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Removal of some pesticides from water using new synthesized apatitic materials

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ABSTRACT

In order to minimize the negative impact of pesticides on the ecosystem, the search of host solid matrix that can trap micro pollutants (heavy metals, pesticides…) is necessary. In this sense, we have synthesized the carbonated phosphocalcics poorly crystallized apatites, analogous to biomaterials (teeth, bones), and which served as an adsorbent for pesticides. The objective of this work is therefore based on the retention of the two pesticides, dicofol and trifluralin, by the apatitic materials cited above. Adsorption of these pesticides in selected apatites was investigated under butch experiments. The concentration of adsorbed pesticides was followed using scintillation counting method. The adsorption isotherms were found to better, described by the linear Freundlish equation. The retention mechanism of these two pesticides by apatitic materials was monitored via infrared spectroscopy.

Keywords: apatites, pesticides, adsorption, desorption, UV-VIS, IR, liquid scintillation.

INTRODUCTION

The transition from an extensive agriculture to an intensive agriculture compelled the agriculturists to the massive utilization of pesticides. Indeed the research of a good production makes these products indispensable to protect cultures against all aspects which could limit or prevent their development. However though today blamed, pesticides are potentially poisonous for no target organisms, including plants and animals. For example, dicofol and trifluralin present an important interest owing to their utilization in the agricultural zones of beets and cereals in Morocco **[1].**

In order to minimize the risk of these pesticides, we have used some of the apatitic materials which we have utilized in the treatment of industrial liquid effluents charged with heavy metals or pesticides **[2, 3]**. The objective of this work is then based on the study of the adsorption phenomenon of dicofol and trifluralin by synthetic poorly crystallized apatites. The cristallinity of some apatites was studied in our laboratory in previous works **[4,5,6].** This study is an extrapolation from that obtained in our previous work, where we have also successfully studied the retention of the some pesticides (imazapyr, atrazine, dicofol…) with apatitic materials to remove these phytosanitary compounds from water **[2,7,8].**

MATERIALS AND METHODS

2 - Experimental methodology:

2-1 - Preparation of apatitic materials:

The poorly crystalline apatites with vacancy and analogous to the biomaterials were prepared by the freeze-drying method which has been described in our previous work **[4,5,6].**Their general formula is given by: $Ca_{10-x}(PO_4)_{6-x}(CO_3)_x(Y)_{2-x}\square_x$ with: $Y=F^-$ (fluorapatite) or $y=OH^-$ (hydroxyapatite) and □ = vacancy. These two categories of apatite materials were used respectively for adsorption studies of dicofol and trifluralin. In the following text,these

apatites will be denoted simply by fluorapatite ($Y=F^-$) and hydroxyapatite ($Y=OH^-$).

2-2 - Adsorption kinetics:

- Case of dicofol:

0.5 g of fluorapatite ($Y = F^-$) is mixed in 10 ml of a hexane solution containing varying concentrations of dicofol at 20 °C with mechanical stirring. After filtration, the determination of dicofol in the filtrate was carried out using UV-VIS spectroscopy **[9].**

- Case of trifluralin:

To determine the kinetics of adsorption, 0.5 g of hydroxyapatite ($Y = OH^-$) were suspended in 5 ml of trifluralin in glass centrifuge tubes of 16 ml. To achieve the adsorption kinetics, tubes are stirred with a stirrer rotating at a constant temperature room at 20 ± 1 °C for 0,15, 30 minutes, 1, 2, 4, 8 and 16 H. After stirring, the solid and liquid phases are separated by centrifugation at 6000 g during 30 min **[10]**.

The radioactivity of the filtrate is measured on an aliquot of 1 ml in the presence of 10 ml of scintillate (Ultima Gold, Packard) by liquid scintillation. The amount adsorbed by apatite product is then calculated taking into account the difference in radioactivity by reference to the initial solution **[10]**.

2-3 - Adsorption isotherm:

The adsorption isotherm of dicofol and trifluralinis carried out analogously to the adsorption kinetics with an equilibrium time set from the latter.

3 - Experimental Results and discussion:

3-1 – Study of dicofol:

We have studied the adsorption kinetics by fluorapatite ($Y=F^-$) in two concentrations of dicofol. The supernatant was analyzed after 2.5, 10, 20, 80 and 150 min of agitation. Figure 1 shows that the equilibrium is reached after only 20 min of stirring.

