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Calcium phosphates as adsorbents for the controlled release of carbofuran

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Abstract

The synthetic calcium phosphates which could be used as fertilizers were studied as carriers for controlled release of pesticides. In this sense the adsorption and desorption of carbofuran on apatitic tricalcium phosphate (PTCa) and brushite (DCPD) were investigated by using batch mode experiments. The equilibrium adsorption data fitted well to the Langmuir adsorption isotherm. The kinetic study shows that equilibrium is quickly obtained for both phosphates. The thermodynamic evaluation of carbofuran adsorption on both phosphates revealed that the adsorption phenomenon was an exothermic and a physical process. The kinetics of desorption showed that the calcium phosphates employed can be served as supports for the slow release of this mobile pesticide, thus controlling its immediate availability and leaching.

Keywords: Synthetic calcium phosphates; Carbofuran; Adsorption; Controlled release.

1. Introduction

Increasing use of pesticides in agriculture and domestic activities for controlling pests is polluting the environment day by day [1]. The contamination of soils, groundwater and surface water by pesticide is currently a significant concern throughout the world because these compounds are detrimental to both human life and environment [2]. Toxicity of parent pesticides and their degradation products is making these chemical substances a potential hazard. When these pesticides are introduced into the environment through spraying on crops, droplets of pesticides fall on soil, plant and water. While some part of these chemicals stays in the area where it is applied, major part gets transported to various environmental compartments [3]. In order to compensate the losses caused by transport and degradation processes, pesticides are applied to agricultural soils in amounts which greatly exceed those required for control of the target organisms, and the excessive quantities added increase the environmental impact of these compounds on environment [4]. The use of controlled release systems of pesticide has been proposed as a strategy to decrease the environmental impact of pesticides, because they release the agent to the target at a controlled rate and limit the amount of pesticide immediately available for undesirable processes such as runoff volatilization and leaching. Different types of sorbent materials and formulation systems have been proposed for such purpose [5-12].This study suggest the potential use of synthetic calcium phosphates as adsorbents of pesticide for their controlled release. The use of brushite (DCPD) and apatitic tricalcium phosphate (PTCa) has been subjected to considerable attention due to their low cost, ubiquitous occurrence in nature, their availability structure, ionic exchange property, adsorption affinity, their characteristic to establish bonds with organic molecules of different sizes, excellent sorbents for different kinds of amino acids [13], and accordingly have been proposed for removal of heavy metal ions [14], fluoride [15], nitrobenzene [16] and dye [17] and also as drug delivery agents for localized treatments [18-19] .

Apatites are often identified by the general formula $M_{10}(XO_4)_6Y_2$, with M: Ca, Sr, Ba, Pb, etc.; X: P, As, Si, etc.; Y: various anions, such as OH^-, F^-, Cl^- or other groups [20]. In nature apatites are very abundant; they are found in phosphate mines where they form the principal constituent. In the biological environment, they constitute the major part of the mineral matter of the vertebra skeleton. These apatites are used as a raw material in many processes of chemical industries, such as for the preparation of artificial fertilizers [21], for the manufacture of catalysts or for osseous prostheses. The release of P from these insoluble phosphates in the soil is an important aspect to make its availability.

In this research work, the carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-methylcarbamate) ,a carbamate nematicide and insecticide, was selected like an adsorbate because in Morocco, this insecticide is applied to the soil of many crops (wheat, bananas, potatoes, sugar cane, carrots, and tomatoes) [22]. Recent studies have shown that due to its moderate adsorption onto soil constituents, carbfuran is fairly mobile and leaching, that can be detected in agricultural soils, lakes, streams and rivers [23], moreover it presents a high persistence in raw milk [24], water [25–28], soil [29,30], atmosphere [31,32], or plants [33–36].Thus, the sorption, mobility and transformation of carbofuran have received particular attention in recent years.

The objectives of this work were to test the ability of two synthetic calcium phosphates for the adsorption of the carbofuran at different conditions and also to assess their usefulness as controlled release systems of this pesticide.

2. Experimental

2. 1. Materials and methods

2.1. 1. Preparation and characterization of the adsorbents

The adsorption tests were conducted on two calcium phosphates: (PTCa) and (DCPD). The first one (PTCa) was prepared at room temperature by a double decomposition method [37]. The solution A (47 g of calcium nitrate $Ca(NO_3)_2 4H_2O$ (from Scharlau, Spain) in 550 ml of distilled water + 20 ml of ammonia solution) was added quickly at room temperature into the solution B (26 g of di-ammonium hydrogen phosphate$(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) in 1300 ml of distilled water + 20 ml ammonia solution). The precipitate was filtered, washed, and dried at 80 °C for 24 hours.

