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Elimination of the Declared Insecticide by Natural and Modified Clay and Montmorillonite Sodium

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Abstract

In this research, we study the comparison of the removal of a domestic insecticide declared as an organic pollutant from the water on the surface of the natural clay (N-C) and Montmorillonite sodium (Mnt-Na), where we reveal general information about adsorbents on organic pollutants, as well as physical and chemical methods for their spectral analyses. In addition, we have a simplified explanation of the adsorption phenomenon and then we study the various factors that affect it, represented by the effect of the initial concentration of the pollutant solution, the effect of the pH, temperature and the contact time, conductivity effect, turbidity analysis, and dissolved oxygen analysis. And we have achieved the results that benefit us by comparing the effectiveness of Natural clay (N-C) and Montmorillonite sodium (Mnt-Na) in the elimination of insecticide, in addition to judging the possibility of describing adsorption by the best adsorbent.

Keywords: Adsorption, Insecticide, Natural clay, Montmorillonite sodium, Antibacterial activity

1 Introduction

Pesticide use worldwide has increased dramatically over the past two decades, co-existing with metamorphoses in agricultural practices and more intensive agriculture [1]. In the areas of pesticide use, the impact on environmental and human health would be 3 to 6 times greater [2]. Pesticides are chemical compounds used to control organisms considered harmful in agriculture, in different industries and by individuals in homes. They have been used in large quantities in recent decades. Simultaneity of these pesticides poses a real challenge of public health, exclusively for farmers who are most at risk, similarly and more of the general population into consideration of exposure to pesticides for domestic use [3]. Micro pollutants are substances likely to have an impact on health or the environment - alone or in combination with other micro pollutants - even at very low concentrations [4]. These are substances that are not naturally present in the media, but come from human activities. Histological studies revealed structural alterations in the spleen and liver, confirming and explaining the variation in some of the parameters studied [5]. In addition, inflammation of the bladder was observed. The results obtained show a slight increase in body weight and a decrease in weight gain, a decrease in the number of white blood cells, peritoneal and alveolar macrophages, splenocytes, and blood platelets [6].

The removal of these pollutants from industrial discharges is very often carried out by conventional chemical treatments such as: coagulation-flocculation, electrocoagulation among others, has proved effective, but in most cases, very expensive [7]. The treatment by the technique of adsorption is more used for its efficiency in the abatement of organic micropollutants, involving liquid solid interactions. The application of natural or modified clay in the case of Mnt-Na in the field of water treatment that began to develop after the Second World War. Because of their remarkable particularity is their ubiquity and reactivity of nano-particles, and also for its adsorbent properties in order to eliminate organic substances and also used both as an adsorbent material and as a bacterial support to lower the content of organic matter and biodegradable matter via the sizes and the leaf structures that provide a large specific surface area [8]. In our study, we will study the removal of a household insecticide declared as a micro pollutant of water on the surface of two adsorbents Natural clay and montmorillonite sodium Thus, the impact of contamination, where we will observe how the process of elimination is affected by changes in concentration, adsorbent mass, temperature, pH and contact time, turbidity, dissolved oxygen.

2 Experimental

In this work, the experimental methodology for the study of the removal of a domestic insecticide declared as an organic pollutant from the water on the surface of the natural clay and Mnt-Na, where we will present the tools, devices and materials necessary to conduct this study, in addition to explaining how to collect and analyze samples, the effect of changes in concentration, temperature and pH and the contact time, conductivity effect, turbidity analysis, and dissolved oxygen analysis.And its effect on elimination capacity, and all the results obtained will be shown. A "household pesticide" (classified as a "Class 5 product") is a product of the family of biocides and the subfamily of pesticides intended to control certain undesirable organisms because it attacks wood, food,

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domestic animals. Products designated as pesticides are products that are used for the prevention, control or disposal of organisms considered undesirable [9].

2.1 Materials

2.1.1 Insecticide used

Domestic insecticide (Figure.1), considered a micro-pollutant of water, is used without any prior purification. The solutions are prepared by dissolving quantities of active matter liquid with Bi-distillate water. An insecticide solution at a concentration of 100 mg/l was prepared by dissolving 1ml in 100 ml of bi-distilled water and then diluting the stock solution to obtain 5 ml of daughter solutions by volume, at a concentration ranging from 50 mg/l to 500 mg/l.

