Elimination of the pesticide 2,4-D by synthesized anion clays starting from marine water

N. Sadik [1], E. Sabbar [2], M. Mountadar [1], M. Lakraimi [3]

[1]Unit of Chemistry Analytical and Sciences of the Environment Faculty of Science of El Jadida
[2]Laboratory of Physicochemistry of Materials. Faculty of Science of El Jadida
[3]ENS Université Cadi Ayyad of Marrakech

Abstract
The layered double hydroxide (LDH) is synthesis from seawater. We studied as potential adsorbents of organic pollutant: herbicide 2,4-D. The adsorption tests were carried out in aqueous medium under air atmosphere, taking into account the effect of some experimental factor, ie as the calcination temperature, contact time, pH, ratio adsorbent / adsorbate and charge density. The results show that the calcined LDH possessed a very high adsorption capacity, and that the adsorption kinetics of 2.4-D by calcined LDH is fast (equilibrium is reached after 20 minutes of contact). The adsorption isotherm of 2,4-D by calcined LDH is the type *S*. This type of isotherm confirms the weak interaction between the solute molecules and the adsorbent.

Keywords: Layered double hydroxides; Anionic clays ; Synthesis; Marine water; Calcinations; Adsorption; Pesticide; Herbicide 2,4-D.

I. Introduction
The widespread use of pesticides in agriculture is now a reality and manifests a serious threat to medium-term quality of groundwater, thus becoming an important environmental problem. This encourages researchers to find cures due to increased use. Adsorption is one of the mechanisms which decrease solute mobility and thus could be suitable in the control of the fate of pesticides in the environment. Previous researches have used various media for the retention of pesticides. Such as clay [1,2], oxide minerals [3,4], activated carbon [5,6] and varied soils [7,8].

The layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, could be suitable to smooth and even prevent the environmental impact caused by pesticides. These materials have very high exchange capacities, and LDHs are the property of being able to regenerate after calcinations and formation of mixed oxide.

The purpose of this study was to assess the retention of pesticides by LDH prepared from sea water [9]. We focused on remove the anion 2,4-D (2,4-dichlorophenoxyacetic acid) as a model for pollutants herbicides because of its frequent use. In order to determine the proper experimental conditions for the elimination of 2,4-D, we study the influence of several parameters on absorption (calcinations temperature, contact time, pH, ratio adsorbent / adsorbate and the charge density). Thus the use of adsorption isotherms allows the determination of the retention capacity.

II.   Materials and methods

II.1. Materials

The synthesis of Mg/Al–CO$_3$ LDHs (with a molar ratio R = Mg/Al = 2, 3 and 4) was conducted using a constant-pH co-precipitation method. The solutions containing of trivalent metal Al$_2$(SO$_4$)$_3$,18 H$_2$O was added very slowly at a constant rate in a reactor initially composed of sea water containing the divalent metal Mg^{2+} (1294 mg/l). The pH of mixture was maintained at a value of 10 by the simultaneous addition of a (NaOH+Na$_2$CO$_3$) basic solution. After curing for 24 hours, the precipitate was recovered by filtration. The collected precipitate was washed three times with distilled and dried at 60 ° C in oven.

II.2. Adsorption experiments

The quantities of LDH compounds were synthesized starting from marine water, calcined at different temperature. These quantities are suspended in a volume V of a solution of 2,4-D whose initial concentrations varied between 0.08 and 4 mmol/L. The herbicide is suspended under anionic form by adding a few drops of soda at the outset. All the tests were carried out under air atmosphere and at room temperature. The pH of the suspension is adjusted to the desired value by adding sodium hydroxide, and after this contact herbicide with LDH. After filtration, the solid products obtained were dried at room temperature and then analyzed by DRX, IR spectroscopy. The supernatants were recovered and analyzed by UV-visible spectroscopy.

The amount of 2,4-D eliminated by LDH (Q) is calculated as the difference between the initial (C$_i$) and the final (C$_e$) (equilibrium) concentrations of the herbicide in solution by mass of LDH (m) in the volume of solution, V:

$$Q = (C_i - C_e) \, V \, / \, m$$

The solubility of 2,4-D in water is low, it is 0.9 g/L. A solution of 2,4-D with a concentration of 4 mM (which corresponds almost to the maximum solubility of 2,4-D) was prepared, other solutions of different concentrations were obtained by simple dilution.

II.3. Analytical techniques

By X-ray diffraction, and IR spectroscopy, the structural characterizations were performed. The LDH phase of as-synthesized has been identified with XRD patterns were recorded on a Siemens D501 diffractometer with copper Kα radiation. The IR spectra were obtained on a FTIR Perkin Elmer spectrometer using the KBr technique. By UV-visible spectroscopy, the 2,4D concentrations in the filtrates were determined. While the absorbance was measured at 230 nm on a Perkin Elmer Lambda 2S spectrometer.