The second one, the (DCPD) powders was prepared by an aqueous double decomposition of the salt of calcium and of phosphate [38]. A calcium nitrate solution ($Ca(NO_3)_2 4H_2O$) (Scharlau, Spain) was added to ammonium dihydrogen phosphate ($(NH_4) H_2PO_4$) (Riedel-de Haën, Germany) at an ordinary temperature and a white precipitate appears. After maturation of 2 hours, the precipitate was filtered and washed with 1 L of distilled water. Finally, the precipitate was lyophilized for 24 hours.

Both phosphates were characterized by chemical and physical analysis. The calcium content in the solid was determined by complexometry with EDTA and the phosphate ion content by spectrophotometry of phospho-vanado-molybdic acid. The specific surface area was determined according to the BET method using N_2 adsorption (Table 1). Infrared spectroscopy IR was carried out after dispersion of anhydrous KBr (about 2 mg product to 200 mg of KBr) using TENSOR 27 spectrophotometer (Bruker Optics, Germany) (Figures 1 and 2).

Table1: Characteristics of phosphates used

Name	Ca/P	Specific surface (m^2/g)
PTCa	1.50	62
DCPD	1	2

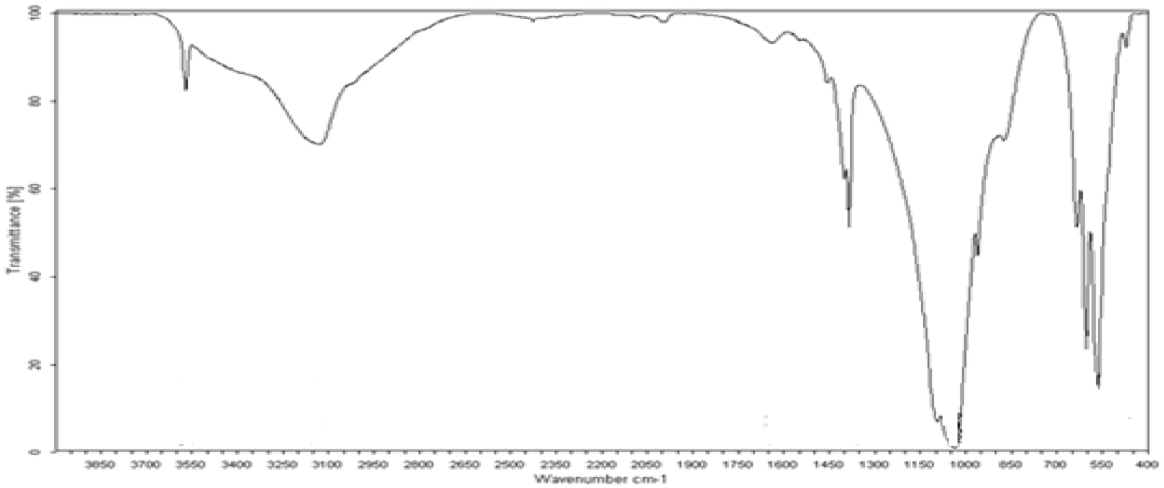


Figure 1: Infrared absorption spectrum of PTCa of Ca / P = 1.5

2.1. 2. Adsorbate

Commercial grade carbofuran formulated as a granule (5G) was purchased from the local market under the name furadan 5G. Stock solution of carbofuran (400 mg/l) in distilled water was prepared. The most important physicochemical properties of carbofuran are collected in Table 2.

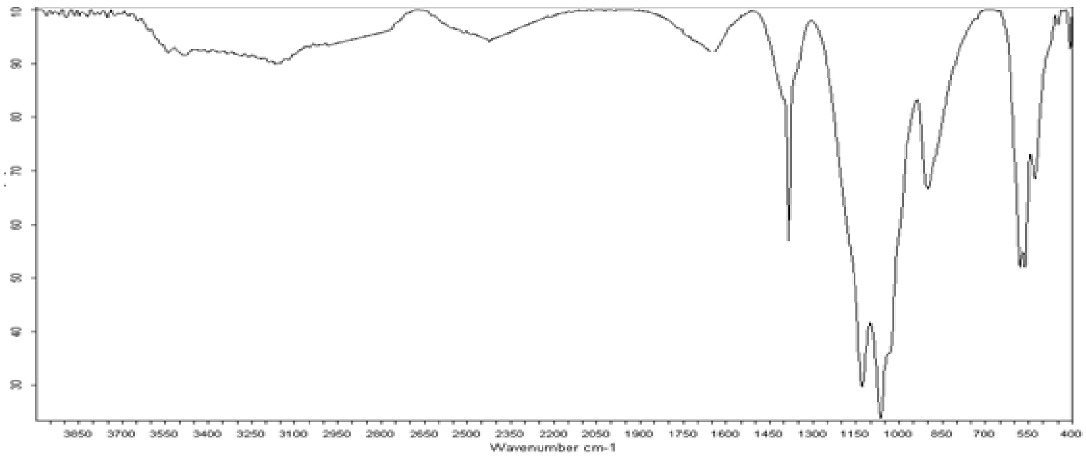
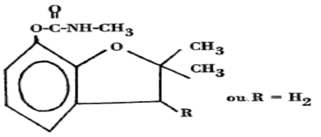