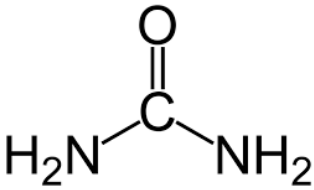

Figure 1 : Chemical structure of cabramide

2.2 Method of analysis

At the end of each adsorption experiment, the adsorbent was removed by centrifugation at a speed of 2500 rpm. The resulting filtrate was then analyzed by UV- Visible spectrophotometer by monitoring the absorbance changes at λ_{max} = 320 nm for the insecticide. The amount of insecticide adsorbed of natural clay and Montmorillonite sodium, Q_e (mg/g), was evaluated using the following

$$Q_e = (C_0-C_t)*V/M \quad (1)$$

where C_0 and C_t (mg/L) referred to the initial and the equilibrium concentration of carmine respectively; V (L) is the volume of the carmine solution and M (g) is the mass of natural clay and Montmorillonite sodium

2.3 Characterization techniques

2.3.1 Adsorbent used

The spectral characteristics of the materials were determined through standard procedures [10]. The application of natural and abundant adsorbents such as crude clay and sodium clay for water treatment is an authorized route to protect water capital. Several techniques were used: The resulting phase analysis was performed by recording X-ray diffracts grams of powder using an Xpert Pro (Panalytical) diffract meter using copper CuKα radiation (λ = 1.5418Å) and infrared spectroscopy. The raw clay and sodium dried at 100°C/ 24h were analyzed by Fourier infrared transform spectroscopy brand spectrometer SHIMADZU FTIR-8000. Both solids were prepared as a solid mixture with (KBr) and analyzed by absorption.

3 Results and discussion

3.1 Material chemical analysis

3.1.1 X-ray diffraction (DRX)

The spectrum presented in (Figure.2) makes it possible to identify the crystalline structure of N-Clay and Mn-Na. Figure .2 shows the diffract gram of the crude clay and the sodium clay according to the XRD diagram obtained, the two clays have an almost identical mineralogical composition, but distances between the layers to 2ϴ practically different.

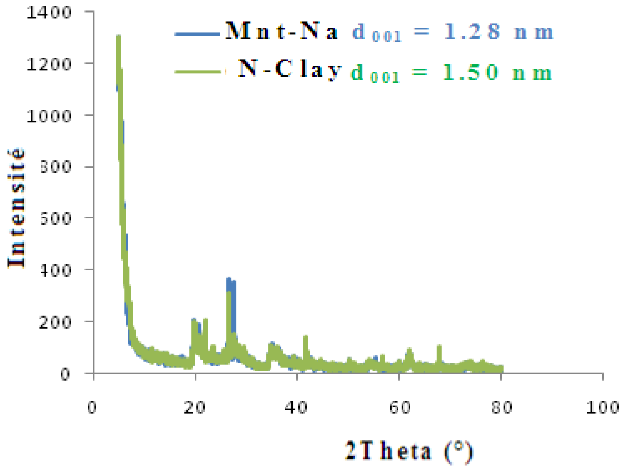

Figure 2: Diffract gram of N- Clay and Mnt - Na

Table.1: Reticular distances of the different clays studied [11]

Type of adsorbent	Reticular distances d_{001} (Å)
(N-C	15
Mnt-Na	12.8

From Figure 2 we can see: The bentonite clay is characterized by four peaks, the first being 15,037 Å (001) and the other three being 4,508Å (110), 2,567 Å (200) and 1,501 Å (060) [12] .He clay -Na has a peak at 2θ=7.033° corresponding to an interfoliar distance d001=12.802 Å with a disappearance of certain lines characteristic of the crystalline phases attributed particularly to quartz (located at 2ϴ = 27°) and an intensification of certain lines, characteristics of montmorillonite, initially hampered by the undesirable crystalline phases localized at 2ϴ = 6 and 29° [13]. The sodium treatment of montmorillonite leads to the decrease of the reticular distance, it goes from 15.037 to 12.802 Å, this decrease is due to the exchange of cations Ca^{+2}, Mg^{+2}, K^{+} by sodium ions Na^{+} which really confirms a good purification of bentonite [14].