III. RESULTS AND DISCUSSION.

III.1. X-ray diffraction

The diffractograms of the clays anion synthesized from sea water are presented in Figure1.
The X-ray diffraction peaks correspond to hydrotalcite, with the appearance of a secondary phase CaCO$_3$ (aragonite). By the relation c/3 = 1/2 (d$_{003}$ + 2d$_{006}$) = d$_{interlamellaire}$, the value of interlamellar distance is the order 7.75 Å. This distance is in good agreement with that found in the literature concerning the intercalation of carbonate ion in anionic clay. We found at 500 ° C, that the lamellar structure of HDL calcined is completely destroyed. Only, the lines corresponding to a type oxide MgO and rays corresponding to the phase CaCO$_3$ are observed.
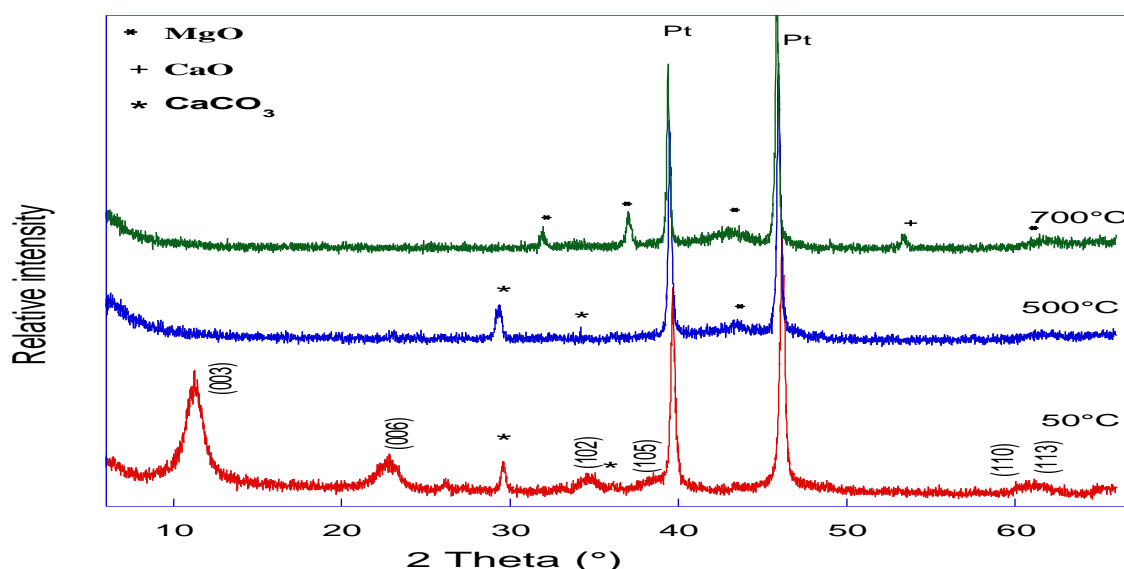
Figure 1: XRD patterns of the LDH phases obtained after different calcinations temperature.

III.2. Infrared spectroscopy

The IR spectra of synthesized anion clays starting from marine water (Figure 2) resemble those of other hydrotalcite-like phases [12,13]. Typical for these spectra are the strong broad absorbance bands between 3600 and 3200 cm^{-1} associated with the stretching mode of hydrogen-bonded hydroxyl groups from both the hydroxide layers and interlayer water. In the lower frequencies, a sharp peak at 1600 cm^{-1} in all the samples can be attributed to the bending mode of interlayer water. It can be seen also the presence of the IR active absorption bands arising from the carbonate anion observed at 1364–1390 (v_3), 855 (v_2) and 685 cm^{-1} (v_4). The main absorption band of the sulphate anions was observed at 1120 cm^{-1} (v_3).
A series of bands are recorded at 450, 560, 799 and 940 cm^{-1} ascribed to $[AlO_6]^{3-}$ condensed groups, Mg/Al-OH translation, Al-OH translation and Al-OH deformation, respectively.
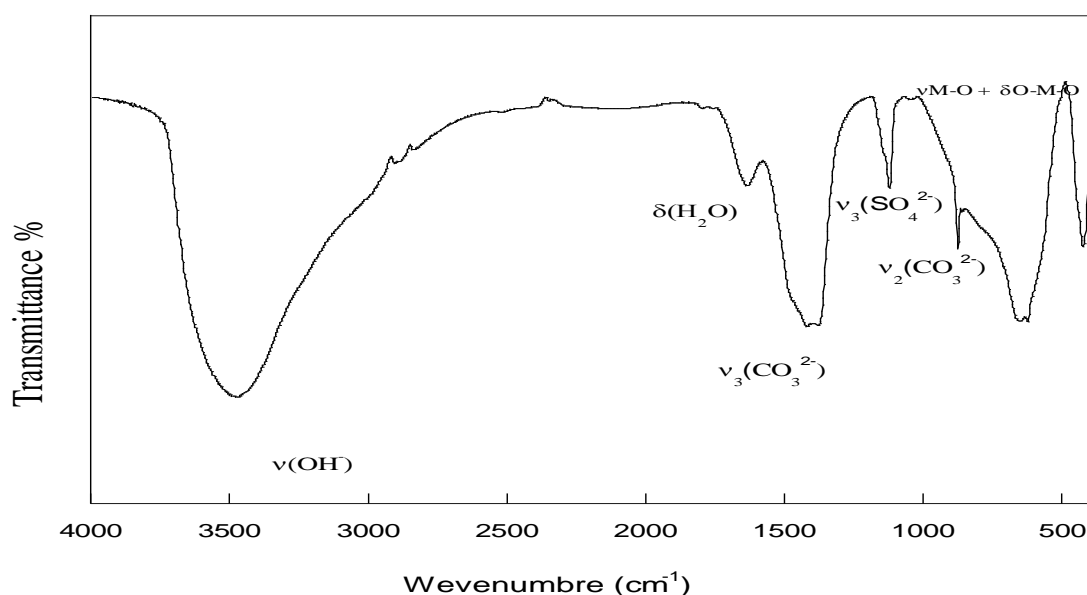

Figure 2: IR spectra of LDH synthesized anion clays starting from marine water

III.3. optimization study of adsorption of 2,4-D on LDH

The study of the influence of parameters on adsorption is needed to determine the proper experimental conditions for the elimination of 2,4-D.

III.3.1. Influence of calcinations temperature

Figure 3 shows the evolution of the adsorption capacity vis-à-vis ion 2,4-D as a function of the calcinations temperature of LDH.

LDH the precursor was calcined in air at different temperature between 200 °C and 800 °C for 16 hours. About 0.2 g of calcined LDH was suspended in 40 ml of a solution of 2,4-D to 2 mmol / L for a contact time of 24 hours. As our goal is to capture such pollutant molecules that can exist in water and knowing that the natural pH of the water in most of the time, between 6 and 7, we proceeded to study at a pH near 6.5.

