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Variation of Some Physicochemical Parameters to Improve the Properties of Clays of Madagascar: Case of Nitrates in Water

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Abstract Clay is a lamellar material made up of elementary layers (phyllosilicates) that pile, aggregate themselves, disaggregate according to the condition of the surrounding environment. This induced arrangement of the internal reactive interfaces, different from external surfaces, and confined spaces which are true nanoreactors. The small size of their layers of which the thickness is on a nanometric scale (millionth mm) confers on clays mineral all the remarkable properties exploited in many application that one daily mixes with since millenia. We applied one of these properties with the process of adsorption to highlight the elimination of certain pollutants in water. The processes of adsorption are the object of this study. They tend to develop quickly and are mainly used for the elimination of polluting compounds. This technique showed great capacities of depollution of waste waters. But, its performance and its effectiveness depend on the nature of the adsorbent. In practice, we will use the adsorbent white clay and green clay. This study makes it possible to determine the effect of the initial nitrate concentration, the effect of the pH and the effect of the load while adsorbing. The best results were got to 76.5% for white clay (WC) and 60% for green clay (GC) with 100mg/L^{-1}. of Nitrate. Indeed, the good output of adsorption is obtained with acid pH for the two adsorbents with 200mg/L^{-1} of Nitrate. However, the percentages of retention of thenitrates ion on the adsorbents used vary 35% and 89% for white clay and 28% and 80% for green clay with 100mg/L^{-1} of Nitrate. The analysis is carried out by visible spectrometry U.V of type SHIMADZU U.V- 160A. The experiment shows that the white clay of the I.M.R.A is good adsorbent power that the green clay of Homéopharma.

Keywords Nanotechnology, Water, Nitrates, Elimination of nitrates, Adsorption, Clay

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1. Introduction

Water, it is before all the source of the life, however it unequally remains distributed and too rare for an important part of humanity. The figures are there, disturbing: nearly 250 million human beings, representing 26 countries, miss water cruelly.

In the countries in the process of development, 80% of the cases of pathologies listed find their origin in a water of poor quality. Diseases that one believed finished for a long time still prevail in Africa, which is intolerable at one time which is said industrialized. Generally, our waterways are polluted by urban, agricultural and industrial waste including of many toxic substances of synthesis which the natural processes do not succeed in breaking up. Even in tiny quality, some of these substances can be very detrimental.

Pollution is not always visible. The water of a river or a lake can seem clean, even if it is still polluted. In the ground waters, on which the majority of the Malagasy people hope to be supplied, the pollutants are particularly difficult to detect. Moreover, the effects of pollution are not necessarily immediate; they can take years to be appeared.

When pollution makes water unfit for consumption, with the leisure, agriculture and industry, it ends up returning the less aesthetic lakes and rivers. What is more serious, it is that when pollution destroyed the aquatic life and reduces its capacity of reproduction, it threatens possibly the human health. Nobody escapes the effects of the water pollution.

One distinguishes several types of pollution, which can have a domestic origin, agricultural or industrial.

Physical pollution destroys the transparency of water (presence of suspended matter), acts on its temperature (thermal pollution) or its radioactivity.

Chemical pollution is due to undesirable substances (nitrates, phosphates) or dangerous (metals and others micro pollutants), which cause deep chemical imbalances (acidity, salinity) having biological effects. Most toxic products come from chemical industry, of the industry of metals, the agricultural activity and the discharges of domestic or industrial waste.

Organic pollution of water, coming from domestic waste

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waters and agribusiness industries, causes an oxygen overconsumption (necessary to its degradation) and can result in the death of the aquatic life. It can also cause the appearance or the setting in solution of bad products (metals, ammonia, sulphides).

Microbiological pollution in the water of the micro-organisms, of which some are pathogenic germs (virus, bacteria). The domestic hearths, the hospitals, the breedings and certain agribusiness industries reject germs likely to present a danger to health.

