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Evaluation of Silica as an Adsorbent for Carbendazim from Aqueous Solutions

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Abstract— **Adsorption of carbendazim onto silica has been studied. The influence of contact time, pH, ionic strength and temperature has been determined. The adsorption isotherms can be described by the Langmuir model. Adsorption appears to be more effective as pH increases and it is not significantly affected by ionic strength of the sample (except at high I values). Spectroscopic and thermogravimetric results suggest that carbendazim is adsorbed in its protonated form. Results indicate that after the treatment with silica, roughly 90% carbendazim can be removed from the aqueous solutions, making this adsorbent as a potential candidate for water treatment processes.**

Index Terms— **adsorption, carbendazim, pesticide, silica.**

I. INTRODUCTION

A pesticide is a substance or mixture of substances used to destroy, prevent and/or repel certain plague. They can be classified as herbicides, fungicides or insecticides. Argentina produces big quantities of pesticides, involving more than 2.3 billion U$S in 2012, being the second country in Latin-America below Brazil, which is top of the list referring to pesticides (8.8 billion U$S in 2012) [1].

The pesticide studied in this work is placed among the most used ones in South America: carbendazim (methyl-benzimidazol-2-ylcarbamate or methyl, 2-benzimidazole-carbamate, see Fig.1) is a systemic fungicide widely used for control of several type of fungal pathogens of cereals, fruits and vegetables as well as a preservative for inks, paints and leathers, fruits and vegetables [2], [3]. Some pesticides have the property of converting into carbendazim as a decomposition product. Such is the case of benomyl or thiofanate [4].

It has been found that 300-600 ppm of carbendazim per day can affect lung and kidney rat tissues, giving adverse hematological and biochemical effects [5]. It has also been reported that carbendazim causes endocrine disruption and adverse effects on the spermatogenesis in male rats [6]-[8].

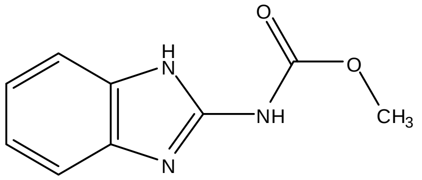

Fig.1: Molecular structure of carbendazim.

As many other pesticides and organic compounds do, carbendazim is adsorbed by a variety of surfaces, and this fact carries several environmental and technological consequences. Previous studies showed that the interaction between soil components and organic compounds bearing basic sites is rather complex, involving several sorption mechanisms [9], [10]. As early suggested by Kah and Brown [11], specific approaches to each compound is required for understanding the adsorption behavior of bases in organic soils. The effect of several variables such as pH, organic matter content and clay type, among others, were already pointed out [12]. In particular, carbendazim is strongly adsorbed on different kind of soils and, due to its relatively high stability, it remains in the environment for a long time [13], [14]. Thus, considerable attention is currently devoted to the understanding of the interaction between carbendazim and solid substrates [3], [15].

The effectiveness and strength of the adsorption process is a crucial factor from the environmental and technological point of view, and it can be estimated by studying the adsorption isotherms of a pesticide on a certain surface.

Pesticide adsorption isotherms depict the amount of pesticide adsorbed versus its equilibrium concentration (at a given temperature, pH and ionic strength) and they can be conveniently grouped into six classes according to the IUPAC classification [16].

Moreover, analysis of solids obtained after adsorption give additional information about the nature of the adsorption process and they have proven effective in the detection and quantification of pesticides. For instance, the analysis of the infrared spectrum of solid carbendazim was suggested as a convenient analytical method [17]. More recently, the surface-enhanced Raman scattering (SERS) technique was also used for the detection of carbendazim in the μM range [18]. Recent quantum chemical calculations suggest the presence of tautomeric equilibrium in carbendazim [19]. Thus, not only the presence of adsorbed carbendazim, but

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also the nature of the adsorbed species can be studied by FTIR.

The objective of this work was to evaluate silica as a potential adsorbent of carbendazim in order to extract this pesticide from polluted waters. To accomplish this aim, adsorption isotherms for carbendazim on silica particles were determined at different conditions (pH, ionic strength, temperature), as well as FTIR and TGA analyses were carried out, making also possible to understand the physicochemical behavior of the system.

II. MATERIALS AND METHODS

A. *Synthesis of carbendazim*

Carbendazim was synthesized and purified, according to a modified version of literature procedures [20], from the reaction between methyl chloroformate and calcium cyanamide, followed by the addition of phenylendiamine in hydrochloric media. The product was characterized and identified by means of FTIR spectroscopy, ^{1}HNMR, ^{13}CNMR and HPLC- MS.

0,063-0,200 mm particle sized silica (Merck) was used for all determinations. Silica particles were dried in a crucible for 15 h at 120ºC and then in a muffle for 3 h at 250ºC and stored in a desiccator.

B. *Kinetics and Isotherms*

All solutions were prepared dissolving pure carbendazim in distillated water. pH was adjusted using 5% aqueous HCl or 5% aqueous NaOH; ionic strength (I) was adjusted using $CaCl_2$ as well.

In kinetic adsorption experiments, 5g of dry silica were added to 100 mL of 5mg/L carbendazim solution (pH=4.5, I=30mM and 25ºC) with continuous stirring. 1 ml supernatant sample were withdrawn at 0, 0.5, 1, 2, 3, 24 and 48 h. Kinetics were carried out in duplicate. All samples were then centrifugated and filtered using Nylon 0,45 µm HPLC filters.