The maximum amount eliminated 2,4-D is achieved for a calcinations temperature of 500 °C. As highlighted by the evolution of diffractgrams X versus temperature (figure 1). At this temperature the lamellar structure is collapsed [11], and only the lines corresponding to a type oxide MgO and lines corresponding to the phase $CaCO_3$ are observed. Based on these results, we carried out the calcination LDH at 500 °C. This value of calcinations temperature was used by most researchers who have worked with LDH precursors calcined [14,15,16,17].
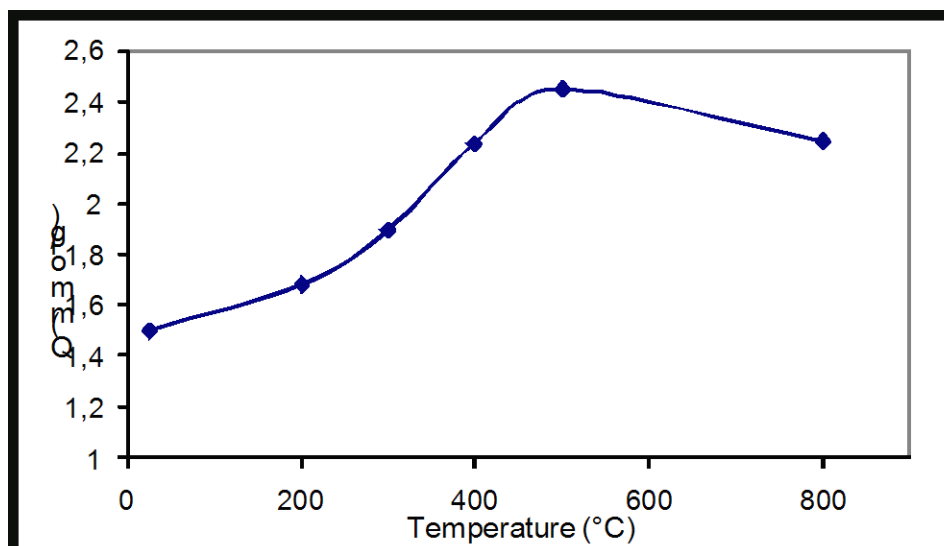

Figure 3: Evolution of the capacity of adsorption with respect to the ions 2,4-D according to the calcination temperature of clay ($C_{Initial}$= 2 mmol/L; $m_{adsorbent}$ = 20 mg; V= 40 ml; neutral pH).

The reconstruction is done by the incorporation of the anion present in the reaction medium. The advantage of such a remediation process is the make it possible, after trapping, to regenerate the anion exchange material by reaction with carbonates in accordance with a further calcination. We can consider several repeated cycles of calcinations, re-hydration and anion exchange.

III.3.2. Kinetic study

The kinetic study was conducted with a mass of 20 mg of LDH calcined at 500 °C, suspended in 40 ml solution of 2,4-D initial concentration of 2 mmol/L.

The results obtained show that the adsorption kinetics of 2,4-D by LDH is very fast and steady state is reached after 20 min (Figure 4). Contact times were obtained by similar Sannino and al. during the adsorption of 2,4-D on montmorillonite [18], and J. Inacio and al during the adsorption of MCPA on Mg_3AlCl [19].
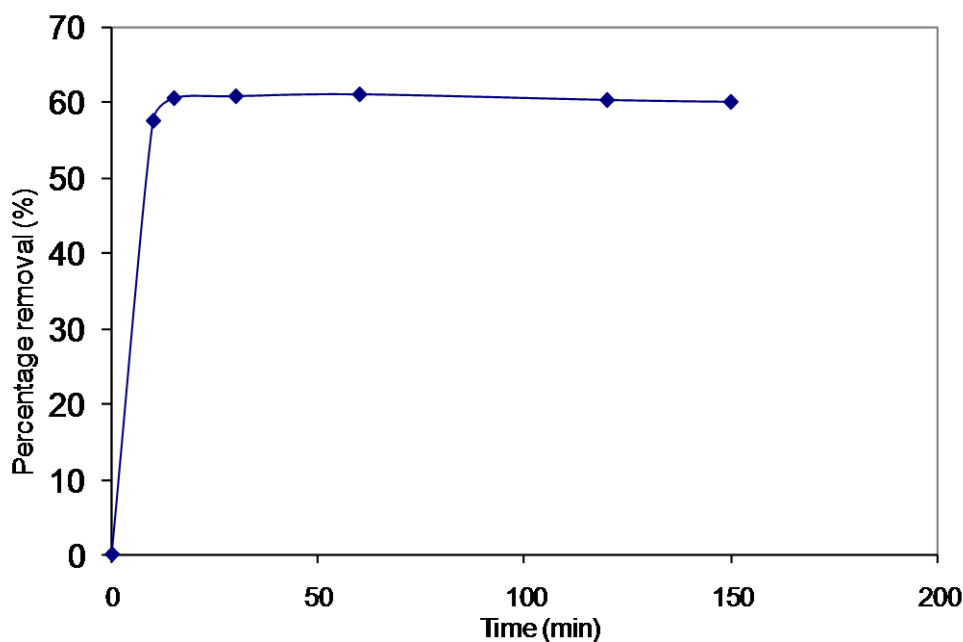
Figure 4: Kinetic study of the adsorption of 2,4-D on LDH calcined at 500 °C. ($C_{Initial}$= 2 mmol/L, $m_{adsorbent}$=20 mg, V=40ml, neutral pH.

In most cases, adsorption or desorption of organic compounds by clays proceeds in two stages: a first stage is fast, and then the next is slower.

The kinetics of adsorption is usually controlled by the rate of molecular diffusion and the activation energy of the reaction at the solid - liquid in the pores. The adsorption reaction and the diffusion processes are relatively rapid processes across the interface but still slower accessibility small pore diameters (micro- or mesopores).

In the remainder of this work, we used a contact time of 2 hours to ensure that the state of adsorption equilibrium is reached.