Figure 2: Infrared absorption spectrum of DCPD of Ca/P=1

Table 2: Physicochemical properties of carbofuran

Common name	Carbofuran
Trade name	Furadan
IUPAC name	2,3-dihydro-2,2-dimethyl-7-benzofuranylN-methylcarbamate
Molecular formula	$C_{12}H_{15}NO_3$
Molecular weight	221,25
Solubility in water	700mg/l
Vapor pressure	3,4.10 mmHg à 25° C - 1,1.10 mmHg à 50°
Formulation	10% GR
Toxicity	Class Ib
Acute oral LD50 for rats	8 mg/kg
Structural formula	

2.2. Adsorption study

2.2.1. Effect of soil mass

Different adsorbent mass in the range 0.1–0.6 g were used in adsorption experiments with 10 ml of the pesticide solution. The initial pesticide concentrations of the solutions were fixed at 92 mg/ l, at normal pH (6.4), room temperature (25 ◦C±2), for contact time 24 h, with occasional agitation.

2.2.2. Effect of contact time

The carbofuran solution at its normal pH (C_0= 224 mg/l) was left in contact with adsorbent (0.2 g/10 ml) at 25 ◦C for different time intervals between 15 and 1440 min. The results indicated that the adsorption equilibrium is attained after about 15–120 min. However, equilibrium time of 24 h was selected to carry out the adsorption experiments.

2.2.3. Adsorption equilibrium

Adsorption equilibrium studies were conducted with an adsorbent quantity of 0.2 g with pesticide concentrations ranges between 23 and 336 mg/l in a test tube of 20 ml capacity containing 10 ml of the pesticide solution. A blank was also maintained to assure the quality control of the experiments .The mixture was stirred at constant speed (500 rpm) for one minute and then placed in a water bath at 25 °C. Calculation of the amounts of pesticide adsorbed was calculated using the formula:

$$Qads = (C_o - Ceq).V/m \qquad (1)$$

where Qads (mg/g) is the amount of pesticide adsorbed, C_o (mg/l) is the initial pesticide concentration, Ceq (mg/l) is the equilibrium pesticide concentration, V (l) is the volume of pesticide solution, and m (g) is the adsorbent mass in contact with pesticide solution.

The solid was separated from the mother solution by filtration through a fritted glass. Samples of carbofuran were analyzed using high performance liquid chromatography (HPLC) (Jasco, UK) with UV detector (MD 2010, PDA) equipped with reversed-phase packed column (Agilent C18) of 15 cm length, with a pore size of 5 µm. Operating conditions were as follows: mobile phase was a mixture of water and acetonitrile (at a ratio of 60:40) and a flow rate of 1 ml /min was maintained throughout the run. Under these conditions, the retention time for carbofuran was 9.5 min. The amounts of pesticide in the samples were derived from the standard curve constructed by plotting the peak area against different concentrations of the active ingredient of the pesticide. The response of the detector to carbofuran concentration was linear with correlation coefficient $R^2 = 0.9999$.
Also, the effect of temperature on the sorption of carbofuran onto PTCa and DCPD was studied in the range of 25 –35 °C at optimum conditions.

2.3. Desorption

Desorption experiments were conducted immediately after the adsorption experiments on both calcium phosphates initially treated with 91,66 mg/l carbofuran solution , by successives dilutions.

First supernatants were replaced with equal volume of distilled water (10 ml), after the tubes were stirring for one minute, and placed in a thermostatic bath at 25° C. At selected times, the solid and solution were separated by fritted glass and the concentrations of carbofuran in the supernatant solutions were measured by HPLC using the same conditions described above for adsorption experiments.