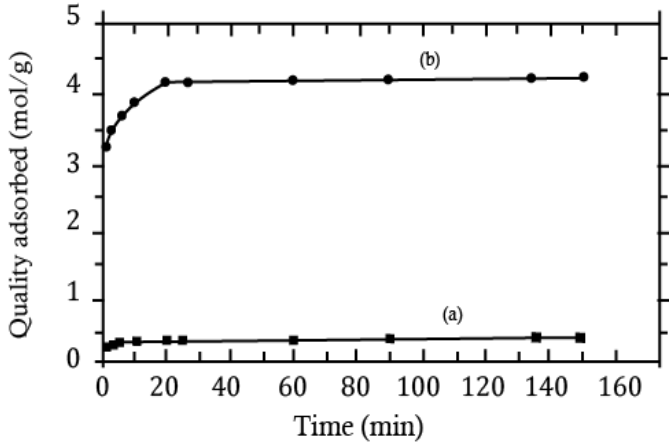


Figure 1 : Adsorption kinetics of dicofol, for two concentrations: (a) $2.1.10^{-4}$M (b) $2.9.10^{-3}$M, in fluorapatite ($Y = F^-$)

The plot of the adsorption isotherm of dicofol in the apatite was performed after 20 minutes following initial concentrations: 212, 297, 594 and 1050 mg / l (Figure 2). This result indicates that the model of Freundlich isotherm perfectly describes the adsorption. Indeed, the Freundlich adsorption isotherms can be described by the following equation (11):

$$\frac{x}{m} = K_f\, Ce^{1/nf}$$

With:

$\frac{x}{m}$: amount adsorbed of dicofol per unit mass of apatite µg / g

Ce: the concentration of the pesticide in the aqueous phase (µg / ml solution) at equilibrium.

K_f and n_f: Freundlich constants, which characterize the isotherm adsorption.

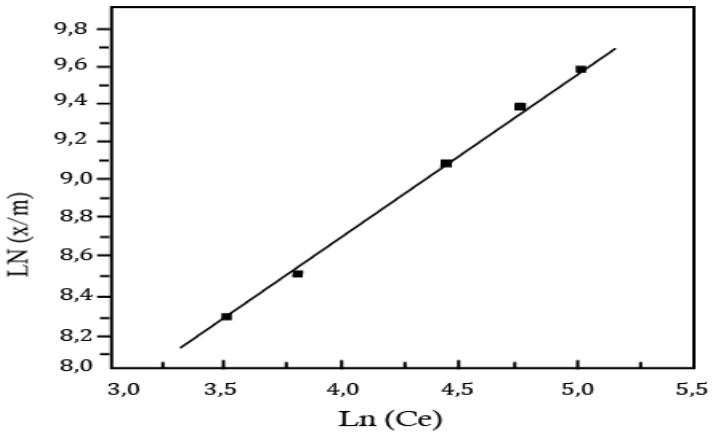


Figure 2: Adsorption isotherm of dicofolin fluorapatite (Y = F^-)

From the experimental values of Ce and X / m, we calculated using the linear regression the values of K_f and $1/n_f$ (Table 1).

Table 1: Parameters of Freundlich adsorption isotherm of the dicofol by fluorapatite (Y = F^-)

K_f	$1/n_f$	r^2
115,7	0,988	0,994

Value $1/n_f$ is close to unity, indicating a linear course of the adsorption isotherm of dicofol in fluorapatite (Y = F^-), reflecting a constant distribution of the solute between the adsorbent and the solution. The adsorption coefficient K_f is a high value which reflects a significant adsorption capacity of apatite for dicofol. In conclusion, this apatite matrix seems to be suitable for the adsorption of this pesticide from water.

The fluorapatite (Y = F^-) obtained after fixation of dicofol at different stirring times, is dried in the open air and analyzed by IR spectroscopy. This technique is a good tool to show the sites of fluorapatite (Y = F^-) of the dicofol adsorption. The IR spectra of fluorapatite (Y = F^-) with different adsorption times (Figure 3) show the presence of the band at 633 cm^{-1}. This band can be assigned to the vibration of OH^- ions in fluorapatite (Y = F^-). Its intensity significantly increases from 5 min to 20 min of stirring time. Consequently, the increase in the intensity of this band during the adsorption of dicofol in fluorapatite (Y = F^-) could then be due to the incorporation of the hydroxyl group (OH^-) of dicofol in the channels of this apatite and also generating the interactions type between F^- of fluorapatite and HO^- of dicofol or into apatitic F^- vacancies. Scheme 1 shows the developed formula of dicofol with the hydroxyl (OH).