III.3.2.1. Determination of kinetic constants of adsorption of 2,4-D

The rate of retention of the herbicide 2,4-D is one of the primary characteristics in determining the efficiency of adsorption. The adsorption kinetics can be studied using the kinetic equations of first order so-called Lagergren (1898) (eq1) [20] and second order (1995) (eq 2) [21,22]:

$$\text{Log } (q_e\text{-}q) = \text{Log } (q_e) - \frac{K_{1,ads}}{2,303} \, t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{K_{2,ads} \times q_e^2} + \frac{t}{q_e} \tag{2}$$

where :
- q_e and q_t (mM / g) are the amounts of 2,4-D respectively adsorbed at equilibrium and at time t , in minutes.
- $K_{1, ads}$ (min^{-1}) adsorption rate constant of first order.
- $K_{2, ads}$ (g / mM / min) adsorption rate constant of second order.
The linearity of variation of t / q_t with t indicates the validity of this equation, and therefore shows that the process follows a second-order kinetics. The rate constant of adsorption of 2,4-D by LDH calcined $K_{2\,ads}$, is deducted from the curve $t / q_t = f (t)$ (Figure 5). The results are shows in Table 1.

Table 1: kinetic constants of adsorption.

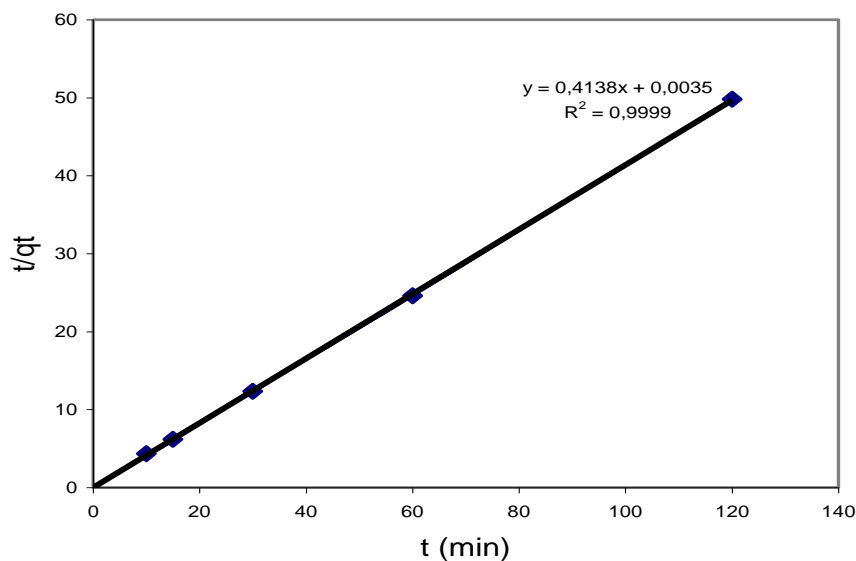| $K_{2,ads}$ (g/mM/min)	q_e (mM/g)	R^2
48,786	2,42	0,999

Figure 5: Curve of the model of second order for the constants speed of adsorption of 2,4-D on LDH calcined at 500°C.

The values of R^2 show that the reaction involved in the adsorption process of 2,4-D, is the second order. The value of q_e calculated from the slope of the f (t) = t / q_t is the same order of magnitude as that found experimentally.

III.3.2.2. Determination of diffusion rate constants

The intra-particle model has been studied in this work and the model adopted is based on theories developed by Weber and Morris [23]:

$$q_t = k_p\, t^{1/2} + C$$

q_t is the amount adsorbed per unit mass of adsorbent (mg/g) at time t and K_p rate constant for intra-particle diffusion (mg/g.min$^{-1/2}$) and C (mg / g) intercept.
    Figure 6 shows the amount adsorbed as a function of the square root of time. The figure shows the existence of a linear part, corresponding to the region or the intra-particle diffusion is the limiting factor of the adsorption kinetics [24]. From the slope of the linear portion of this curve determines the diffusion constant K_p. While its intercept obtained by extrapolation, is proportional to the thickness of the boundary layer [25].
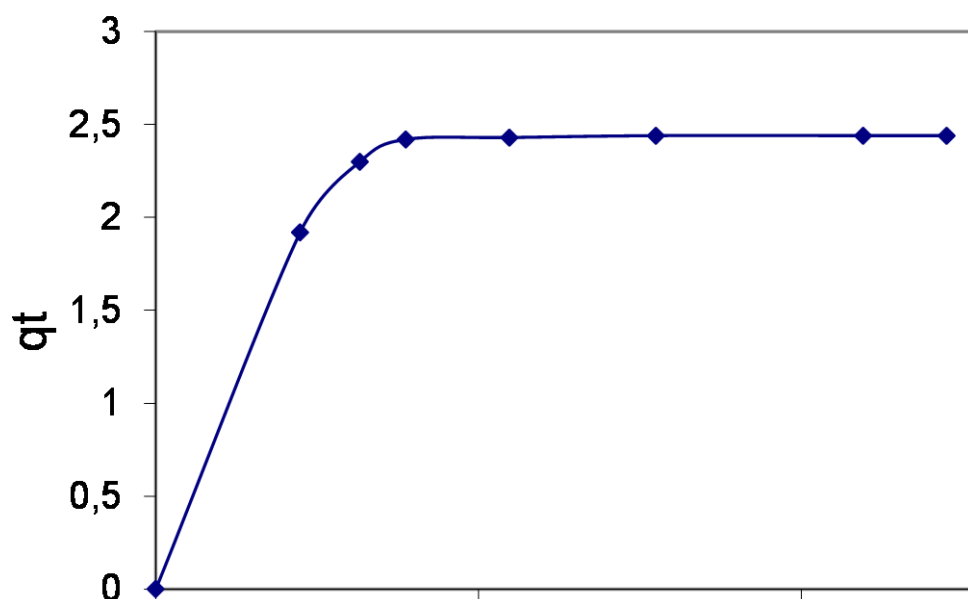
Figure 6: Curve of diffusion intra-particle for the adsorption of 2,4-D by LDH calcined at 500°C ($C_{Initial}$= 2 mmol/L, $m_{adsorbent}$=20 mg, V=40ml, neutral pH.

III.3.3. Influence of pH

The influence of pH on the retention phenomenon was examined using 20 mg of calcined LDH and a solution concentration of 2 mmol/L 2,4-D. Then the suspensions were adjusted to initial pH values between 5 and 9. The results of retention of 2,4-D by LDH calcined at various initial pH are given in Table 2.