3. Results and discussion

3.1. Effect of solid quantity

The results are given in Fig. 3 for PTCa; similar trends (not shown) were obtained for DCPD. It was noted that the amount adsorbed of carbofuran formulation increases with the increase of solid quantity up to 0.2 g and reached to 0.3 mg/g. The influence of adsorbent amount is mainly related to increase in surface area, which leads to an increase in the number of available binding sites. Therefore, these increase the rate of reaction between adsorbent and adsorbate. However it is observed that after a dosage of 0.2 g of PTCa, there was no change in amount adsorbed of pesticide. This may be due to the overlapping of adsorption sites at higher dosage as a result of over-crowding of adsorbent particle [39]. So, 0.2 g was considered as the optimum dose of both phosphate powders and was used for further study.

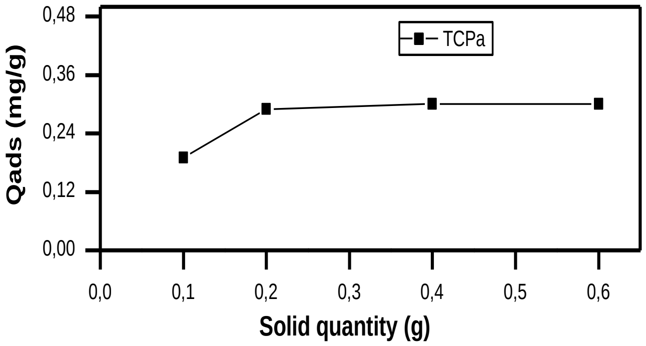


Figure3: Effect of calcium phosphate (PTCa) mass on adsorption of carbofuran (Initial insecticide concentration: 92 mg/l, pH: 6.4, stirring time: 1 min, T: 25 °C)

3.2. Kinetics of adsorption

Kinetics of carbofuran adsorption on two phosphates was studied and the results are presented in Fig.4. The adsorption kinetics exhibited two phases, a very rapid adsorption in the initial stages followed by an equilibrium phase represented by an adsorption plateau. The pseudo-equilibrium was reached within 15 min in case of PTCa and 120 min in case of DCPD. However, similar trend was observed while studying the adsorption characteristics of fluoride [40], protein [41] on synthetic phosphates and carbofuran adsorption on fertilizer industry waste [42].

The rapid step is probably due to the abundant availability of active sites on the material and the adsorption plateau indicating the complete occupancy of these sites.

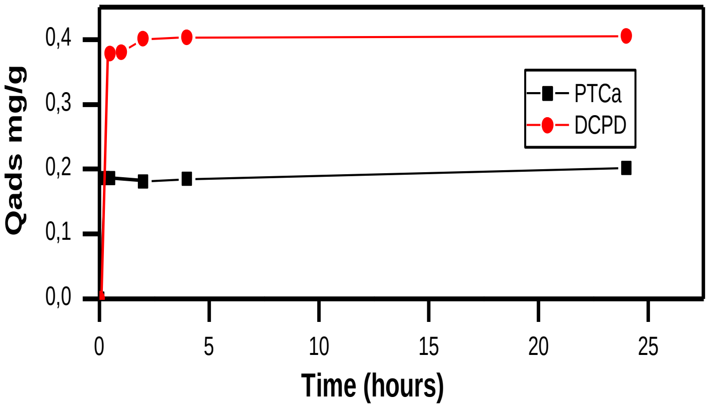


Figure 4: Kinetics of adsorption of carbofuran on DCPD and PTCa at 25 °C (Solid Quantity: 200 mg, initial pesticide concentration: 224 mg/l, pH: 6.4, stirring time: 1 min)

The sorption kinetics describes the pesticide sorption rate, which in turn governs the residence time of sorption reaction and also the efficiency of sorption process. Out of the several kinetic models available to examine the controlling mechanism of the sorption kinetic process and to test the experimental data, the Lagrangian equation or pseudo-first-order kinetics equation [43] and pseudo-second-order kinetics equation [44] have been used for carbofuran sorption kinetics of both phosphates.

The linearised form of pseudo-first-order equation:

$$\ln(Qe - Qt) = \ln Qe - k_1 t \qquad (2)$$

where Qe (mg/g) and Qt (mg/g) are the amount adsorbed of pesticide at equilibrium and at time t, respectively, and k_1 ($\min^{-1}$) is the rate constant of pseudo-first order adsorption. The application of this equation to the data of carbofuran on PTCa or DCPD (data not shown) indicated the inapplicability of the model.

The pseudo-second order kinetic model is linearly expressed as (Eq. (3)):

$$t/q_t = 1 / k_2.q_e^2 + t/q_e \qquad (3)$$

where k_2 (min.g/mg) is the pseudo-second order rate constant, which can be calculated from the intercept of the straight line obtained from plotting t/Qt vs. t.

