.

5.3.1.1 Experimental method

The batch tests were carried out by shaking in vessels always the same amount of **clay suspension (80 g/L)** with different **diclofenac concentrations (1, 5, 10 mg/L)** in distilled water. For each contaminant concentration and each clay three tests were performed in order to have a reliable result. Moreover a blank run per clay (without test substance) and one control sample (with only the test substance) were subjected to the same test procedure. The former serves as a background control during the analysis to detect interfering compounds and the latter in order to check the stability of the test substance in solution and its possible adsorption on the surfaces of the test vessels (OECD, 2000).

The used clay materials are taken from the uniform samples obtained as described in Chapter 4.

The experimental procedure consisted in the following steps:

- 0,8 grams of clay powder were weighted (through an electronic scale precise till the order of magnitude of milligrams).
- From the stock solution (Chapter 4) a defined amount of diclofenac was taken and diluted in 10 ml of distilled water in order to obtain the desired solute concentration.
- The diclofenac solution is mixed with the clay powder in a glass vessel.
- The clay suspensions were continuously mixed by shaking and equilibrated for 24 hours, as suggested by OECD (2000) for reaching equilibrium, at the room temperature (20 ± 2 °C) by the use of an agitation device, illustrated in Figure 5-9.

Figure 5-9 Agitation device mixing clay suspensions in glass vessels for 24 hours.

- The vessel was then centrifuged at 3000 rpm for 15 minutes to separate the solid and aqueous phases. A rough measurement of the pH was taken.
- Solid phase extraction (SPE) was applied in order to remove the impurities from the aqueous phase. This process was carried out by the use of Oasis HLB 60 mg cartridges and a vacuum manifold. The chosen solvent was methanol, due to its slight polarity, while the sorbent on the cartridge was made by a non polar compound.

  First the packing of the cartridges were conditioned injecting 6 ml of methanol and 6 ml of distilled water (Figure 5-10). Then 5 ml (over 10 ml of the batch solution) of the centrifuged sample were added, assuming that a uniform distribution of the diclofenac was obtained in the aqueous phase. The result was that diclofenac was retained by the cartridge sorbent. The impurities were rinsed through the cartridge by selectively washing them with 6 ml of distilled water. The sorbent was then dried and finally the diclofenac retained in the cartridge was eluted into a flask with 6 ml of methanol (Figure 5-11).

Figure 5-10 Solid Phase Extraction: conditioning step.

Figure 5-11 Solid Phase Extraction: elution step.

- The extracted 6 ml solution of diclofenac was then dried by the use of Rotavapor at a temperature of 40 °C and an average pressure of 200 mbar till a volume of approximately 0,5 ml.
- The solution was transferred in vials and the volume was brought to 1 ml with methanol (Figure 5-12). This sample was then put in a box and stored at 4°C (Figure 5-13) waiting for being analysed.

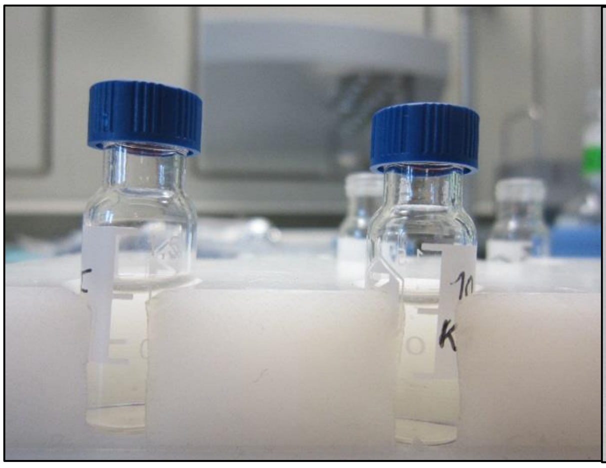

Figure 5-12 Example of vials with 1 ml of diclofenac solution.

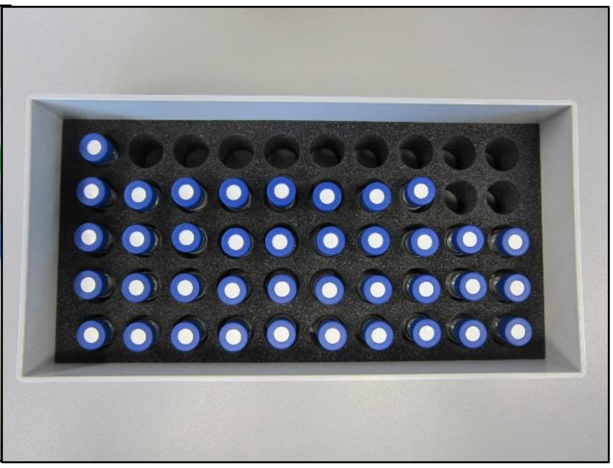

Figure 5-13 Vial samples ready for HPLC analysis.

- The sample was analyzed by High Performance Liquid Chromatography in order to detect diclofenac and measure its quantity in the aqueous phase. HPLC analysis was carried out by using a mixture of water and methanol (50:50 v/v) as eluent and a flow rate of 0,6 ml/min. The detection limit of the HPLC device was 1 ng/µL.

5.3.1.2 Results and discussion

The results obtained with HPLC were chromatograms. The area of each peak was calculated.
In order to make a quantitative analysis 2 calibration lines were constructed using different standards from stock solution: one with standards of diclofenac in concentrations below 10 ng/µl and one with standards of diclofenac in concentrations between 10 and 100 ng/µl.
Two graphs with the correlation between concentrations and areas were created, using for each standard the initial concentration of the contaminant and the corresponding area of the peak in chromatogram after HPLC analysis. Basing on the equations of the calibration lines, the concentrations of the samples resulting from the batch test were calculated. In Figures 5-14 and 5-15 the calibration lines are reported.