3.1.2 FTIR Analysis

The FITR tests confirmed that the analyzed materials have a crystalline structure. The spectra obtained are illustrated by (Figure 3) .We note:

Figure 3: FTIR spectra for N- Clay and Mnt – Na

The analysis of this spectrum shows the main absorption bands of the vibration modes of the different functional groups:

- **Natural clay**

An absorption band centered around 3620 cm^{-1} that is relative to the elongation vibrations of the OH groupings related to the octahedral cations Al (Al-OH-Al) [15]. The band centered at 1642 cm^{-1} is attributed to the H-O-H deformation vibrations of water molecules [16]. The adsorption bands from 1000 to 500 cm^{-1} are attributed to the valence and deformation vibrations of the octahedral ions substituted for the hydroxyl groups and the intense band observed at 1030 cm^{-1} which corresponds to the valence vibrations of the Si-O bond in the plane. The band cantered at 915 cm^{-1} is not only attributed to the deformation vibrations of the Al-OH-Al bonds but is also attributed to the presence of kaolinite [17].

- **Montmorillonite sodium**

The band that spans between1600 - 1700 cm^{-1} may be attributed to the valence vibrations of the OH group of the constituent water, in addition to the binding vibrations of the adsorbed water located at 1646 cm^{-1}. An absorption band centered on 3620 cm^{-1} is due to the valence vibrations of the OH groups bound to the octahedral Al cations (Al-OH-Al) [18]. The Si-O bond is characterized by: The intense band located between 900 - 1200 cm^{-1} and center around 1008.9 cm^{-1} corresponds to the valence vibrations of the Si-O bond [19].

3.1.3 Drawing the absorbance λmax curve (UV-Visible)

Using a spectrophotometer, the absorbance of the primary domestic insecticide solution was measured and the maximum wavelength was obtained, λ_{max} = 320 nm, which is absorbance in terms of change of concentration.

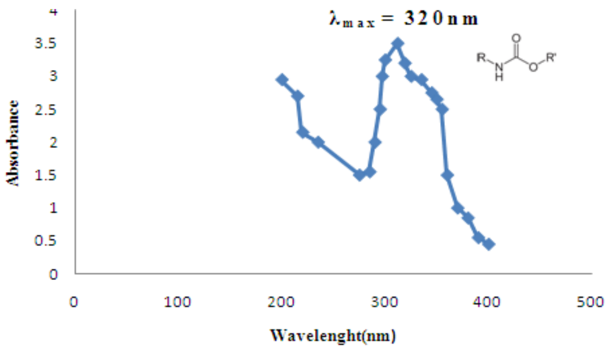

Figure 4: Absorbance of insecticide

To track the impact of insecticide concentration in water, we used a UV- Visible spectrophotometer to determine the maximum wavelength of uptake of the insecticide and also to determine the concentration of chemical species [20]. The absorption wavelength at a value of 320 nm, and thus there would be no sign of the visible light of absorption of the insecticide which confirms that the insecticide is colourless. The wavelength that corresponds to the highest absorption is usually called lambda-max (λmax).

3.1.4 Adsorption Isotherms

To do this, we place a fixed mass of natural clay and Mnt-Na, m = 1000 mg, in each of the insecticide solutions at different initial concentrations (100, 200, 300,400,500 ppm) in a volume of 5 ml at constant pH and temperature, and after the end of the experiment the samples are placed in a centrifuge for 5 minutes at 2500 rpm, then we filter the solutions and measure the absorption ratio with a spectrophotometer. Figure. 5 below show the results:

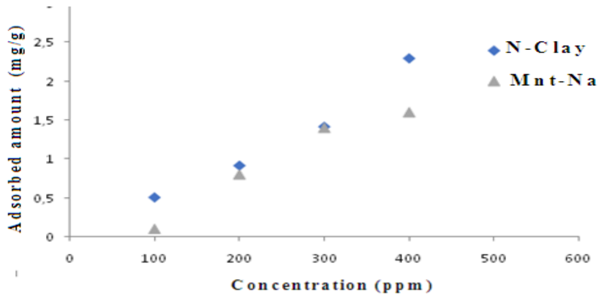

Figure 5: Initial concentration effects

Where it is noted that the higher the initial concentration, the greater the adsorption capacity to reach a maximum value at the highest concentration (2.5 mg/g for natural clay and 2 mg/g for Mnt-Na, a concentration of 500 ppm). We can also note the difference in adsorption capacity between natural clay and sodium clay because it is greater in the former than in the latter. This result is due to the fact that the presence of deliberate interfoliar layers of the sodium element in the natural clay. In addition, the high adsorption capacity of natural clay relative to Mnt-Na is due to its large interfoliar surface, which can absorb more polluting particles than sodium clay [21].

3.1.5 Effect of pH and temperature

To do this, we place a mass of 1 g of natural clay and 1g of sodium clay separately in 10 ml of water contaminated with domestic insecticide for 5. After placing the samples in a centrifuge, filtering them and measuring the pH as a function of temperature, we obtained the results shown in Figure 6. We find that the raw clay has maintained the acidity of the medium in the acid domain and that the influence of temperature has not much influence on the pH [22]. Whereas the acidity in the Mnt-Na has moved into the basic domain, this means that the variation is very dramatic between N-C and Mnt-Na. Natural clay can be said to play a major role in adsorbing organic micro pollutants even at very high temperatures without the pH varying. The low adsorption capacity in the acid field is due to the presence of large quantities of H^+ hydrogen ions competing with insecticide molecules for adsorption sites [23]. In addition, the absence of this hydrogen ion effect in the basic range where adsorption capacity is large and more stable. The reason for the decrease in adsorption capacity with the increase in temperature is due to the fact that the adsorption process is an exothermic process, in addition, high temperature molecules have a high kinetic energy [24]. Which reduces the risk of them accumulating on the surface of the adsorbent material.

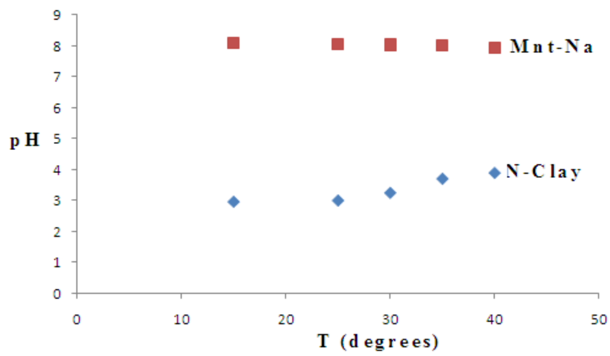

Figure 6: The effect of changing the pH

3.1.6 Effect of conductivity

Electrical conductivity characterizes the situation of a material or a solution to let the electric charges move freely and thus allow the passage of an electric current, and it is determined by the content of dissolved substances, ion load, ionization capacity, mobility and water temperature. We mixed 10 ml of concentration insecticide 500 ppm with 1 g of N-C and 1 g of Mnt-Na separately in two 50 ml bechers, and then we determined the conductivity as a function of time.

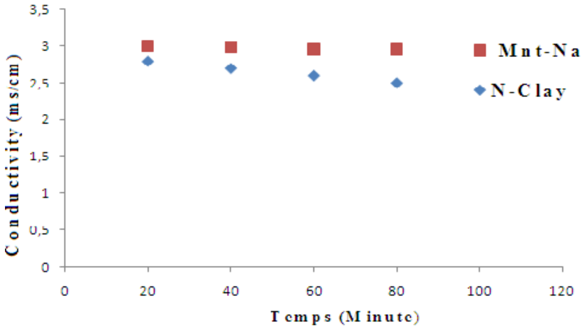

Figure 7: The impact on conductivity

Across the curve Figure.7, we observe that the conductivity of the mixed natural clay/ insecticide it is decreasing, against the conductivity sodium clay/ insecticide it is constant. So we conclude that the insecticide applied to both clays, mobilizes the mineral elements in the Mnt-Na by count in the N-C the electric charge decreases from the mineralogical elements present in the natural clay [25].