The other bands present in the IR spectrum (Figure 3) are assigned to the vibration of the phosphate ions (PO_4^{3-}) and carbonate (CO_3^{2-}) [6,9].

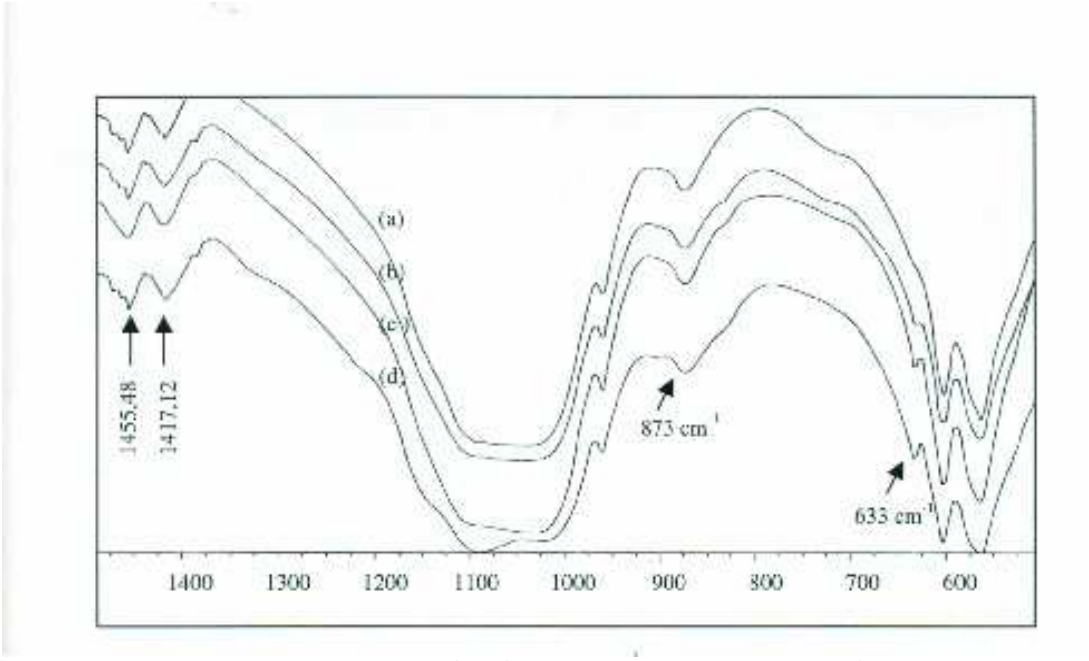
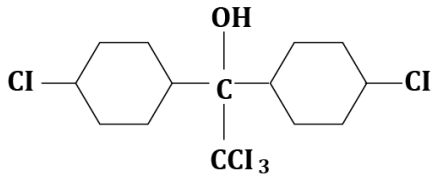


Figure 3: IR spectrum adsorption of dicofol, with stirring time periods:(a) pure fluorapatite (Y = F^-) (b) 5 min, (c) 10 min and (d) 20min.



Scheme 1: developed formula of the molecule dicofol

3-2 – Study of trifluralin:

The adsorption kinetics is shown in Figure 4 where observed maxima and minima with a relatively intense adsorption during about one hour and followed by a marked drop at time
(t = 2 hours). Equilibrium is reached after eight hours.

The evolution of the adsorption kinetics presents the phenomenon called "overshoot phenomenon" [10], which could be attributed to the significant changes of the apatite in contact with the aqueous solution of trifluralin. There is then a competition between the herbicide and water with respect to the adsorbent.