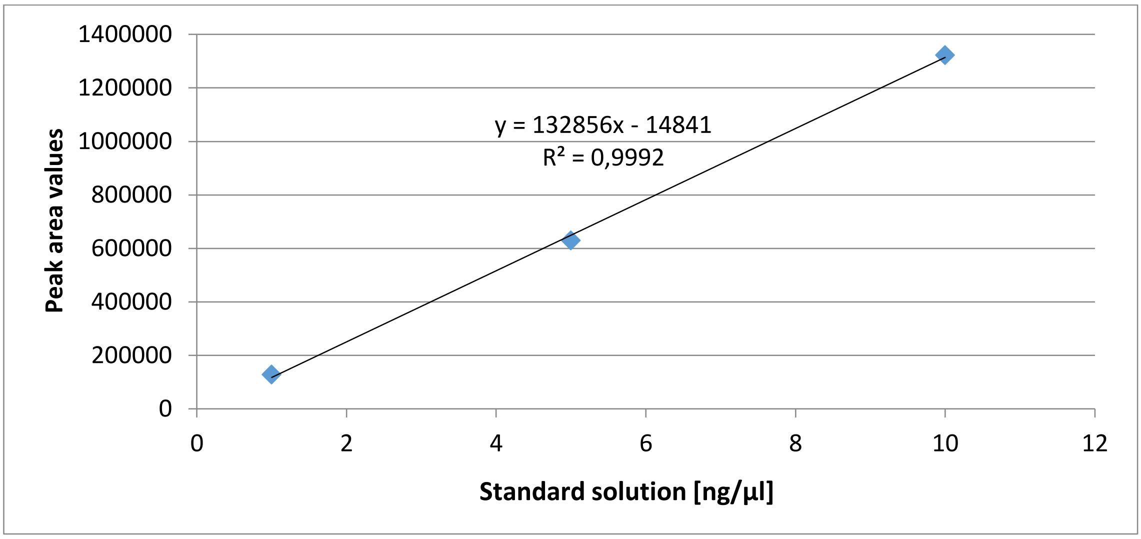

Figure 5-14 Calibration line for standard concentration lower than 10 ng/µl. Values of peak areas from chromatograms vs concentration of Diclofenac standards [ng/µl].

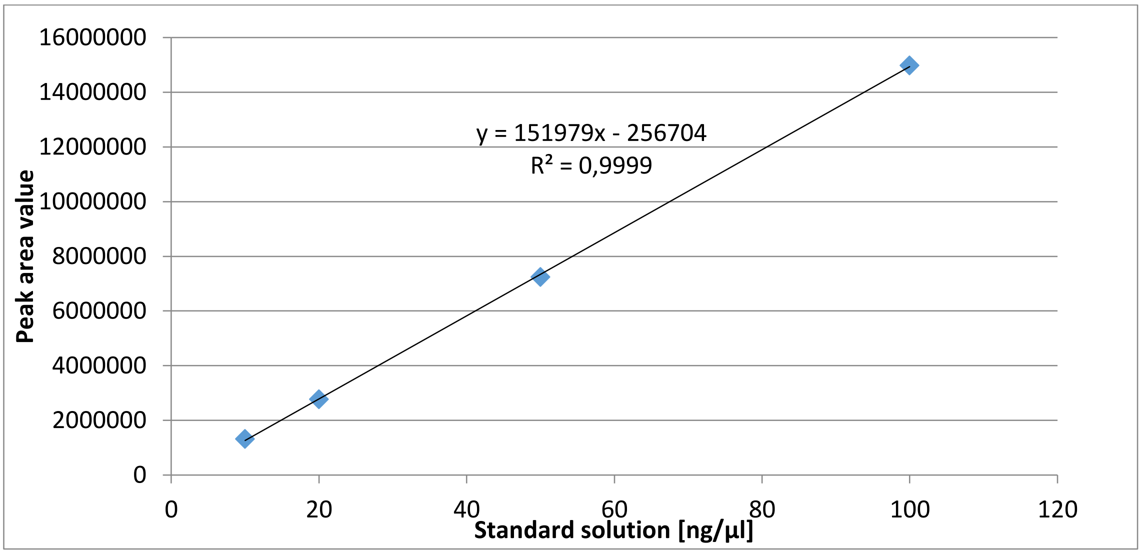

Figure 5-15 Calibration line for standard concentration between 10 ng/µl and 100 ng/µl. Values of peak areas from chromatograms vs concentration of Diclofenac standards [ng/µl].

The resulting concentrations of the analysis are reported in Table 5-2 for kaolin and in table 5-3 for red clay.

Table 5-2 Batch test results with kaolin. Volume of solution: 10 ml. Mass of clay: 0,8 g. Clay/ solution ratio 1:12,5.

Sample Nr.	Initial DCF concentration in solution: C_0 [mg/L]	DCF at equilibrium in 5 ml solution [μg]	DCF concentration at equilibrium: C_e [mg/L]
1 K1	1	4,27	0,85
1 K2	1	4,63	0,93
1 K3	1	4,48	0,90
5 K1	5	3,99	4,24
5 K2	5	21,21	4,03
5 K3	5	20,17	3,71
10 K1	10	47,74	9,55
10 K2	10	39,56	7,91
10 K3	10	39,43	7,89

Table 5-3 Batch test results with red clay. Volume of solution: 10 ml. Mass of clay: 0,8 g. Clay/ solution ratio 1:12,5. DCF=diclofenac

Sample Nr.	Initial DCF concentration in solution: C0 [mg/L]	DCF at equilibrium in 5 ml solution [μg]	DCF concentration at equilibrium: C_e [mg/L]
1 RC1	1	4,14	0,83
1 RC2	1	4,33	0,87
1 RC3	1	3,99	0,80
5 RC1	5	21,68	4,34
5 RC2	5	21,77	4,35
5 RC3	5	21,54	4,31
10 RC1	10	41,15	8,23
10 RC2	10	52,08	10,42
10 RC3	10	47,82	9,56

The blank run tests confirmed that there were not significant interferences due to the presence of impurities or organic matter.