Table 2: Adsorption of 2,4-D on LDH calcined at 500°C with different pH ($C_{Initial}$= 2). mmol/l, adsorbant=20 mg, V=40ml)

| pH initial	pH final	Q	%
5	10	2,18	54,5
6	10	2,44	61
7	10	2,42	60,5
9	10,5	2,26	56,5

We note that there is maximum retention for pH values between 6 and 7. For pH values below 7, the decrease in the retention of 2,4-D can be attributed to a dissolution of the matrix by hydrolysis.

For pH = 9, contamination by carbonates is obviously causing of the decrease in retention. There is a competition between the anions carbonate and organic molecules for accessibility to the hydroxylated surface [19].

The following experiments in this work will be performed at a pH between 6 and 7, while knowing that such a value of 2,4-D is in anionic form in aqueous solution (pK_a = 2.64).

We note that the final pH of the solutions is always higher than the initial pH of the solutions. Such effects have been reported by other authors on the sorption of organic pollutants (2,4-D, MCPA, and Picloram, ...). I Pavlovic and al., and LP Cardoso and al. [26,27], could be justified by the fact that the materials LDH, during the rehydration process, release of OH-ions. This results an increase in solution's pH.

So in addition to adsorption processes on the external surface, there is also a process of intercalation of anion, during the reconstruction of the interlayer domain, according to the following mechanism:

$Mg_{1-x} Al_x O1 x / 2$ (x) x-(1 (x / 2)) → H_2O [$Mg_{1-x} Al_x (OH)_2$] (x) XOH-x

Where X is the anion intercalated.
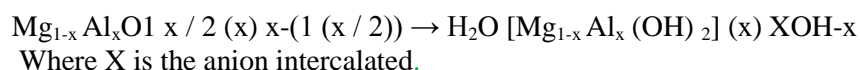
III.3.4. Influence of the Mg/Al ratio

Figure 7 shows the variation of adsorbed amount of 2,4-D as a function of molar ratio Mg/Al (R = 2, 3, 4). In these measurements, 20 mg of LDH have been suspended for 24 hours in 40ml of solution of 2,4-D. From this figure we see that the adsorption capacity as well as the affinity of the anion 2,4-D for LDH increases when the charge density increases.

This result is a consequence of decreasing of the metal ratio Mg / Al. The amounts of 2,4-D retained by the sorbent is higher than their anionic exchange capacity, it may be possible that the intercalation is in the form of multilayers between the sheets of LDH.
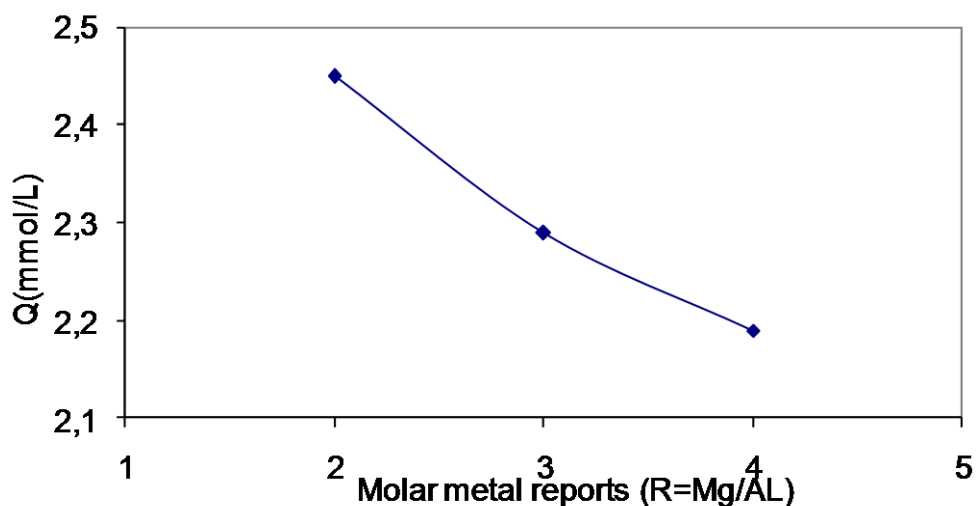

Figure 7: Quantity of the 2,4-D retained by 20 mg of LDH calcined at 500°C for various molar metal reports Mg/Al (R = 1,2,3) ($C_{Initial}$= 2 mmol/L, $m_{adsorbent}$=20 mg, V=40ml, neutral pH).

III.3.5. Effect of adsorbent mass

The evolution of the retained quantity of 2,4-D as a function of the mass of the calcined LDH is shown in Figure 8.
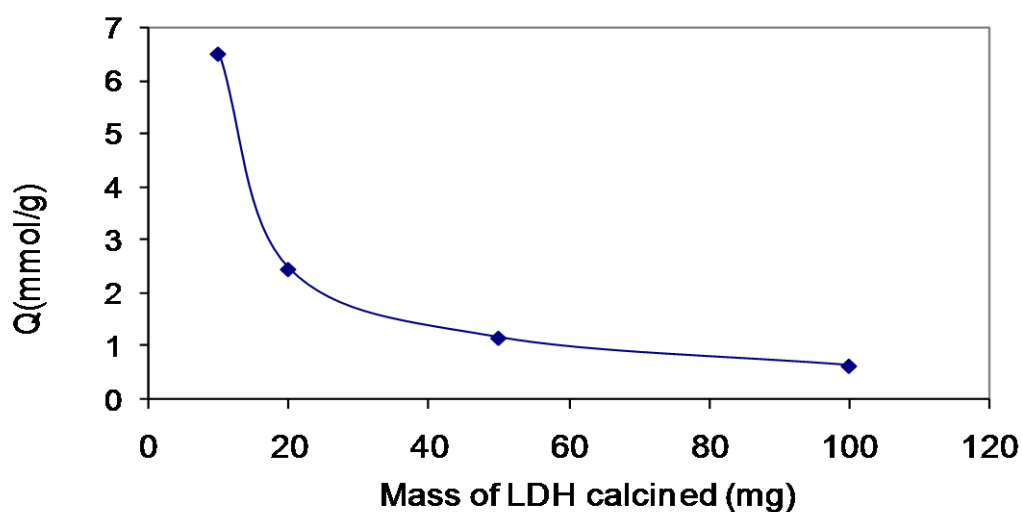

Figure 8: Quantity of 2,4-D retained according to the mass of LDH calcined at 500°C (Mg/Al = 2, $C_{Initial}$= 2 mmol/l, V=40ml, neutral pH).