We will be interested more particularly in chemical pollution because it is the most widespread pollution in the world. A molecule strongly used in the rural areas drew our attention, it is the nitrate which is polluting coming from several types of, in particular, agricultural and animalist waste. To try to solve the problem of water polluted by this input we used a cheap raw material which is also in the countryside, clay. Our topic of study is entitled “Variation of some physicochemical parameters to improve the activity of clays of Madagascar: case of nitrate in water”. In the first part, we will carry out a bibliographical study concerning clay and nitrate and the technique (adsorption) used to determine the variation of concentration of nitrate when it is in contact with clay. In the second part booked with the various physicochemical characterization of the precursors in particular the potassium nitrate solution, the clay solution and the adsorption of nitrate in clay. For that, we used two types of clay, green clay and white clay. The third part relates to the discussion of the results got compared to the bibliographical data. And finally, we will finish the article by a conclusion and the prospect for research around the polluting agent others that the nitrate.

2. Bibliographical Studies

A. Clay [1, 2]

1. Definition [3]

It is a material of elementary layers (phyllosilicates) which pile up, incorporate themselves, disaggregate according to the condition of the surrounding environment. This induced arrangement of the internal reactive interfaces, different from external surfaces, and spaces confines which are true nanoreactors. The small size of their layers of which the thickness is on a nanometric scale (millionth mm) confers on clays mineral (aggregation layers in particles, then in aggregates on increasingly large scales) all the remarkable properties exploited in many application that one daily mixes with since millenia.

2. Structure of clays minerals [4]

The phyllosilicates are hydrated aluminium silicates corresponding to the formula $(Si_2O_5)_n$. One can also consider that their structure is a combination of two fundamental structural layers formed by the assembly of the ion of the types O_2, OH^- and some cation: Al^{3+}, Mg^{2+}, and Si^{4+}.

The first unit is represented by tetrahedrons. Each tetrahedron is consisted a superposition of a hexagonal layer and a compact layer. The hexagonal layer is formed by six ion of oxygen laid out in hexagon and thus form cavities called “hexagonal cavities”.

The superposition of these two layers generates tetrahedrons formed exclusively by all three ion O_2 which clearly seems component of the called hexagonal layer “basal layer”. These three oxygen ion cap an ion O_2 of the sub-base called “apical layer”. In the center of each formed tetrahedron exists a vacuum occupied by a cation. Generally Si^{4+} (R=0,41 Å) can be replaced by other ion Al^{3+}, K^+, Na^+, Mg^{2+}, or Fe^{3+} (R=0,50Å)

The second unit is represented by the octahedral ones. Each octahedral is formed by a superposition of two compact layers of ion O^2 and OH^- and octahedral form what is called layer.

The tops of each octahedral are occupied by ion of oxygen or hydroxide such as the whole of three ion is registered in an equilateral triangle pertaining to the roadbase. This last cap a similar structure belonging to the roadbase and the sub-base but laid out of such way that the top of the lower triangle is opposed higher triangle. In the center of each tetrahedron exists a cavity called “tetrahedral cavity”. Each cavity tetrahedron occupies more often Si^{4+}. Dans each cavity octahedral contains a cation like Al^{3+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Li^+ but Al^{3+} and Mg^{2+} are most frequent.

Thus, the cavity inside a tetrahedron is smaller than the octahedral cavity. If the cation which occupy the cavities are bivalent for example: ion Mg^{2+}, all the cavities are occupied and of the phyllosilicates are known as “trioctaedric”. On the other hand if the octahedral cavities contain the ion Al^{3+} trivalent, two thirds of the cavities are only occupied and the corresponding phyllosilicates are called “octahedral”. The ion O^{2-} and OH^- are charged negatively then they will tend to be pushed back between themselves. Thus the positive loads of the cation placed in the tetrahedral or octahedral cavities will balance them and ensure the stability of the unit.

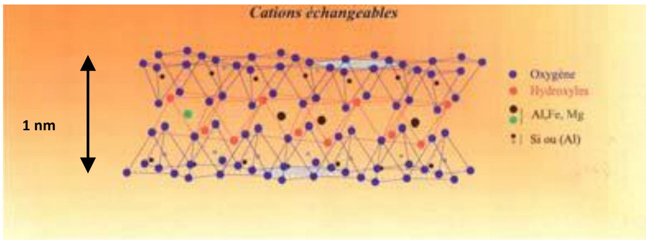

Figure 1. Structure of the clay layers[1]

B. GENERAL INFORMATION ON NITRATES

1. Nitrogenized parameters [2, 5]

The nitrogenized parameters are fixing, the assimilation, the ammonification, nitrification and denitrification.

Fixing: it is the passage of atmospheric nitrogen nitrogen combined under the action of certain organization.