The perfect fit of the experimental data of carbofuran on phosphates according Eq. (3) (Fig. 5 and Table 3) indicates the applicability of model for the adsorption of carbofuran on both types of phosphates.

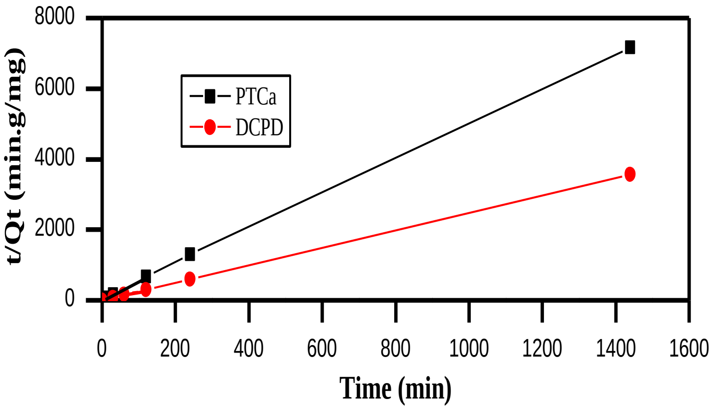


Figure 5: Determination of rate constants of pseudo second order adsorption of Carbofuran by DCPD and PTCa

Table 3: Rate constant of pseudo second order

Adsorbents	Qe (mg/g)	k_2(min.g/mg)	R^2
PTCa	0.201	0.688	0.999
DCPD	0.404	2.590	1

3.3. Adsorption equilibrium

Equilibrium isotherm equations are used to describe experimental adsorption data. The equation parameters of these equilibrium models often provide some insight into both the sorption mechanism and affinity of the adsorbent. The importance of obtaining the best-fit isotherm becomes more and more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the adsorption system designs.

Using Furadan formulation that affording initial concentration of carbofuran ranging between 23.83 and 336 mg/l, it is observed that the amount adsorbed (mg/g) on the two phosphates increases more quickly for low concentrations in solution and then reaches a plateau; that can be explained by a monolayer adsorption type Fig.6.

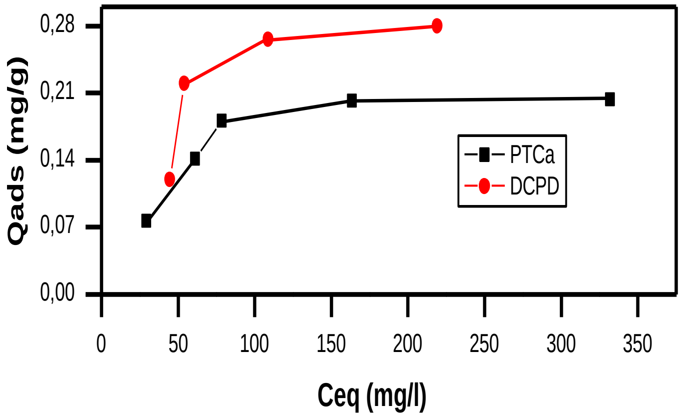


Figure 6: Adsorption isotherms of carbofuran by DCPD and PTCa, (Solid quantity: 200 mg, stirring Time: 1 min, T: 25 °C)

Langmuir and Freundlich isotherm models were used to calculate the isotherm constants and maximum adsorption capacity of carbofuran on two types of phosphate.

3.3.1. Freundlich sorption isotherm

The Freundlich sorption isotherm is an empirical expression describing the exponential distribution of active centers, characteristic of heterogeneous surfaces and infinite surface coverage. The linearized form of Freundlich isotherm is tested in the following form [45]:

$$\ln(Qads) = 1/n \ln Ce + \ln K_F \qquad (4)$$

where 1/n is a characteristic constant related to sorption intensity, Qads is the sorbed concentration of sorbate onto sorbent (mg/g), Ce represents equilibrium concentration of sorbate in solution (mg/l), and K_F is the multilayer sorption capacity of sorbent (l/mg). A plot of ln(Qads) versus lnCe would exhibit in a straight line with a slope of 1/n and intercept of $\ln K_F$ as shown in Fig.7. The results are listed in Table 4.
The value of $1/n < 1$ indicates that adsorption capacity is slightly reduced at lower equilibrium concentration [46].

3.3.2. Langmuir isotherm

The Langmuir model represents monolayer sorption on a set of distinct localized sorption sites with uniform energies and with no transmigration of sorbate in the plane of the surface. The sorption data obtained was applied to the following linearized form of Langmuir isotherm [47].

$$Ce/Qads = 1/ Q\infty\, b + Ce / Q\infty \qquad (5)$$

where Q∞ is the monolayer sorption saturation capacity (mg/g), and b represents the enthalpy of sorption (l /mg), independent of temperature. A plot of Ce/Qads versus Ce yields a straight line with its slope of 1/ Q∞ and intercept of 1/ Q∞ b as shown in Fig. 8, the results are recorded in Table 4.