As can be seen from this figure, the ratio solid / liquid is low. This favours the retention of 2,4-D. Also, an increase in the amount of adsorbent causes agglomeration of particles thus reducing surface contact with the adsorbent. This aggregation does not promote the accessibility of organic molecules on the surface [28,29]. For this, we decided to use a solid / liquid ratio low to be in the optimum conditions for trapping a maximum of 2,4-D.

III.3.6. Influence of initial concentration of 2,4-D

Figure 9 shows the influence of the initial concentration of 2,4-D on the retention phenomenon of 2,4-D on LDH calcined at 500 °C. As the initial concentration of 2,4-D increases from 0.2 to 4 mM, the residual concentration increases and the adsorbed amount and the percentage adsorption decreases.

The adsorption isotherms of 2,4-D by LDH calcined is shown in Figure 10. This isotherm is of type *S* according to the classification of Giles then modelled by the Freundlich equation (Table 3) [30]. For small value of the solute's concentration, the adsorption increases gradually then by an abrupt increase when the values of concentrations grow. This type isotherm is observed when, in the presence of weak interactions between molecules of solute and adsorbent. This would involve hydrogen bonds between the carboxylic function of the pesticide and the hydroxyl groups or oxygen atoms of the layers. The shape of the curve also reflects strong competition between the solute and solvent or other species present on the surface adsorption sites [31].
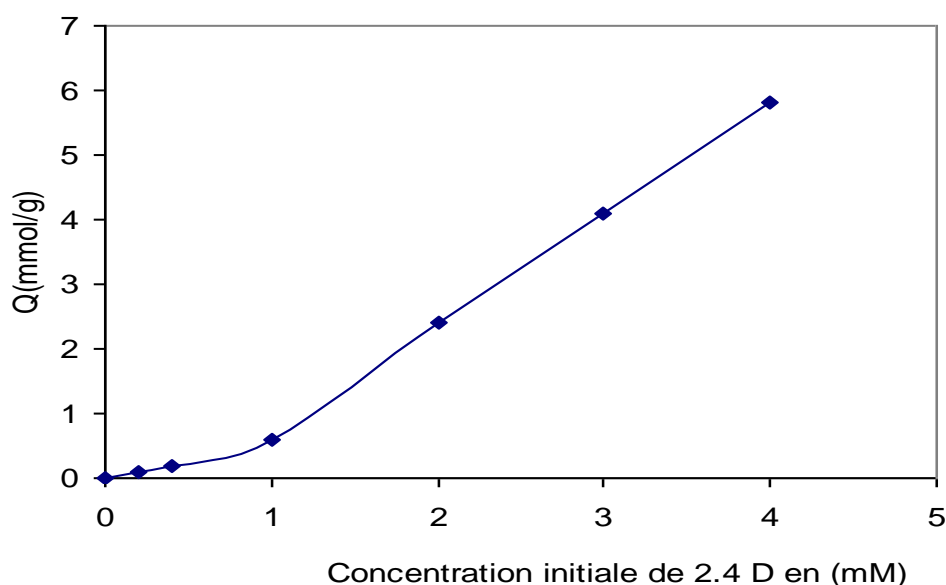

Figure 9: Quantity of 2,4-D retained according to the initial concentration of 2,4-D (Mg/Al = 2, $m_{adsorbent}$=20 mg,V=40ml, neutral pH).

In 2002, You and Zhao have obtained this type of isotherm for adsorption of the herbicide Dicamba on Mg-Al-CO_3 calcinated [32]. Thus in 2009, J. S. Valente and al. have obtained for adsorption of 2,4-D on Mg-Al-CO_3 calcinated [33].

The realization of organo-clays can increase the clays adsorption capacity by modifying the properties hydrophyles - hydrophobic subject of clay. Thus moderate attraction (physical absorption) between the aromatic groupings and other species present in solution makes that adsorption becomes easier whereas the concentration in 2,4-D increases.