Assimilation: it is the transformation of mineral or organic nitrogenized matter inert into living matter.

The ammonification: it is the ammonium release starting from organic nitrogenized matter.

Nitrification: it is the oxidation of ammoniacal nitrogen (NH_4^+) nitrates some then out of nitrite via nitrifying bacteria.

Denitrification: it is the reduction of gas nitrogen nitrates via denitrifying bacteria.

In waste waters, the nitrogen can be organic or mineral (either nitrogenizes ammoniacal, or nitrite, or nitrate). It is presented in four forms:

- organic nitrogen

The organic nitrogen which is transformed into ammoniacal nitrogen (NH_4^+).

- ammoniacal nitrogen

The ammoniacal nitrogen (NH_4^+) comes from the organic matter of origin natural or related to the human activities (spreadings). In deep waste waters, the presence of the ion ammonium can also be due to the reducing condition reigning in a tablecloth. Its presence in water is an indicator of pollution [2].

- Nitrites

The nitrites can be met in water, but generally with low dose. They come nitrification from ammoniacal nitrogen or denitrification from nitrates. The nitrous nitrogen (NO_2^-) is unstable and is quickly transformed into nitrates by the reaction of nitrification [2].

- Nitrates

The nitrates are naturally with weak concentration in water. The nitric nitrogen (NO_3) can be of artificial origin, due to their use as fertilizers for the cultures (mineral and organic manures, animal manure) [6]. The excesses not absorptive by the plants are washed by the rains and join groundwaters and surface waters. The nitric nitrogen is very stable and very water soluble.

Thenitrates ion constitute the last stage of the bacterial degradation of nitrogen. Its presence in water indicates, the matter organics [1] water pollution. It is a reaction of oxidation which is done by enzymatic catalysis connected to bacteria in water. The chain reaction is:

$$\mathbf{NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^-} \qquad \textbf{Reaction: 1}$$

$$\mathbf{2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+} \qquad \textbf{Reaction: 2}$$

$$\mathbf{NH_4^+ + 2O_2 \longrightarrow NO_3^- + H_2O + 2H^+} \qquad \textbf{Reaction: 3}$$

$$\mathbf{2NO_2^- + O_2 \longrightarrow 2NO_3^-} \qquad \textbf{Reaction: 4}$$

2. Origin of nitrates in water [1, 7]

In water nitrates are naturally present at amounts varying according to the seasons and the places. The concentration of nitrates in surface water and underground are generally expressed in milligrams per liter. The main sources of nitrates in water are:

- Wastes industrial and domestic;
- Rejection of effluents of breeding;
- Food of surface waters by polluted table cloths;
- Chemical fertilizers employed to improve the growth of the cultures;
- Waste of animal origin coming from barns and places of storage of manure;
- Waste of human origin coming from fields of purification, or septic tanks or no tight tanks of retention;
- Animal manure

C. GENERAL INFORMATION ON ADSORPTION

1. Definition of adsorption

Adsorption is the fixing of a gas or a liquid (adsorbate) on the surface of a solid (adsorbent). It occurs with the interface of an adsorbing adsorbate 2.

The solid which is the seat of this adsorption is called adsorbent while the liquid or the gas which undergoes adsorption is called adsorbate. Figure 2 below watches the phenomenon of adsorption.

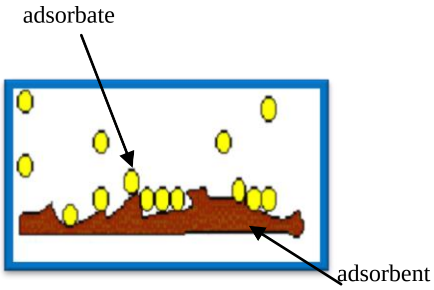

Figure 2. Phenomenon of adsorption

3. Various Kinds of Adsorption

According to the nature of the forces which retain the molecule adsorbed on the surface of the solid. There exist two types of adsorption: chemisorption, and physical adsorption.