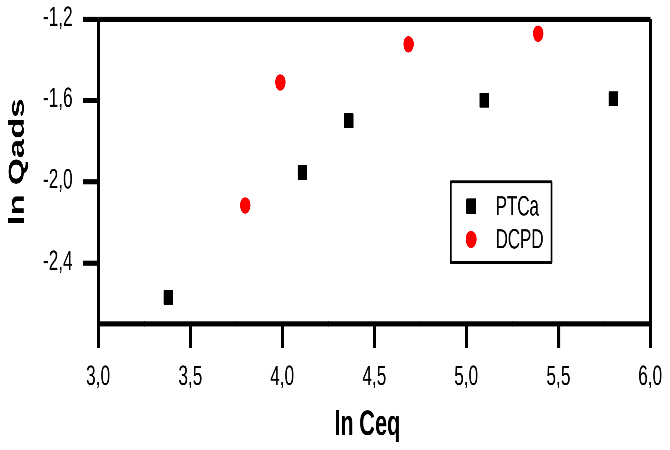


Figure7: Freundlich plot for carbofuran on DCPD and PTCa

The correlation coefficient values (R^2) show that the data fitted well with Langmuir isotherm model (R^2> 0.95) than Freundlich model (R^2> 0.79). The adsorption capacity (measured by K_F) of sorbents is higher on DCPD (0.0314 l /mg) than on PTCa (0.0268 l/mg). Further the value of intensity of adsorption (n) is greater than unity signified that the forces within the surface layer are attractive [48]. The results in this study indicate that both monolayer adsorption and heterogeneous surfaces conditions exist under the experimental conditions used.

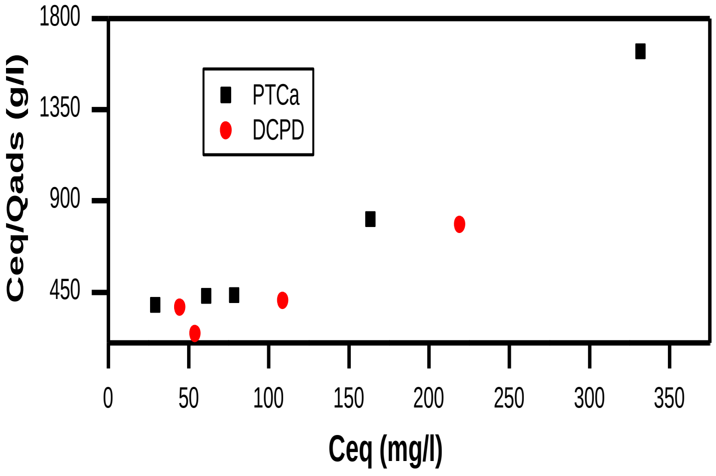


Figure 8: Langmuir plot for carbofuran on DCPD and PTCa

Table 4: Parameters obtained from adsorption models

ParametersAdsorbants	Freundlich isotherm K_F	 $1/n$	 R^2	Langmuir isotherm Q ∞	 b	 R^2
PTCa	0.0268	0.381	0.862	0.232	0.025	0.99
DCPD	0.0314	0.425	0.791	0.364	0.017	0.95

3.4. Adsorption thermodynamics

In order to understand the effect of temperature on the adsorption of pesticide, adsorption experiments were conducted at 25, 30, and 35 ◦C. The evolution of the amount adsorbed as a function of temperature was represented on the Fig. 9.

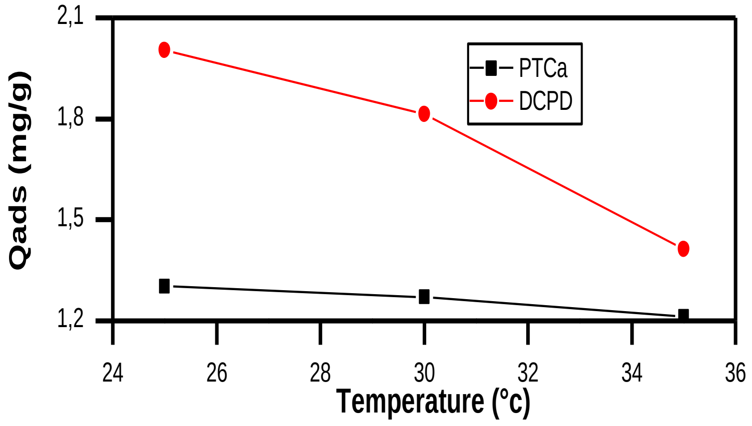


Figure 9: Effect of temperature on the equilibrium adsorption of Carbofuran on DCPD and PTCa. (Solid quantity: 200 mg, initial pesticide concentration: 104.851 mg/L, contact time: 24 h)