The isotherm is modelled by the Freundlich's equation. The capacity of adsorption and the coefficient of affinity are given starting from the curved log (Q) in function log (C_e) (Figure 11), and the results are represented in table 3.
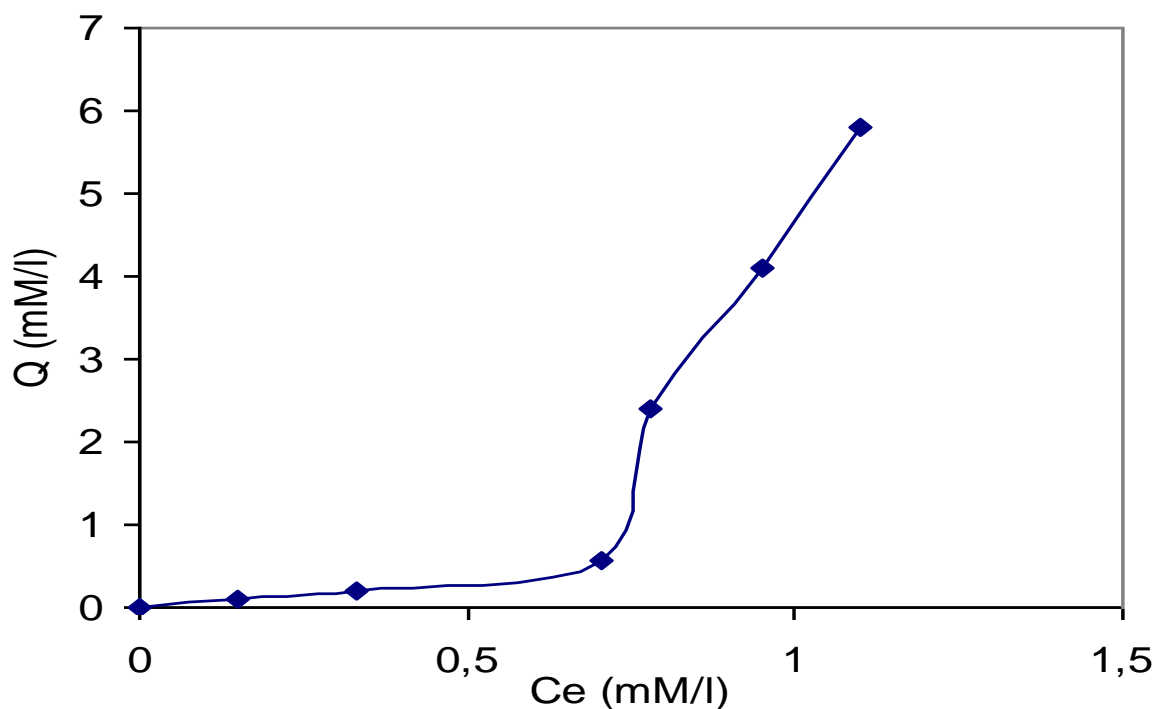
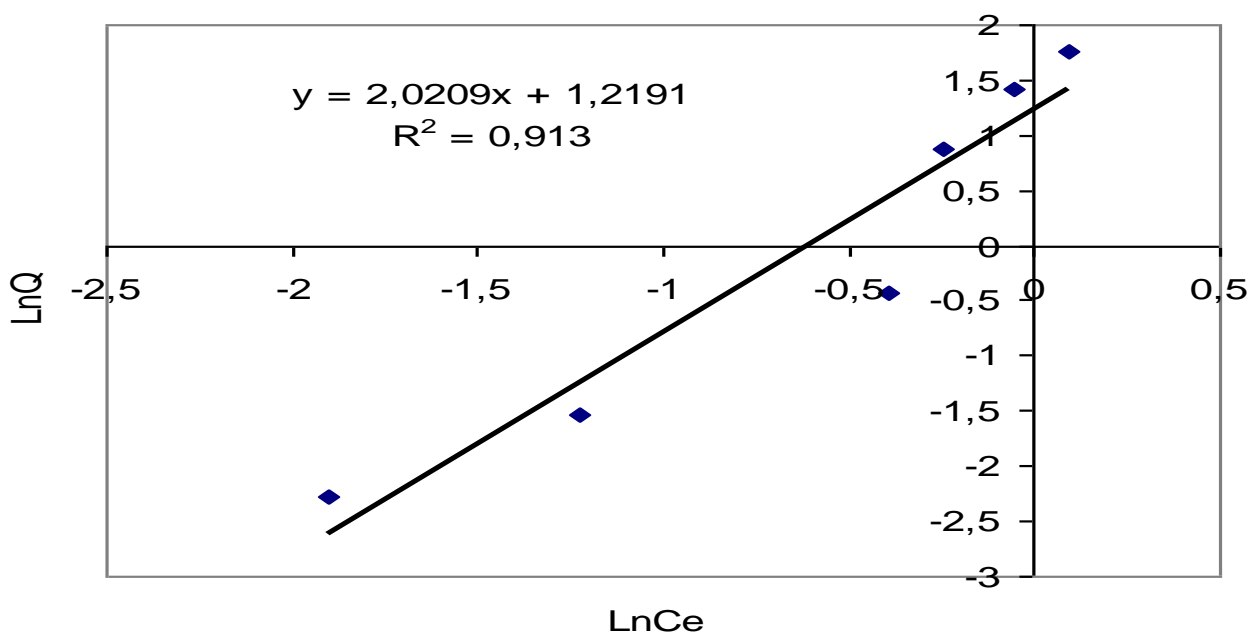Figure 10: Isotherm of adsorption of 2,4-D on calcined LDH.

Figure 11: Linear transform of the isotherm of Freundlich.

In the spectrum of the LDH synthesized anion clays starting from marine water of 2,4-D is given in Figure 12. The characteristic bands of the organic anion are observed on all spectra along side the absorption bands of the hydroxylated layers, confirm that the pesticide is adsorbed in LDHs in its anionic form [34].

Table 3: parameters of Freundlich for the retention of 2,4-D by LDH.