3.1. Chemical Adsorption or Chemisorption

Chemical adsorption is generally irreversible. It brings into play one or more covalent bonds or ionic between the adsorbate and the adsorbent. This kind of adsorption brings into play energies of high attraction. The heat of adsorption is relatively high. It is of the order 200 $KJ.mol^{-1}$ [8]. The various chemical bonds in chemisorption are:

- The purely ionic bond of the atoms donors or acceptors of electrons,

- The covalent bond or metal,

3.2. Physical Adsorption

Physical absorption is characterized by the forces between the molecules of liquid or gas and solid. These forces are of type Van Der Waals. It is reversible. Put energy concerned is weak, it is of the order 20 KJ.mol^{-1} [9].

Chemisorption and physical absorption are differed by their energy, their temperature of process, their nature of connection and their kinetics. Table 1 represents these differences.

Table 1. Differences between physical adsorption and chemical adsorption

Properties	Physical Adsorption	Chemical Adsorption
Energy of adsorption	20 kJ.mol^{-1}	200kJ.mol^{-1}
Temperature of process	Lower than the boiling point of the adsorbate	high
Nature of the bonds	Physical (Van Der Waals)	covalent bond
Desorption	More or less perfect	Difficult
Energy of activation	Weak	High
The kinetics	Very fast	Low
Quality of the surface	Multilayer formation	One layer

3.3. Factors Influencing Adsorption [1]

The factors influencing adsorption are the temperature, the load of the adsorbent, the nature of the adsorbate and specific surface.

- Temperature

Adsorption is an exothermic process and consequently its unfolding must be favored at low temperature.

- Charge of the adsorbent

The capacity, the speed and the heat of adsorption decrease when the load (adsorbed fraction) of the adsorbent increases.

- Nature of the adsorbate

To have a good adsorption, it is necessary that there is initially an affinity between the solid and the aqueous solution. In general, the polar solids, adsorb other polar bodies preferentially. On the other hand the nonpolar solids, adsorb nonpolar substances preferentially. Consequently, affinity for the substrate grows with the molecular mass of the adsorbate.

- Specific Surface [10, 11, 12]

Specific surface gives primarily the characterization of the solids and porous materials. More, it is large, more adsorption is better.

4. Results of the Tests of Adsorption

A Experimental methods

We chose potassium Nitrate like adsorbent and we tested the adsorbing power of two clay samples, the white clay of the IMRA and the green clay of Homeopharma. The adsorption of nitrate is analyzed with a UV-visible spectrophotometer. The maximum wavelength of detection of nitrates is of 220 Nm. We tried to vary various parameters such as the nitrate concentration, the pH, the load while adsorbing and the temperature of adsorption in order to optimize the requirements to have a maximum adsorption.

1. Effect of the initial nitrate concentration

The outputs of retention of thenitrates ion were given for the two clay samples: white clays and green clays under the same operating condition, namely: 5g of clay per liter of distilled water and the initial nitrate concentration of 100 mg. L^{-1}, 350 mg. L^{-1} and 700 mg. L^{-1}. The tests of adsorption were carried out at temperature 25°C under agitation during 60 mn [13].

It should be noticed that as the output of adsorption decreases, the initial concentration of nitrates increases with the same quantity of adsorbent (20.029% for white clay and 13.914% for green clay with the same initial concentration).

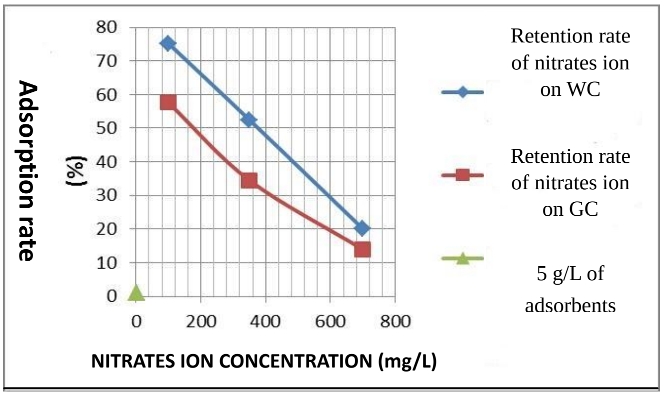

Figure 3. Average output according to the concentration in $N0_3^-$ ion at room temperature (25°C) with 5 g.L^{-1} of adsorbent

2. Effect of the pH

The study of the effect of the pH on the adsorption of the nitrates ion was carried out by varying the pH from 4.15 to 8.30 with an initial concentration in ion NO_3^- fixed at 200 mg. L^{-1} and a load by adsorbing white clay and of green clay fixed at 5 g.L^{-1}. It was carried out with the room temperature. The initial pH of the solution was measured with a pH-meter and was adjusted with the values wished using the solution of HCl and NaOH 0,01N.