The control sample verified that there were no significant losses of diclofenac due to sorption on the glass flask. This result is also in accordance with the literature (Sungjun et al, 2013).

The pH measurement gave for all the samples an approximated value of 6.

Since the main aim of this test is to assess the sorption behaviour of diclofenac on the clays, these results were used to build sorption isotherm for both kaolin and red clay.

Therefore the results of the three experiment conducted with the same clay and the same contaminant initial concentration (C_0) were used to calculate an average value of the concentration at equilibrium (C_e). Values obtained from samples 10 K1 and 10 RC2 were not considered reliable. The former presented a significant deviation compared to the other tests, while the latter gave an inconsistent result with C_e value higher than C_0. They were considered as random errors of the HPLC device. Once obtained average values, they are used to calculate the amount of diclofenac sorbed by the clay through the relation reported also in Chapter 2:

$$q_e = \frac{(C_0 - C_e)\,V}{M}$$

Where: q_e = amount of diclofenac sorbed per unit of clay at equilibrium [mg/Kg]

C_0 = initial diclofenac concentration in solution [mg/L]

C_e = diclofenac concentration in solution at equilibrium [mg/L]

V = volume of solution [L]

M = mass of clay in suspension [Kg]

The elaboration of the obtained values leaded to the results reported in Table 5-4.

The sorption rate was calculated as the percentage of contaminant which was removed from solution by sorption.

Table 5-4 Results of batch tests: amount of sorbed contaminant on clay and percentage of removal for kaolin and red clay.

Clay	C_0 [mg/L]	Average C_e [mg/L]	q_e [mg/Kg]	Sorption rate [%]
Kaolin	1	0,89	1,35	10,82
	5	3,99	12,57	20,11
	10	7,90	26,26	21,01
Red clay	1	0,83	2,12	16,93
	5	4,33	8,33	13,33
	10	8,90	13,78	11,03

Basing on the calculated values of C_e and q_e sorption isotherm were developed. Linear and Freundlich isotherm trends were assessed. In fact they are the most used in literature for low contaminant concentrations (Xu et al, 2009).

The linear trend was evaluated by plotting on x-axis C_e values and on y-axis q_e values for each clay material (Figure 5-16).

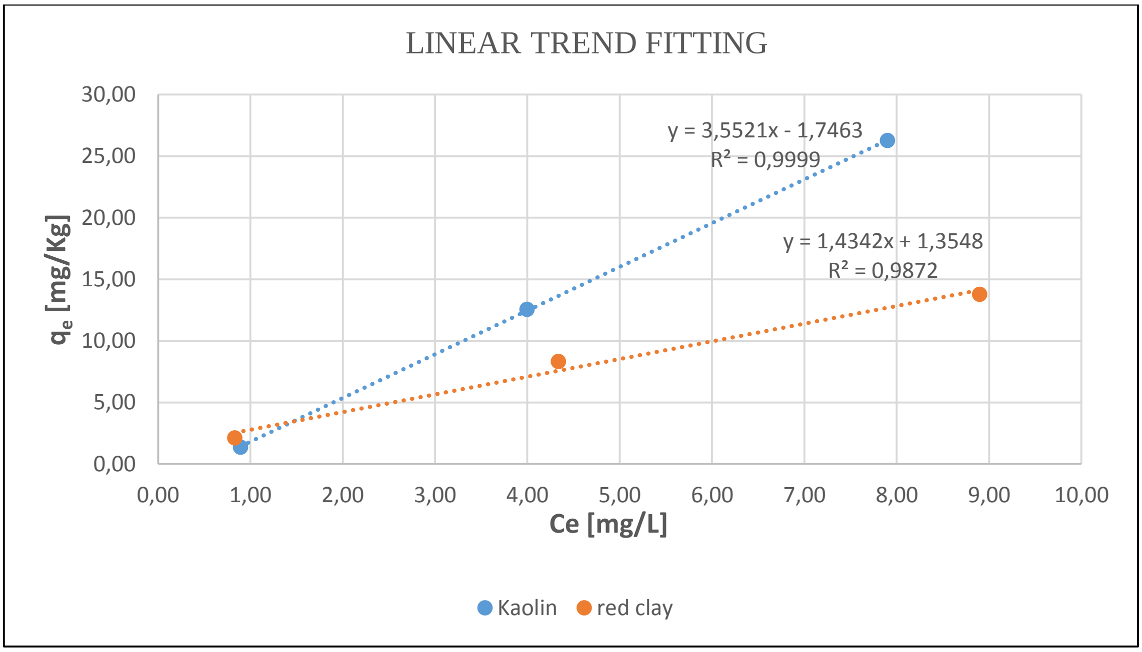

Figure 5-16 Isotherm linear trend fitting for kaolin and red clay.

The Freundlich trend could be described by plotting on the x-axis $\log(C_e)$ values and on y-axis $\log(q_e)$ values, as reported in Figure 5-17. In fact, Freundlich isotherm behaviour is given by the formula reported in Chapter 2, but it can be formulated also in the following way:

$$\log(q_e) = \frac{1}{n} \cdot \log(c_e) + \log(k_f)$$

Where: K_f = Freundlich adsorption capacity parameter [(mg/Kg) (L/mg)$^{1/n}$] represents the y-intercept of the straight line interpolating the log values

$1/n$ = Freundlich adsorption intensity parameter [-] represents the slope of the same line.