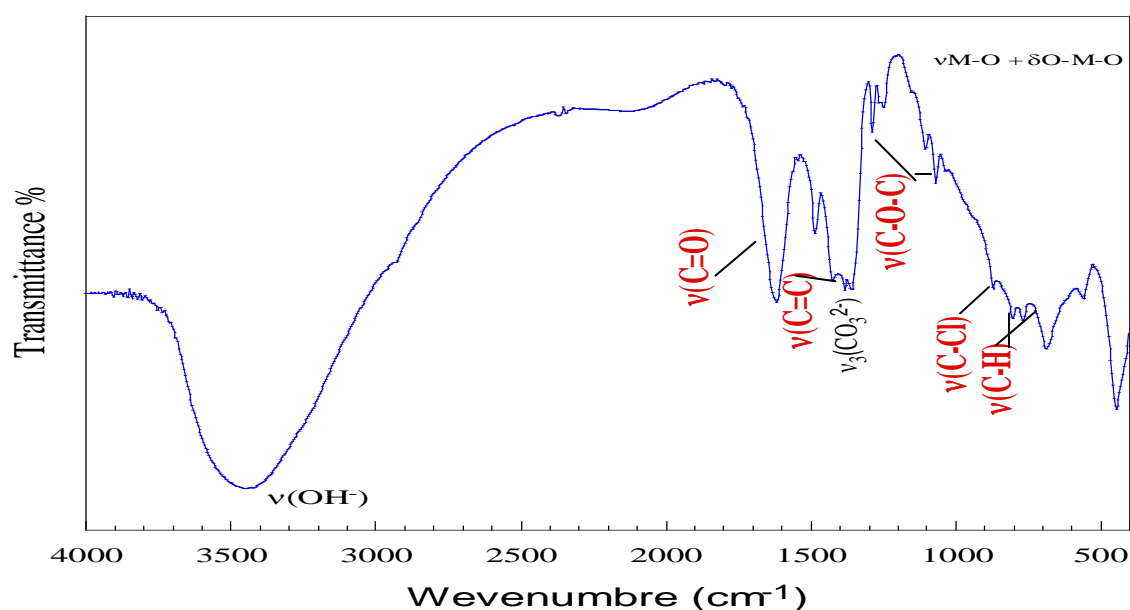| K_f (mmol/g)	n_f	r^2
3,384	0,50	0,913

Figure 12: IR spectra of LDH obtained after retention of 2,4-D

Conclusion

We used in this study LDH in the process of removing organic pollutants: the herbicide 2.4-D.The adsorption of the herbicide and its affinity for clays are a function of interactions adsorbate / adsorbent interactions but also adsorbate / solvent. Other parameters also influence the adsorption process. We have seen that the adsorption capacity of calcined LDH and its affinity to-2.4-D herbicide depended on the calcination temperature, pH, density of charge on the sheets, also report adsorbent / adsorbate.

The calcined LDH have higher adsorption capacities starting precursors. The results obtained show that the adsorption kinetics of 2.4-D by calcined LDH is fast (equilibrium is reached after 20 minutes of contact) and adsorption tests were carried out in aqueous medium at pH 7 for which the herbicide 2,4-D is in anionic form.

The adsorption isotherm of 2,4-D by calcined LDH type S. This type of isotherm suggests weak interactions between the solute molecules and the adsorbent and the shape of the curve also reflects strong competition between the solute and solvent or other species present on the surface adsorption sites.

References

1. Draoui, K., Denoye, R., Chgoura, M., Rouquerol, J., *J. Thermal Anal* 51 (1998) 831.
2. Legrouri, A., Lakraimi, M., Barroug, A., De Roy, A., Besse, J. P., *Water Research* 39 (2005) 3441.
3. Waston, J. R., Posner, A. M., Quirk, J. P., *J. Soil S* 24 (1973) 503.
4. Kavanagh, B.V., Posner, A. M., Quirk, J. P., *J. Soil Sci* 31(1980) 33.
5. Beltran, J., Hernandez, F., Lopez, F. J., Morell, T., *Int.J.Environ. Anal.Chem* 58 (1995) 287.
6. Belmouden, M. Thése de Doctorat, Université IbenZohr, Faculté des Sciences, Agadir (2000).

7. Inacio. J., Thèse de l'université Blaise   Pascale, Clermont- ferrand (2002).

8. Boivin, A., Amellal, S., Schiavon, M., Th. M., Genuchten, V., *Environmental Pollution* 138 (2005) 92.

9. Sadik, N., Sabbar, E., Mountadar. M., *Phys. Chem. News* 51 (2010) 122.

10. Reichle, W.T., *Solid State Ionics* 22 (1986) 135.

11. Roelofs, J. C. A. A., Bokhoven, J. A. V., Dillen, A. J. V., Geus, J.W., De Jong, K. P., *Chem. Eur. J* 8 (2002) 5571.

12. Zhang, L., Feng, L., Evans, D. G., Duan, X., *Mater. Chem*. Phys 87 (2004) 402.

13. Benito, P., Labajos, F.M., Rocha, J., Rives, V., *Micropor. Mesopor.Mater* 94 (2006) 148.

14. Sato. T., Okuwaki. A., *Solid State , Ionics* 45(1991) 43.

15. Bruna, F., Celis, R., Pavlovic, I., Barriga, C., Cornejo, J., Ulibarri, M.A., *Journal of Hazardous Materials* 168 (2009) 1476.

16. Lazaridis, N. K., Asouhidou, D. D., *Water Research* 37 (2003) 2875.

17. Lakraimi. M., Thèse d'Etat de l'Université Cadi Ayyad, Marrakech (2002).

18. Hermosin, M. C., Cornejo, J., *Chemosphere*, 24(1992) 1493.

19. Inacio, J., Taviot-Guého, C., Forano, C., Besse, J. P., *Applied Clay Science* 18(2001) 255.

20. Lagergren, S., Zur Theorie der sogenannten Adsorption gelostn. Stoffe. Stcok. k. Handl.Bihay. 24 (Afd. 1) (1898) 39.

21. Ho, Y. S. PhD Thesis, Birmingham,UK, University of Birmingham. (1995).

22. Ho, Y. S., Mckay, G., *Water Res*., 34(2000) 735.

23. Weber, W. J., Morris, J. C., *J. Sanit. Eng. Div. ASCE* 89(1963) 3.

24. McKay, G., Poots, V.J.P., *J.Chem. Tech. Biotech* 30 (1980) 279.

25. Panday, K.K., Gur, P., Singh, V.N., *Water Research* 19(1985) 869.

26. Pavlovic, I., Barriga, C., Hermosı´n, M.C., Cornejo, J., Ulibarri M.A., *Applied Clay Science* 30 (2005) 125.

27. Cardoso, L.P., Valim, J.B., *Journal of Physics and Chemistry of Solids* 67 (2006) 987.

28. Gorover, R., Hance, R., J. Soil Sci., 109 (1970)136.

29. Inacio, J. Thèse de l'université Blaise Pascale, Clermont- ferrand (2002).

30. Giles, C.H. MacEwan, T.H., Nakhwa, S.N., Smith, D., *J. Chem.Soc*. 3973 (1960).

31. Tzompantzi, F., Valente, J.S., Cantu, M.S., Gomez, R. in: S.R. Schmidt, (Ed.), Catalysis of Organic Reactions, CRC Press Taylor and Francis Group, Florida, 55 (2007).

32. You, Y., Zhao, H., Vance, G.F., *Applied Clay Science* 21(2002) 217.

33. Valente, J. S., Tzompantzi, F., Prince, J., Cortez, J. G.H., Gomez, R., *Applied Catalysis B: Environmental* 90 (2009) 330.

34. Lakraimi, M., Legrouri, A., Barroug, A., De Roy, A., Besse, J.P., *J. Mater Chem* 10 (2000)1007.

(2012) http://www.jmaterenvironsci.com/