The pH plays a significant role in the mechanism of retention of the nitrates ion. Indeed, the fixing of the molecules of NO_3^- on clays depends on the pH. An increase in the pH decreases the capacity of fixing of white clay and green clay because of the competition of ion OH^- and ion NO_3.

The results of analysis are shown in figures 4 and 5. It is observed there that the percentage of displacement of thenitrates ion on clays decrease with the increase in the pH. This makes it possible to state that the increase in the pH of the solution does not support the fixing of the ion in question (adsorption is weak in basic medium). However, the examination of these results shows that the best output of the pH is lower or equal to 6.6. Adsorption increases with acid pH.

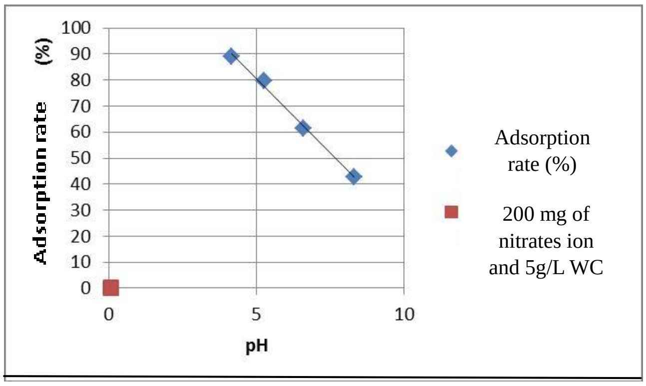

Figure 4. Effect of the pH on the adsorption of the nitrates ion at T=25℃ for 5g.L^{-1} with white clay and 200 mg. L^{-1} of NO_3^-

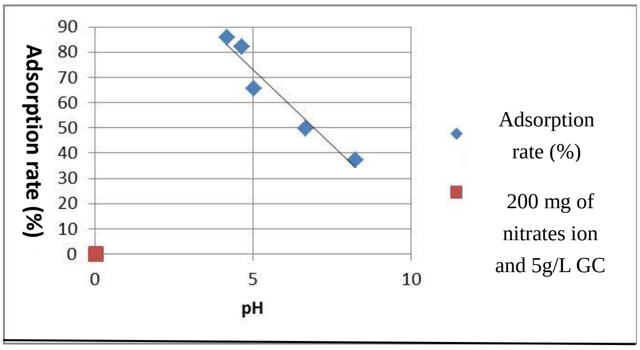

Figure 5. Effect of the pH on the adsorption of the nitrates ion at T=25℃ for 5g.L^{-1} with green clay and 200 mg. L^{-1} of NO_3^-

3. Effect of the load while adsorbing

The effect of the load while adsorbing was observed with room temperature for an initial NO_3 concentration of 100mg. L^{-1} under agitation during 60mn. The various concentration of adsorbent are of 1, 5, 6, and 10 green clay and white clay g.L^{-1}.

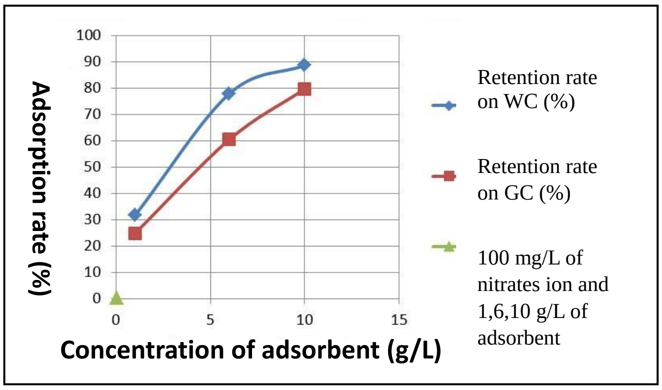

Figure 6. Output of adsorption of nitrate according to the concentration while adsorbing in T= 25℃

The results of analysis are summarized on figure 6. It is noticed there that the output of adsorption increases as far as the load while adsorbing. By comparing the already got results, for the same initial concentration and the various values of the load while adsorbing, it is announced a more important retention for white clay than for green clay (fig 6). On this figure, it is also observed a strong growth as of the beginning up to 10 g/L of adsorbent, but the best outputs of adsorption take place with 10 g/L of adsorbent. These outputs are respectively of 88.6% for white clay and 79.6% for green clay. Indeed, the white clay of the I.M.R.A and the green clay of Homéopharma give almost the same output on the adsorption of nitrate. That makes it possible to conclude that two clays of Madagascar are effective to reduce the nitrate rate in water.