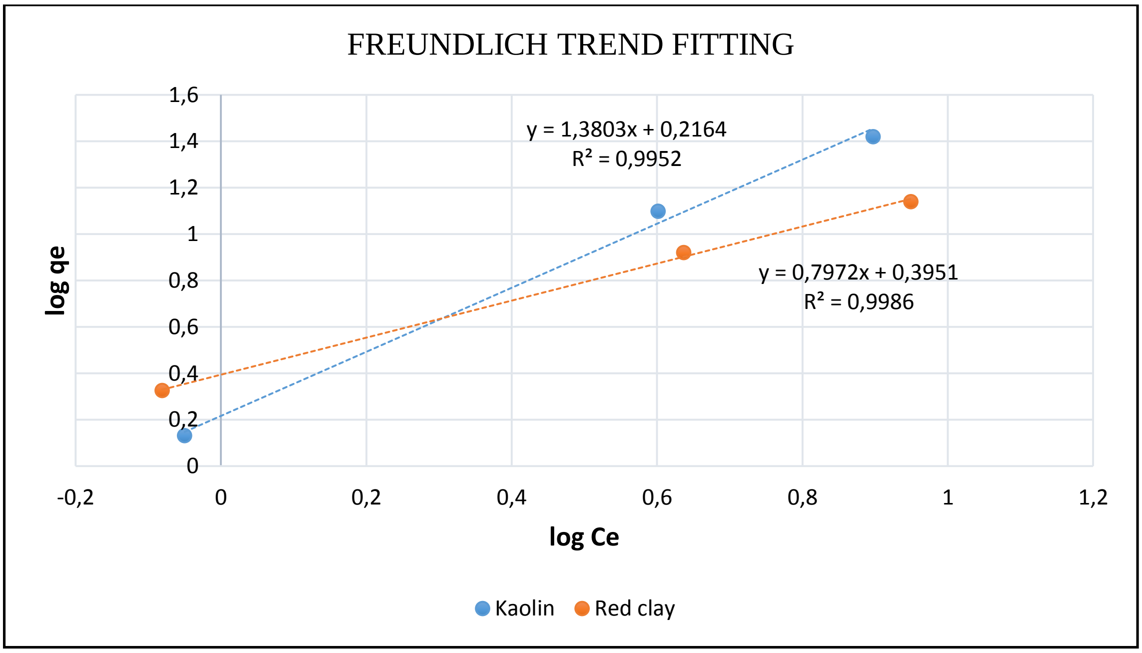

Figure 5-17 Freundlich isotherm trend fitting for kaolin and red clay.

A higher value of the correlation index R^2 suggests a better trend approximation. Therefore for describing the sorption behaviour on **kaolin a linear isotherm** (R^2 =0,9999) was chosen. Instead a **Freundlich isotherm (1/n = 0,7972; K_f = $10^{0,3951}$ = 2,4837)** fitted the **red clay** sorption trend (R^2 = 0,9986). These isotherms are reported in Figure 5-18.

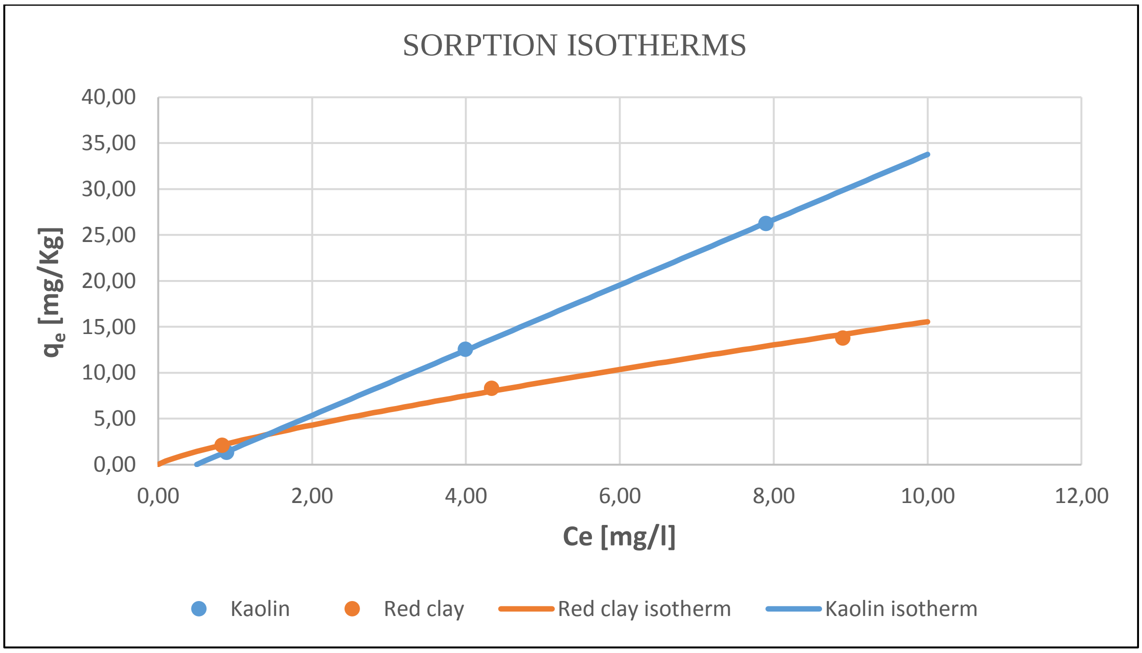

Figure 5-18 Sorption isotherms for kaolin and red clay obtained from batch tests with diclofenac.

These isotherms showed that the sorption process at low diclofenac concentrations occurred at a higher extent for red clay, while it is the opposite at higher concentrations, as it was expected to be, due to the characteristics of the two materials.

The diclofenac sorption on clays results were comparable to the findings of Xu et al (2009) reported in Chapter 2 for agricultural soil. This was a good indicator for the suitability of the injection of clay suspension for the remediation of sandy soil, which presents lower sorption properties.