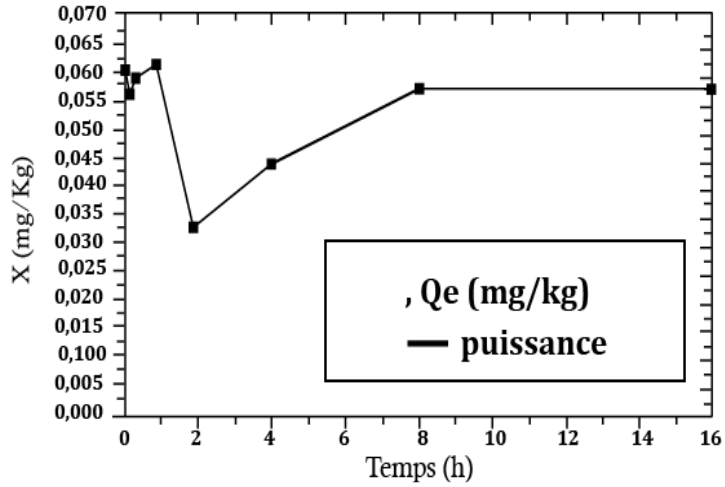


Figure 4: Adsorption kinetics of trifluralin in hydroxyapatite (y = OH^-)

The adsorption isotherm of trifluralin by the hydroxyapatite (y = OH^-) (Figure 5) has a linear curve. The Freundlish model described by the equation also represents it:

$$\frac{x}{m} = K_f Ce^{1/n}$$

The results of adjusted K_f and $1/n_f$ values are given in table 2.

Table 2: Parameters of Freundlich adsorption isotherm dicofol by hydroxyapatite (y = OH^-)

K_f	$1/n_f$	r^2
7,978	0,904	0,998

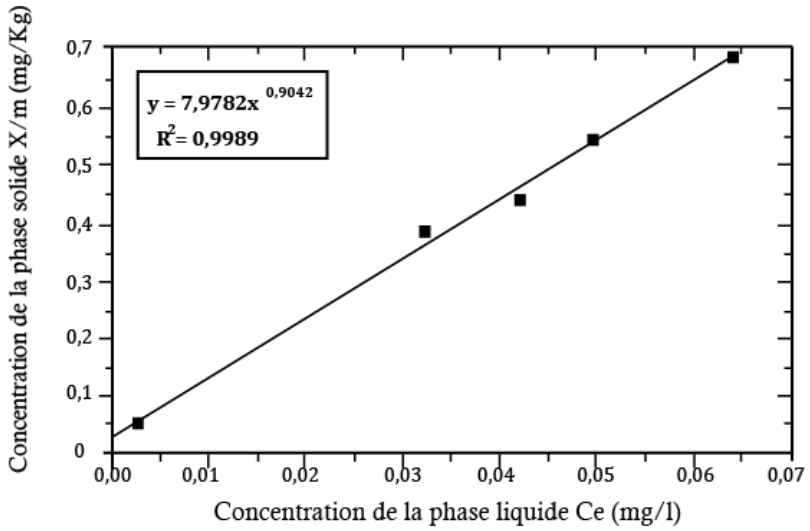


Figure 5: Isothermal adsorption of trifluralin in hydroxyapatite (y = OH^-)

According to the Freudlish model, the adsorption isotherm shows that trifluralin adsorption constant K_f is of the order of 7,978, which suggests that the apatite matrix has a significant adsorption capacity for the trifluralin. The mechanism of adsorption of trifluralin in this apatite can be predicted by IR spectroscopy. This technique is used to specify the mechanism of interaction between trifluralin and hydroxyapatite (Y = OH^-). Figure 6 shows the IR spectra of the apatite with and without trifluralin. The analysis of the IR spectra (Figure 6-b) shows that the bands located around 630 and 3560 cm^{-1} are in fact due to the OH groups of this hydroxyapatite. These two bands disappear almost completely when the trifluralin solution is brought into contact with this apatite (Figure 6-a). This suggests that the fluoride ion of trifluralin (Scheme 2) could interact with the OH^- ions of the hydroxyapatite. It can be suggested that the fluoride ions of this pesticide tend to partially replace the OH^- ions on the surface of the tunnel of this apatite or into apatitic OH^- vacancies.