4. Test of the temperature on adsorption

Adsorption is favoured at low temperature thus when it increases, it is observed a reduction in the output of adsorption. The nitrates are fixed badly on white clay or green clay at a higher temperature at 25℃. The results of the treatment are summarized in table 2 hereafter.

Table 2. Measure of adsorption of nitrates on white clay and green clay at temperature 48℃

Adsorbents	White clay	Green Clay
Initial contents in mg.L^{-1}	100	
Temperature in ℃	48	
Absorptance	0,205	0,261
Contents with balance out of mg.L^{-1}	41	52,2
Average of adsorption in (%)	59	47,8

5. Discussion

White clay is also called Kaolin. It has a good adsorbent power. It is a clay of the Smectite family. For the smectite, the capacity of fixing is very important, thanks to the loads (negative of the layers, positive between the layers) and on the considerable specific surface of 100 m^2 for one gram. These interaction can be done in three different sites:

- in the layers for the simple ion, between the layers for the molecules punts or small, with the periphery for the macromolecules.

Green clay belongs to the family of the illite. Its quality is lower than those of smectite.

It has a good power of absorption but a small power of adsorption [14].

According to the results which we got while varying some physicochemical parameters, clays have a power adsorbing for the nitrate molecules. We chose this pollutant because it is most widespread as well in urban environment as rural. Variation of the initial nitrate concentration of 100 mg. L^{-1}, 350 mg. L^{-1} and 700 mg. L^{-1} for the same quantity of clay (5g.L^{-1}) showed that white clay has a power adsorbing higher than that of green clay. Indeed, the highest output of adsorption of the nitrates ion (75.2%) is observed on white clay, for an initial nitrate concentration corresponding to 100 mg. L^{-1} while the proportion does not exceed the 57% for green clay for the same initial nitrate concentration. In agreement with BOUALLA [15], it should be noted that the agitation of the solution should not exceed the 60 minutes to have a maximum output. The increase in the pH supports the adsorption of the nitrates ion on clays because one eliminates the ion OH- which return in competition on fixing. When one increases the concentration while adsorbing, one observes a growth of the output of adsorption up to 10 g.L^{-1}.

6. Conclusions

This work aims to reduce the quantity of nitrates present in water. The adapted method is the adsorption of white clay of the I.M.R.A and green clay solution of Homéopharma.

To be able to conclude it, the interest of this study concentrated on the effect of the initial concentration innitrates ion, the pH and the load while adsorbing. The tests of adsorption were analyzed with visible spectrometry U.V. The interpretation and the confrontation of the results got through this proportioning, made it possible to draw the following conclusion:

- The highest output of adsorption of the nitrates ion (75.2%) is observed on white clay and to 57.6% on green clay, for an initial nitrate concentration corresponding to 100 mg. L^{-1}. It decreases when the initial concentration of nitrates increases with the load while adsorbing retained.
- The pH is an important parameter for adsorption. An increase in the pH can decrease the capacity of fixing of white clay and green clay of Madagascar. Adsorption is ineffective for a basic pH. On the other hand, it is effective for a pH lower or equal to 6.6. The best output of adsorption is observed with strongly acid pH.
- The output of adsorption of the nitrates ion is almost identical for two clays used. The percentages of retention of the nitrates ion on the adsorbents used vary from 31.6% to 88.6% for white clay and from 24.8% to 79.6% for green clay with 100 mg. L^{-1} of Nitrate. The maximum values of adsorption are respectively of 88.6% and 79.6% for white clay and green clay.
- The output of adsorption of nitrates decreases when the temperature thus increases adsorption is ineffective with high temperature.

Adsorption is a very effective method to retain pollution present in water, in particular thenitrates ion. The experiment shows that white clay is a good adsorbing compared to green clay (to be able adsorbent fairly). All in all, the white clay of the I.M.R.A and the green clay of Homéopharma produce a positive effect to reduce the nitrate rate present in water.

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