This clay/solution ratio (1:12,5) provided with a removal of diclofenac in aqueous phase between 10 and 21 %. OECD (2000) suggested to use a soil/solution ratio with a removal higher than 20% in order to minimize the errors on the sorption calculations.

However this test was performed in order to give an estimation of the sorption properties and the use of 1:12,5 clay/solution ratio is justified by the need to make all the experiments comparable.

5.3.2 Column test

The column test was the final step of the experiment. Its purpose was to implement a method to assess the **remediation capacity** of clay suspensions basing on the properties found in the previous tests. In order to achieve this objective an injection of a clay suspension into a contaminated soil was simulated. In this way it was also possible to verify both the infiltration and the sorption capacities of red clay and kaolin nano-to-micro particles.

The column test was designed in order to make all the experiments comparable. The same clay/water proportion of the infiltration test and the same contaminant concentration of the batch test were utilised in a bigger scale test.

The main aim of this test was to measure the amount of diclofenac sorbed by the clay which effectively could infiltrate through the soil sample.

5.3.2.1 Experimental method

This test consisted in injecting **50 ml of clay suspension (80 g/L)** into a column filled with **190 g of contaminated coarse sand by diclofenac**. This amount of soil was determined in order to guarantee a uniform and complete suspension distribution through all the sand pores. In fact,

basing on the loose coarse sand porosity (ε = 0,4) a volume of 125 ml was calculated to be effective for 50 ml of suspension. Moreover the density of the loose coarse sand was 1,5 Kg/L. The soil was contaminated with three different amount of diclofenac: 50, 250 and 500 µg. If all the contaminant amount was brought from sand into the 50 ml solution, the removal rate by clay would have approached the batch test results for 1, 5, 10 mg/L respectively.
The effective soil contamination concentrations were:
50 µg/190 g = **0, 26 µg/g**
250 µg/190 g = **1, 32 µg/g**
500 µg/190 g = **2, 63 µg/g**

Nine column tests were performed: three injecting red clay suspensions, three kaolin and three with only distilled water. The latter was implemented to assess the wash out effect on contaminant from soil. Each kind of injection was also tested for every diclofenac concentration in soil.
Moreover a blank run per clay (without test substance) and one control sample (with only test substance in order to test the losses of contaminant due to filtering) were subjected to the same test procedure.
The used clay materials are taken from the uniform samples obtained as described in Chapter 4.
The coarse sand sample used for the granulometric analysis (Chapter 4) was taken for this experiment and stored in a dry environment at room temperature.
The experimental procedure consisted in the following steps:

- 190 grams of coarse sand were weighted and divided into 5 samples with the same weight (through an electronic scale precise till the order of magnitude of milligrams)
- From the stock solution (Chapter 4) a defined amount of diclofenac was taken and diluted in 10 ml of distilled water.
- With the column Teflon valve closed, the column was filled in 5 steps and the soil was contaminated. Each step consisted in placing the 5 coarse sand samples one over the other in different times. Between two layers of sand 2 ml of diclofenac solution were injecting by a pipette providing a uniform distribution. After the injection of all the solution the contaminated sand was gently mixed.

- After 2 hours, 4 grams of clay were weighted (through an electronic scale precise till the order of magnitude of milligrams) and mixed in a flask with 50 ml of distilled water.
- The obtained clay suspension (or only distilled water) was infiltrated with a pipette providing a uniform and slow rate injection (Figure 5-19).

Figure 5-19 Injection of red clay suspension into the contaminated soil in column test.

- After 24 hours the column Teflon valve at the bottom was opened and the suspension flowing out of the column was collected in a glass flask (Figure 5-20). The retention time of 24 hours was defined in order to compare the test results with the others obtained in the previous infiltration and batch tests. The valve allowed only clay particles to pass through and retained the sand media in the column.

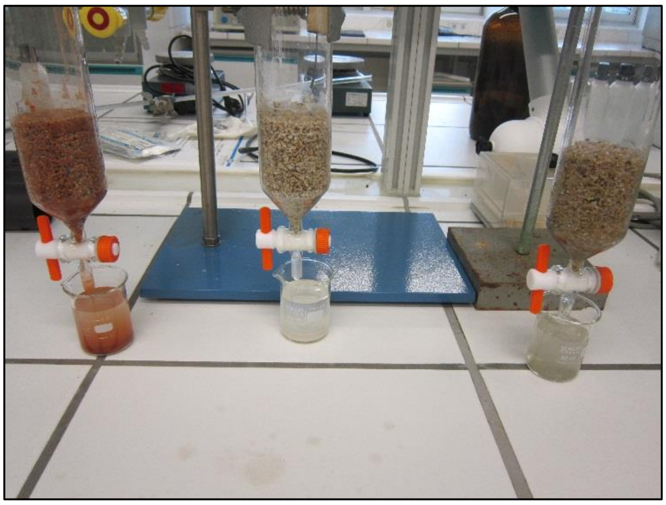

Figure 5-20. Column valves were opened after 24 hours of injection and clay suspension. Clays were then collected in flasks.

- The collected clay suspension settled for 2 hours. Assuming a uniform diclofenac distribution, 10 ml of the aqueous phase was then extracted through a syringe (Figure 5-21), filtered (through a cellulose acetate membrane syringe filter with 0,45 µg porosity) and injected into a glass vessel (Figure 5-22). This step was done to improve the efficiency of the diclofenac analysis removing the more impurities as possible. A rough measurement of the solution pH was taken.