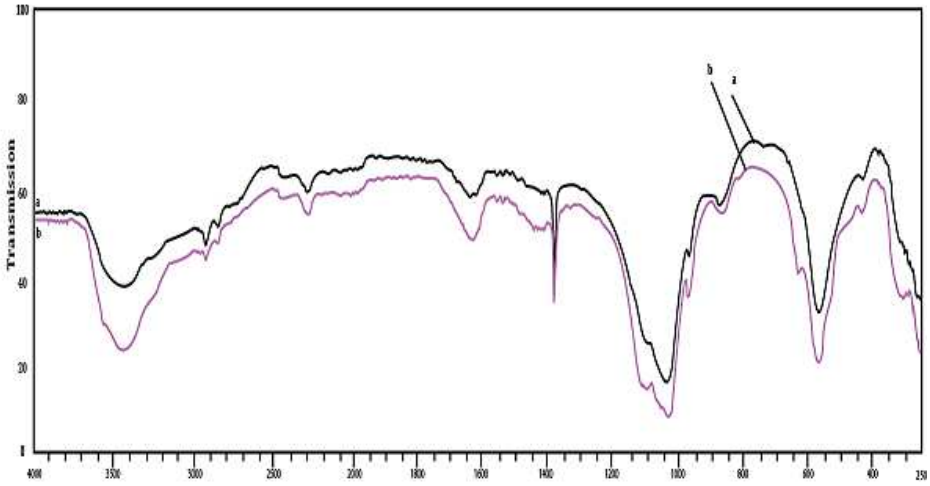
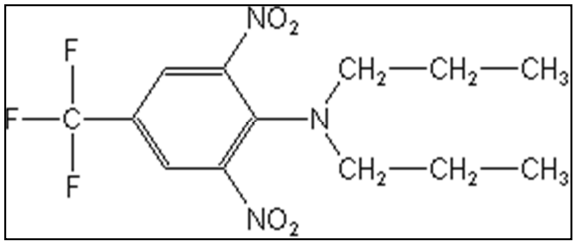


Figure 6: IR adsorption: (a) with trifluralin (b) without trifluralin(pure hydroxyapatite (y = OH^-)



Scheme 2: Developed formula of the trifluralin molecule

CONCLUSION

In this work, we have shown, using adequate two spectroscopic methods (UV and IR) and liquid scintillation that the poorly crystalline apatites analogous to biomaterials (teeth, bones) can be used as adsorbents of dicofol or trifluralin. These apatites are then able to catch micro-pollutants (pesticides, heavy metals…) to decontaminate the water.

With reference to previous Works in apatitic biomaterials [12, 13, 14], this study may have biological implications because it is also known that pesticides exist in trace amounts in both surface water and groundwater. So, these phytosanitary compounds can cause negative adverse effects on human and animal health. Indeed, they can be easily absorbed by human young bones and teeth, via water, fruits, cereals, and meat.

REFERENCES

[1] M. El AzzouziA.Dahchour, A.Bouhaouss. *Weed Research*, vol.38, p.217 (**1998**)
[2] A.Bensaoud, M.ElAzzouzi, E.Mechrafi, A.Bouhaouss, *Fresenius Environ. Bull*, Vol.8, p. 486 (**1999**)
[3] A. Bensaoud, T. Marghich, N. Elhrech, M. El Moussaouti, A. Bouhaouss, *Ann. Chim. Mater*.;vol. 25; p.103 (**1999**).
[4] A.Bouhaouss, A.Bensaoud, M.ElAzzouzi, M.Ferhat, *Phos.Res.Bull*. vol.11, p. 75 (**2000**)
[5] A. Bensaoud, A. Bouhaouss, *Phos.Res.Bull*. vol.10, p. 289 (**1999**)
[6] A.Bensaoud, Doctorat, Université Mohammed V- Agdal –Rabat/Morocco (**2000**).
[7] A.Bouhaouss, A, Bensaoud, M. El Azzouzi, C.P.Ganier, M.Schiavon, *Phys.Chem.News*, vol.1, p.115 (**2001**)
[8] K. Aboufadl, A, Bensaoud, K. Elkacemi, M. El Azzouzi, A. Bouhaouss, M. Schiavon ; Fresenius *Environ. Bull*, Vol 10 ; N° 2 : P. 174 (**2001**).
[9] K.Aboulfadl, Doctorat, Université Mohammed V- Agdal – Rabat/Morocco (**2001**).
[10] E.Mechrafi, Doctorat, Université Mohammed V- Agdal – Rabat/Morocco (**2002**).
[11] M.A.Luke, M.T.Masumoto, T.Cairns, M.K.Hundley, *J.Assoc.offAnal.Chem*, vol.71, p.415 (**1988**).
[12] O. Suzuki, Y. Yagishita, T.Amamo, and T. Aoba, *J.Dent.Res*. vol.74, N°11, p. 1764 (**1995**)
[13] E.I.F. Pearce, *Calcif. Tissue Int*, vol.33, p.395 (**1981**)
[14] Carole Kérvéran-Moreau, Doctorat National, Université d'Orléans-France (**1998**)