3.1.8 Turbidimetry analysis

The measurement of turbidity gives an indication of the suspended solids content, it is measured in NTU (Nephelometric Turbidity Unit) by a HANNA (HI88713-02), we calibrated the device with calibration solutions of the order of 0.1 NUT and 5 NUT, then we centrifuged and filtered the insecticide-treated solutions at a concentration of 500 ppm and we read the turbidity values at each time interval.
The turbidity values of a treated as a function of time are presented in Table 2.

Table 2: Turbidity values of water polluted with time

Temps (min)	10	20	40	60	120
Insecticide (NTU)	2,52	2,43	2,42	2,40	2,39
N- Clay (NTU)	2,19	1,18	1,19	1,31	1.00
Mnt-Na (NTU)	2.25	2.17	2.13	2.12	1.98

In order to identify the most effective adsorbent material in the removal of insecticide is it Mnt-Na or N-C, we will trace the turbidity curve in function of time to make a comparison, and we obtain Figure 8. Home insecticide is more troublesome, with half the turbidity treatment with N-C clay significantly reduced the turbidity values of the polluted water compared to the Mnt-Na clay. The turbidity of the insecticide treated with N-C clay was reduced by 72% and 20% for Mn-Na clay [26]. The reduction of the turbidity of the insecticide on both clays is visible in Figure 8.

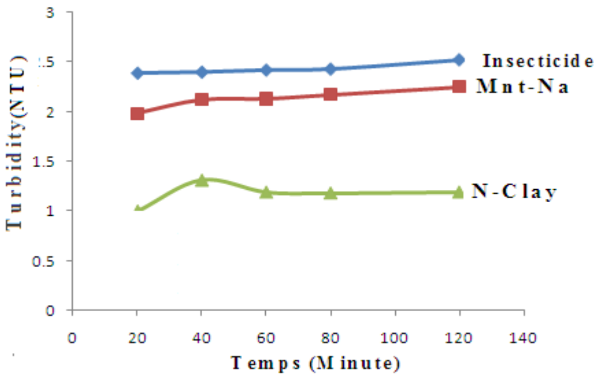

Figure 8: The impact on turbidity

3.1.9 Dissolved oxygen analysis

The oxygen is the manometer on the degree of the water pollution, the dissolved oxygen measures the concentration of the oxygen dissolved in the water and it is expressed mg / l or in percentage of saturation there. It contributes to the chemical and biological processes in aquatic environment. According to (Figure.9), the solubility of the oxygen decreases according to the factor of dilution, this modification is a dominating influence by organic matters reveal in the insecticide that prevent the oxygen from dissolving it in the water, besides they cause the decrease of the oxygen in every dilution [27]. We filled the OD vial with the sample to be measured, and then we left the sample at rest for 120 min. Then we started to read oxygenate dissolved in insecticide and adsorbent/insecticide mixture as a function of time. The results are shown in Table .3

Table 3: Dissolved oxygen values of water polluted with time

Temps (min)	20	40	60	80	120
Insecticide/O_2 (mg/l)	6.5	5.5	4.7	4.5	4.3
N-Clay /O_2 (mg/l)	11.1	10.2	8.4	7.1	6.90
Mnt-Na / O_2 (mg/l)	9.6	9.2	7.10	6.90	6.50

In order to identify the most effective adsorbent material in insecticide removal is Mnt-Na or N-C, we will plot the dissolved oxygen (DO) curve over time to make a comparison, and we obtain Figure 9. At first glance, insecticide treated with N-C clay generally maintained the highest DO concentration at the slow 120 minutes in heterogeneous medium gives many of the DO values would differ between insecticide treated with Mnt-Na and insecticide in homogeneous medium. This trend is supported by almost total elimination of the insecticide. The average content in waters of not polluted surface is 8 mg /l in 20°C and exceeds hardly 10 mg / l [28].