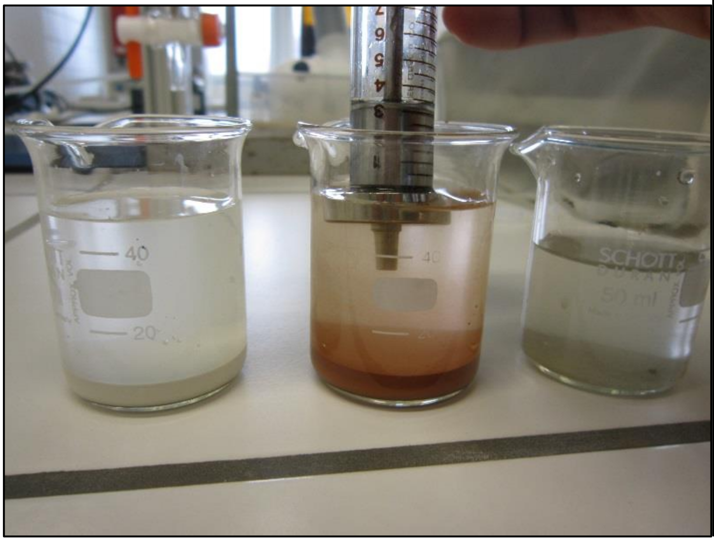

Figure 5-21 Extraction of diclofenac solution aqueous phase come out of the column test.

Figure 5-22 Filtration of the 10 ml extracted clay suspension aqueous phase.

- Solid phase extraction (SPE) was applied in order to remove the impurities from the aqueous phase. This process was carried out by the use of Oasis HLB 60 mg cartridges and a vacuum manifold. The chosen solvent was methanol, due to its slight polarity, while the sorbent on the cartridge was made by a non polar compound.
  First the packing of the cartridges were conditioned injecting 6 ml of methanol and 6 ml of distilled water. Then the 10 ml solution was added. The result was that diclofenac was retained by the cartridge sorbent. The impurities were rinsed through the cartridge by selectively washing them with 6 ml of distilled water. The sorbent was then dried and finally the diclofenac retained in the cartridge was eluted into a flask with 6 ml of methanol.
- The extracted 6 ml solution of diclofenac was then dried by the use of Rotavapor at a temperature of 40 °C and an average pressure of 200 mbar till a volume of approximately 0,5 ml.
- The solution was transferred in vials and the volume was brought to 1 ml with methanol. This sample was then put in a box and stored at 4°C waiting for being analysed.
- The sample was analyzed by High Performance Liquid Chromatography in order to detect diclofenac and measure its quantity in the aqueous phase. HPLC analysis was carried out by using a mixture of water and methanol (50:50 v/v) as eluent and a flow rate of 0,6 ml/min. The detection limit of the HPLC device was 1 ng/µL.

5.3.2.2 Results and discussion

The results obtained with HPLC were chromatograms. The area of each peak was calculated.
In order to make a quantitative analysis 2 calibration lines were constructed using different standards from stock solution: one with standards of Diclofenac in concentrations below 10 ng/µl and one with standards of Diclofenac in concentrations between 10 and 100 ng/µl.
Two graphs with the correlation between concentrations and areas were created, using for each standard the initial concentration of the contaminant and the corresponding area of the peak in chromatogram after HPLC analysis. Basing on the equations of the calibration lines, the concentrations of the samples resulting from the column test were calculated. In figures 5-14 and 5-15 the calibration lines are reported.

The resulting diclofenac concentrations are reported in Table 5-5.

Table 5-5 Column test results. Volume of solution: 50 ml. Mass of sand: 190 g. Mass of clay: 4 g. Soil/ solution ratio 1:12,5. DCF = diclofenac. K=kaolin. RC= redclay. W= distilled water.

Injected material	**Sample Nr.**	**Initial DCF concentration in soil: q_i [µg/g]**	**Max potential DCF concentration in solution: C_0[mg/l]**	**Final DCF amount in 10 ml sample[µg]**	**Final DCF concentration in 50 ml solution: C_e[mg/l]**
Kaolin	CT 1K	0,26	1	4,99	0,50
	CT 5K	1,32	5	17,18	1,72
	CT 10K	2,63	10	23,22	2,32
Red clay	CT 1RC	0,26	1	8,14	0,81
	CT 5RC	1,32	5	21,29	2,13
	CT 10RC	2,63	10	28,59	2,86
Distilled water	CT 1W	0,26	1	1,82	0,18
	CT 5W	1,32	5	15,94	1,59
	CT 10W	2,63	10	14,29	1,43

The blank run tests confirmed that there were not significant interferences in the analysis due to the presence of impurities or organic matter.

The control sample verified that there were no significant losses of diclofenac due to cellulose acetate filtration: the recovery of the filtered stock solution was higher than 99,7 %.

The pH measurement gave for all the samples an approximated value of 6.

A first interpretation of the results suggested that the highest amounts of diclofenac which were removed from soil and brought into solution were detected with the **injection of red clay (RC)** suspensions. This consideration was developed comparing the concentrations at equilibrium of the three kind of tests for a specific initial C_0.

The contaminant removal effect (wash-out) which was not due to the presence of clay was estimated by the tests performed injecting 50 ml of only distilled water (W).

The wash-out removal efficiencies were calculated (for samples CT 1W, CT 5W, CT 10W) removing from the initial diclofenac amount in soil the final amount of contaminant present in 50 ml solution. They are reported in Table 5-6:

Table 5-6 Wash-out effect for diclofenac in column tests performed with the injection of distilled water. DCF = diclofenac.

Initial DCF concentration in soil: q_i [µg/g]	**Final DCF concentration in 50 ml solution: C_e[mg/l]**	**Final DCF concentration in soil: q_f [µg/g]**	**Wash-out removal efficiency [%]**
0,26	0,18	0,22	18,21
1,32	1,59	0,90	31,89
2,63	1,43	2,26	14,29

The wash-out removal efficiency represented also an indirect measure of the **capacity of the soil to adsorb diclofenac**. In these experiments no precise correlation was found between the initial and the final contaminant concentrations.