It is seen from Fig. 9 that adsorption increases with decrease in temperature, indicating that the process is apparently exothermic. The effect of temperature can be explained on the basis of solubility. With increase in temperature the solubility of the pesticide increases and this would cause pesticide to be more soluble and, therefore, exhibit lower tendency to go to the adsorbent surface and get adsorbed.

The thermodynamic parameters of the adsorption process could be determined from the experimental data obtained at various temperatures using the following equations [49]:

$$\Delta G = -RT \ln K_C \quad (6)$$

$$\ln K_C = \Delta S/R - \Delta H/RT \quad (7)$$

$$K_C = nF_e / (1 - F_e) \quad (8)$$

$$\Delta G = \Delta H - T\,\Delta S \quad (9)$$

With:

K_C: Equilibrium constant
ΔG: Gibbs free energy (Joule / mole)
ΔH: Enthalpy (Joule / mole)
ΔS: Entropy (Joule / mol K)
T: Absolute temperature (K)
Fe: fraction sorbed at equilibrium
R: Gas constant.

The values of ΔH and ΔS can be calculated from the slope and intercept of the plots of ln K_C against 1/T (Figs. 10 and 11). Three temperatures represent a threshold for obtaining data to be used for drawing the relation ln K_C vs. 1/T. We agree that as the number of points increases the reliability of the results increases, however, literature data include a huge number of examples that depended on only three points of temperature to draw such relation. We see that a straight line through three points with good value of R^2 is acceptable to rely on in our calculations. The different parameters obtained from such treatment are collected in Table 5. The small negative value of ΔH indicates exothermic nature and that the adsorption is physical in nature involving weak forces of attraction. Negative ΔS values indicate that there is decrease in state of disorderness in the molecules during process, which in turn is due to the binding of molecules with adsorbent surface. The positive ΔG values indicate non-spontaneous nature of carbofuran adsorption reaction with phosphates and, that has governed with the gain of energy from surroundings [50, 51]. By increasing concentration of the reactants, it may often be possible to make the reaction to proceed even if ΔG has a positive value.