3.1.10. Antibacterial activity

Microbiological analysis of insecticide-sprayed water is to provide information on water quality, under certain conditions, the quantity of micro-organisms may exceed the tolerance threshold of the organism and be responsible for infections that cause disease [29]. It is therefore essential to take certain precautions to reduce the rate of proliferation of its microorganisms and thus avoid the deterioration of food. These pathogenic microorganisms include viruses, bacteria, protozoons and helminths. In our case, common sense is to express or reduce contamination after treatment. Four strains of bacteria (Pseudomonas Aeruginosa, Klebsiella pneumonia, Escherichia coli, and Staphylococcus aureus [30]. Were used to see the impact of these bacteria. The reading of four boxes of betri incubated at 37°C for 48 hours informs us that water contaminated with insecticide has a domestic use, has a significant antibacterial activity revealed by the rings that locks out bacterial strains of a visible diameter.

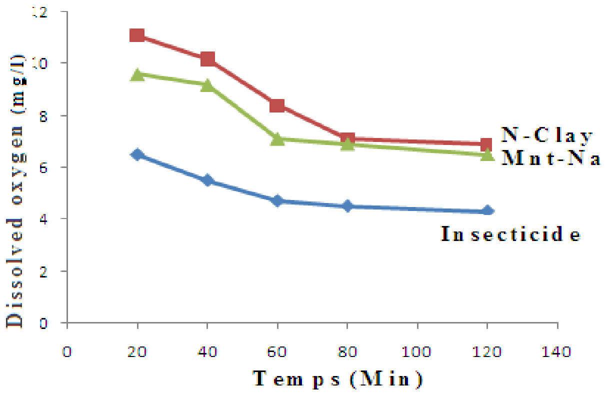

Figure 9: The impact on Dissolved oxygen

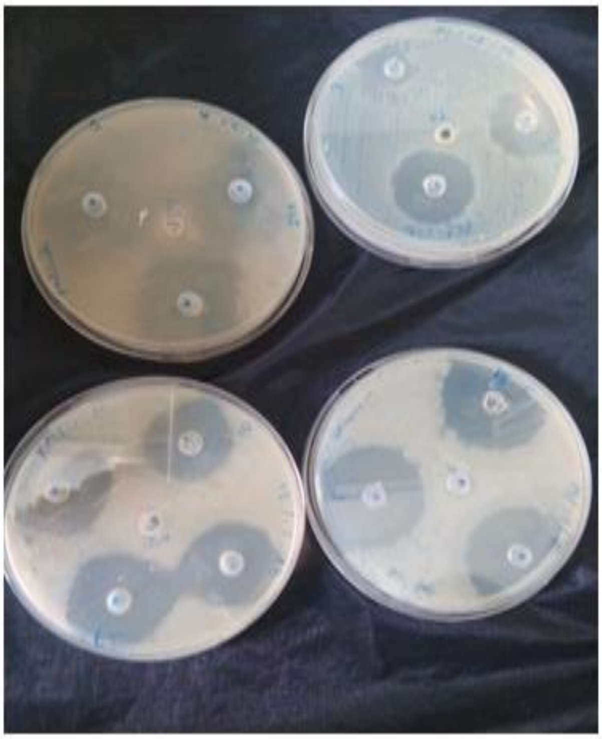

Figure 10: Antibacterial activity

4 Conclusions

In this research, we studied the process of adsorption of a domestic insecticide to the surface of natural clay and modified clay and determined the effectiveness of each under different conditions.It can be concluded that N-C was an appropriate adsorbent to Mn-Na in the removal of household insecticide. Heterogeneous treatment (natural clay/insecticide) by adsorption of various samples of polluted drinking water has proven effective in preserving the acidity of the environment, ensuring the good conductivity of the water, reducing turbidity, stabilizing dissolved oxygen. It is interesting to note that antibacterial activity is observed on water polluted by the method of discs on four bacteria in the gelosed culture medium, from where it can be said that there is a sensitivity to antimicrobial agent's against the insecticide. In addition, the results obtained during this study confirm the practical interest of the use of clays in the field of pollution of water contaminated by the pollutants.

Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that the submitted work is original and has not been published elsewhere in any language. Also, all procedures performed in studies involving human participants were following the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards. All procedures performed in this study involving animals were following the ethical standards of the institution or practice at which the studies were conducted.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution to data collection, data analyses, and manuscript writing.

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