However these results gave an order of magnitude of the removal efficiency, confirmed the coarse sand capacity to sorb diclofenac and justified the use of clay suspensions for its remediation.

In order to assess the amount of diclofenac sorbed by the infiltrated clay an estimation was done using the sorption isotherm relations found for kaolin and red clay from the batch test results in Chapter 5.3.1.2. Given the final diclofenac solution concentrations at equilibrium (C_e) for the column test, these isotherms could be used to provide an estimation of the amount of contaminant present in clay materials (q_e).

Remembering that the isotherm trend for kaolin was linear and a Freundlich trend was found for red clay sorption, the estimated q_e value were calculated for each contamination concentration. They are reported in Table 5-7 along with a comparison with the maximum q_e values achievable in a batch test if all the diclofenac present in the soil was brought in solution (C_0 [mg/l] in Table 5-5).

The amount of the diclofenac retained on clay was found by using the calculated q_e value for the total amount of clay (4 grams). This value was then compared to the initial amount of diclofenac in order to provide an estimation of its final sorption on clay (Table 5-7).

Table 5-7 Estimation of diclofenac sorption on clays for column tests and comparisons with batch tests evidences. DCF = diclofenac.

COLUMN TEST RESULTS					**BATCH TEST RESULTS**	
Clay	**C_0 [mg/l]**	**C_e [mg/L]**	**Estimated q_e [mg/Kg]**	**Estimated DCF sorption on clay [%]**	**Max potential q_e [mg/Kg]**	**Max potential DCF sorption on clay [%]**
Kaolin	1	0,50	0,03	**0,21**	1,35	10,82
	5	1,72	4,36	**6,97**	12,57	20,11
	10	2,32	6,50	**5,20**	26,26	21,01
Red clay	1	0,81	2,11	**16,86**	2,12	16,93
	5	2,13	4,54	**7,26**	8,33	13,33
	10	2,86	5,74	**4,59**	13,78	11,03

These results confirmed the evidences of the batch tests, since at low pollutant concentrations red clay was a better sorbent for diclofenac than kaolin. In general, at the tested concentrations, red clay presents better results in terms of remediation.

Anyway the estimated **removal efficiencies** obtained by sorption on clays were **low** (except for red clay at $C_0 = 1$). It has also to be taken into account that these clays had not good sorption properties and the maximum removal efficiency from batch test was about 20% of the total contaminant. Moreover the coarse sand sorption properties were not negligible as the study (reported in Chapter 2) conducted by Scheytt et al (2005) on sandy sediments confirmed.

The estimations made on the diclofenac sorption on clay particles were made assuming:

- A uniform distribution of clay particles and diclofenac in the column.
- An equilibrium between the contaminant concentrations in solution and in soil after 24 hours of test.
- The same sorption behaviour found in the batch tests for both clay materials.

- A high clay particles recovery in the glass flask collecting the suspension flowing out of the column after 24 hours of test.

The batch test isotherm could be used since the the same main parameters were taken for both the experiments: **retention time, clay/solution ratio, diclofenac initial concentrations and pH**.

Since the main aim of this thesis was to evaluate the remediation by clay particles which could effectively infiltrate, a high recovery of them was necessary. In this column test, contrary to the infiltration tests, a further straining effect occurred due to the funnel shape of the bottom of the column and to the valve. This accumulation of clay is illustrated in Figure 5-23.

Figure 5-23 Example of straining effect on column. The bottom part of the column retained clay particles after the test end.

Basing on the concentrations of diclofenac in solutions and in the clays a further estimation of the soil effective remediation could be done for each test.

The effective amount of diclofenac present in the soil at the end of the test was estimated by removing the quantities of pollutant in solution and in clay substrate to the initial contaminant concentration in soil. The removal percentages estimations are summarized and reported in Table 5-8 for each test.

Table 5-8 Estimation of removal efficiencies of diclofenac from soil for each column test.

Clay	Initial DCF concentration in soil: q_i [µg/g]	Final DCF concentration in soil: q_f [µg/g]	DCF removed in solution [%]	DCF removed on clay [%]	Total removal efficiency [%]	Wash-out removal efficiency [%]
Kaolin	0,26	0,13	49,90	0,21	**50,11**	18,21
	1,32	0,77	34,36	6,97	**41,33**	31,89
	2,63	1,88	23,22	5,20	**28,42**	14,29
Red clay	0,26	0,005	81,40	16,86	**98,26**	18,21
	1,32	0,66	42,59	7,26	**49,84**	31,89
	2,63	1,76	28,59	4,59	**33,18**	14,29

The total estimated removal efficiencies were due to the double effect of injecting water (a sort of physical and chemical soil flushing) and clay particles. The effect of the introduction of clay nano-to-micro particles was evident since the total percentages of removal were significantly higher than the ones obtained with only distilled water (wash-out effect), especially at low diclofenac concentrations.