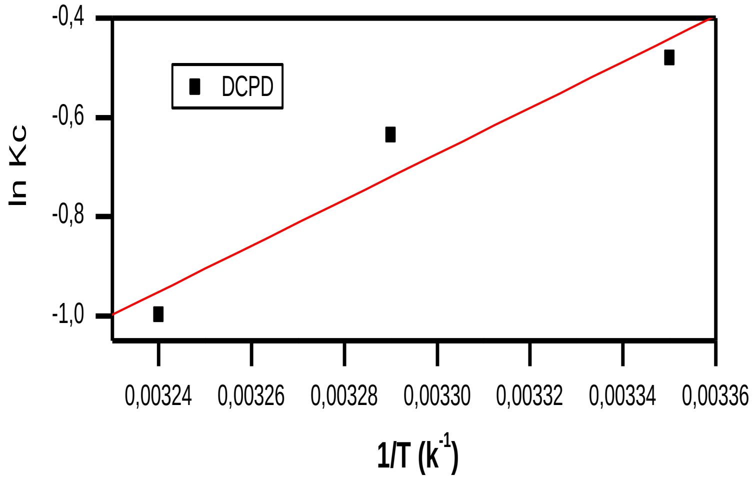


Figure 10: Plot of ln Kc vs. 1/T for carbofuran on DCPD

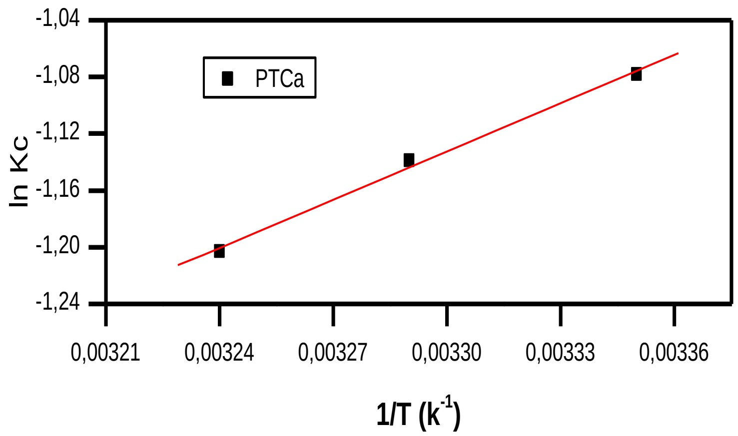


Figure11: Plot of ln Kc vs. 1/T for carbofuran on PTCa

Table 5: Thermodynamic parameters for adsorption of the carbofuran on phosphates

Adsorbents	ΔH (K Joule/mole)	ΔS (Joule/mole K)	T (K)	ΔG (K Joule/mole)	R^2
PTCa	-9.414	-40.467	298.15 303.15 308.15	2.667 2.865 3.076	0,9978
DCPD	-38.5	-132.649	298.15 303.15 308.15	1.181 1,602 2.554	0,96175

3.5. Desorption

The desorption of carbofuran was assessed on the calcium phosphates initially treated with 91.66 mg/L carbofuran solution. Before the desorption process was initiated, the amounts of carbofuran sorbed by the DCPD and PTCa were calculated to be 1.34 mg/g and 1.11 mg/g respectively. We calculated the desorption rate (R) according to Eq. (10).

$$R = C_{S0} - C_{St}/C_{S0} \times 100 \qquad (10)$$

where C_{S0} (mg/g) and C_{St} (mg/g) are the amount of a compound sorbed by sorbents before and after desorption process, respectively.

Figure 12 shows the desorption of carbofuran from both calcium phosphates during the six successive (27 days) desorption steps, expressed as percentages of the initial amount adsorbed (desorption rate) .

The release profiles corresponding to these phosphates are similar (Fig. 12), and less than half of the pesticide sorbed by DCPD and PTCa was desorbed after 4 days. The results revealed that both phosphates prepared displayed slow release properties. These results are in agreement with our previous studies whereas the commercial formulation released the pesticide instantaneously.

In addition the reversibility of the pesticide sorption may provide information about the interactions involved between the chemical and the calcium phosphates used. Therefore the adsorption of carbofuran by synthetic calcium was mainly by physical forces rather than chemical forces (chemical adsorption is irreversible), the same type of interactions was observed between the tribenuron methyl (herbicide) and the hydroxyapatite [52].

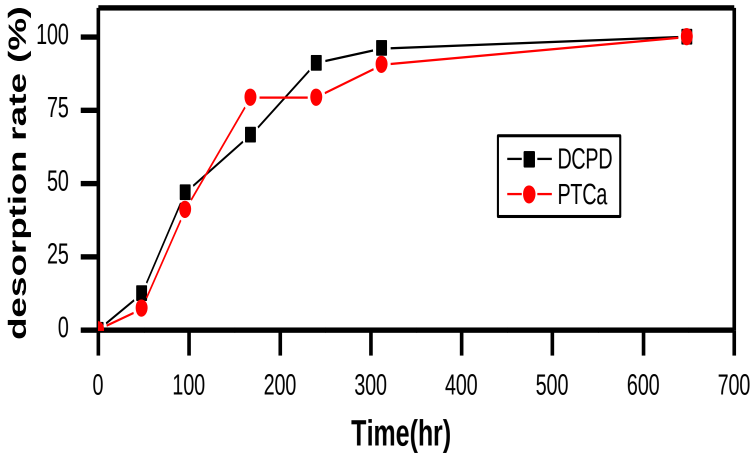


Figure 12: Desorption of carbofuran from PTCa and DCPD

Conclusions

In this study, the adsorption and desorption experiments of carbofuran were carried out using two synthesized calcium phosphates. Both phosphates can be used as synthetic adsorbents for the controlled release of carbofuran. The sorption behavior of carbofuran at different experimental conditions was examined and the results obtained are summarized as follows:

- Increase in mass of adsorbent leads to increase in pesticide adsorption due to increase in number of adsorption sites. Maximum uptake was obtained at adsorbent dose of 0.2 g for which may be considered as optimum adsorbent dosage level at the specified conditions.
- Experimental data showed that the pesticide is adsorbed quickly on DCPD and PTCa.
- The kinetic analysis showed that the pseudo-second-order model had the best fit to the experimental data.
- Langmuir adsorption model was better fitted for the adsorption of carbofuran. The highest monolayer adsorption capacity was obtained 0.232 mg/g for adsorption of carbofuran on PTCa and 0.364 mg/g on DCPD.
- Thermodynamic studies indicated that the carbofuran adsorption process onto both phosphates was physical and exothermic.
- The calcium phosphates could be suitable as supports for the slow release of carbofuran, reducing the amount of pesticide immediately available and decreasing the risk of ground water contamination.

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