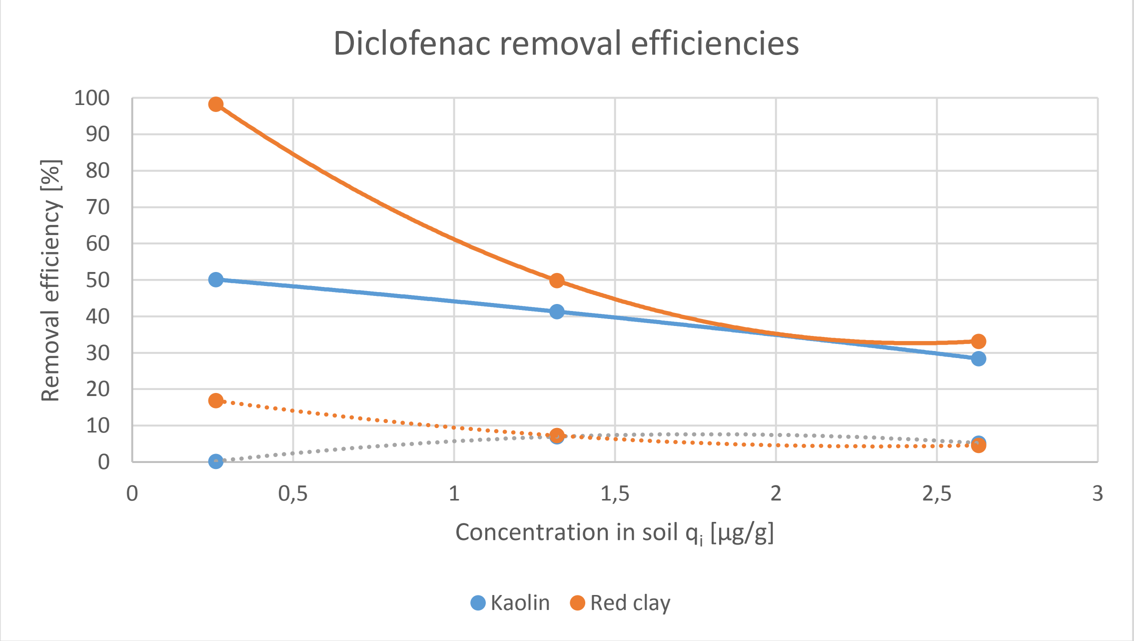

Figure 5-24 Trend of the diclofenac removal efficiencies for kaolin and red clay. The dotted lines refer to the removal due to sorption; the continuous lines to the total removal.

Therefore with the injection of clay suspensions a significant amount of the contaminant was brought from soil into solution. The remediation of the soil was achieved but the water injected is still highly contaminated. Only a small part of the initial diclofenac was sorbed into clay: Figure 5-24 shows the estimated total removal efficiency trends compared to the ones due sorption on clays on the basis of values reported on Table 5-8. At low contaminant concentrations red clay showed the most relevant properties.

6 CONCLUSIONS AND SUGGESTIONS

In this thesis nano-to-micro clay particles were taken into consideration as low cost sorbents with the purpose of remediate contaminated soil. The adopted approach consisted in the injection of clay suspensions into porous media as a new remediation technique. Since no specific literature was available, this thesis aim was to conduct a preliminary laboratory study on its feasibility.

The investigated clay materials were sodium-modified bentonite, kaolin and a secondary clay material (red clay) derived from a gravel washing process. Bentonite, mostly containing montmorillonite minerals, is known in literature for its applications as sorbent while kaolin and red clay were interesting for their low viscosity properties. Nano-to-micro particles of these materials were obtained by grinding and sieving (by a 63 µm sieve) the raw clays.

Diclofenac was chosen as tested contaminant due to its emerging presence in soil and water ecosystems and its toxicity. Previous studies conducted by Xu et el (2009) and Scheytt et al (2005) assessed the diclofenac sorption capacity in different kind of soil.

The first part of the experiment was aimed at evaluate the infiltration properties of the different clays into different porous media and therefore at find a clay content which allowed a high mobility of the injected suspension. The first screening tests evidences suggested to discard bentonite as a possible clay material for the implementation of this remediation technique due to its high viscosity, even in an anticoagulant solution. Performing a further percolation tests, suitable clay contents for kaolin and red clay suspensions were found to be 80 g/L and 100 g/L respectively for a coarse sand porous media.

In order to make all the experiments comparable a 80 g/l clay concentration was chosen for the development of the successive tests, which assessed the sorption properties.

The batch tests leaded to the construction of sorption isotherms. Kaolin showed a linear isotherm behaviour and low sorption capacity at low diclofenac concentrations (1 mg/L), while red clay isotherm could be described by Freundlich relation ($1/n = 0,7972$; $K_f = 2,4837$) with lower removal rate of contaminant at higher concentrations (10 mg/L). However the clay/solution ratio (1:12,5) utilized provided with a removal of diclofenac in aqueous phase between 10 and 21 %.

These relations were then used in order to assess the results obtained from the column tests, which were performed simulating the injection of 80 g/l clay suspensions into soil contaminated with different concentrations of diclofenac (0,26-1,32-2,63 µg/g).

The findings showed that a significant amount of diclofenac was removed from soil but only a part of it was estimated to be adsorbed on clay particles (up to 17% of the total pollutant amount in the case of red clay at 0,26 µg/g contamination) . It was assumed that diclofenac was removed from soil due to the double effect of injecting water (a sort of physical and chemical soil flushing) and clay particles.

The effect of the presence of clay in the soil is evident since the contaminant removal efficiency is significantly higher than in the case of injection of distilled water. In this sense red clay showed a better remediation capacity compared to kaolin, especially at low tested concentrations.

Therefore the feasibility of this approach as a remediation technique was confirmed.

Since this thesis consisted in a preliminary study, many aspects of this approach may be subjected to further detailed investigations:

- In order to better assess the extent of the remediation a more precise mass balance in the column test could be develop by measuring the diclofenac present in the infiltrated clay.
- Moreover, since the tested materials had good infiltration properties but scarce sorption capacity, it could be interesting to investigate on bentonite with a lower clay content in suspension and compare the sorption results. In the same way could be useful to treat the red clay by removing the quartz minerals in order to improve its sorption efficiency.
- As regards the infiltration tests a less empirical method could be developed in order to find a relation between the characteristics of the porous media (porosity, permeability, grain size) and the clay content which guarantee an effective mobility of the suspension.
- Real soil test should be taken into account in order to assess the influence of organic. matter and biological activity on the sorption process.
- A natural continuation of this thesis could be the performance of large scale percolation tests, where suspensions with a selected clay content are infiltrated at different times through the same contaminated soil sample. This test could provide with more reliable information about remediation duration and efficiency.

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