Adsorption isotherms were determined adding 2,0g of dry silica to 10 mL of aqueous solutions bearing different concentration of carbendazim (ranging from 1 to 5mg/L in all experiments except the ones in Section III.F — Temperature Effect —, where carbendazim initial concentrations ranged from 0.2 to 1.5mg/L), adjusting their ionic strength with solid $CaCl_2$ and their pH with HCl or NaOH (depending on the case). The mixtures were thermostatized at 25ºC (except in Section III.F, where temperatures were 25, 30 and 40ºC) and magnetically stirred at 120 rpm for 24 h. pH value was continuously monitored and re-adjusted using HCl or NaOH in order to keep it constant. Samples were then centrifugated and filtered using Nylon 0,45 µm HPLC filters. All adsorption isotherm experiments were carried out in duplicate.

Carbendazim concentrations were measured by means of HPLC-ESI, using an HPLC-MS Agilent 1100 LC-MSD equipment. Chromatographies were developed using methanol:aqueous formic acid (5%) 50:50 as solvent and measuring the signal at m/z=192 (protonated carbendazim) in positive mode. The election of this method relies on its high sensitivity and reproducibility in pesticide quantification [21].

C. *Solid Analysis*

Solid samples were prepared as follows: (a) pure neutral carbendazim was directly obtained from synthesis, (b) carbendazim chlorydrate was obtained dissolving 0.5g of carbendazim in the minimum amount of aqueous 5% HCl and then evaporating the solvent in a rotary evaporator at 60ºC and 10mmHg, (c) adsorbed carbendazim was prepared adding 1g of dry silica to 10mL of 5mg/L carbendazim solution at pH 4.5, I=30mM in $CaCl_2$ and 25ºC, stirring the mixture for 24h, and then filtrating the system through a Buchner funnel, (d) blank silica was prepared as in case (c), only without dissolved carbendazim. All four samples were dried in a vacuum dessicator for 12 h at 80ºC and 10mmHg and then stored in a desiccator.

FTIR measurements were performed on FTIR Bruker Equinox 55, between 400 and 4000 cm^{-1}, with a resolution of 2 cm^{-1}. The whole spectra are given as Supplementary Information.

Thermogravimetric analysis (TGA) were performed in a thermobalance Shimadzu model TGA-50H, in helium current under atmospheric pressure. Studies were carried out at a constant heating rate of 10ºC min^{-1} in He stream (30 cm^3 min^{-1}) flowing onto the cylindrical sample holder.

III. RESULTS AND DISCUSSION

A. *Adsorption Kinetics*

Fig.2 depicts concentration profile vs. time. As it can be seen, equilibrium is reached after 24 h approximately.

In order to determine the type of adsorption kinetics, the experimental data was fitted to two different theoretical models (pseudo first order and pseudo second order), assuming c_{eq} as 1,88 ppm. The corresponding k_1, k_2 and correlation coefficients r^2 are given in Table 1. As it can be seen, the model that better fits the experimental data is pseudo-first order, determining a half-life adsorption time of 2.1 h under these conditions.

Table 1: Statistical parameters of Pseudo-first order and Pseudo-second order kinetic models.

Pseudo-first order model		Pseudo-second order model	
k_1 (min^{-1})	$(5.4\pm0.6)x10^{-3}$	k_2 ($L.mg^{-1}.min^{-1}$)	$(6.0\pm0.9)x10^{-3}$
r^2	0.967	r^2	0.933

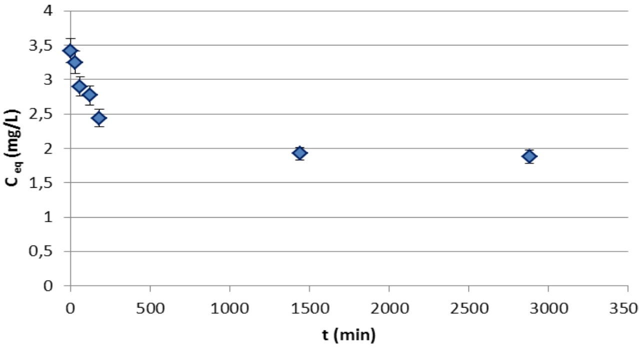

Fig.2: Carbendazim concentration vs. time.

B. Adsorption Isotherms

With the purpose of knowing the characteristics of adsorption of carbendazim on silica, analysis of the adsorption isotherms have been made, as well as a fitting to different theoretical adsorption models.

Fig.3 shows the equilibrium concentration of carbendazim after adsorption of solutions of different initial concentration at 25ºC, pH= 4.5 and I= 30mM in $CaCl_2$.

The graph obtained is a type I isotherm, indicating that adsorption becomes more difficult as concentration increases. These data were fitted to Langmuir and Freundlich adsorption models in their linear forms.

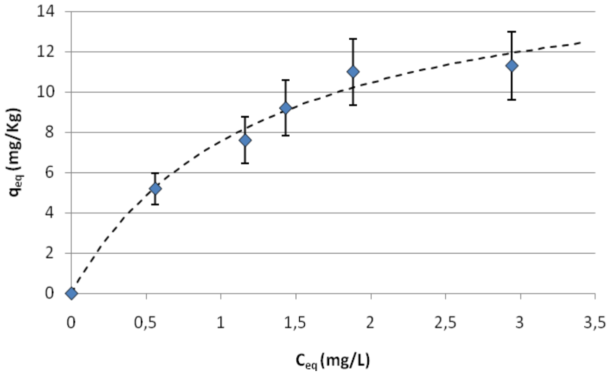

Fig.3: Carbendazim adsorption isotherm on silica at 25ºC, I= 30 mM and pH= 4.5. Langmuir fitting shown in dashed line.

Equation 1 describes the Langmuir model in its linear form, which relates the solute adsorbed mass and the equilibrium concentration *C*.

$$\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0} \qquad (1)$$

where *q* is the mass of solute adsorbed at equilibrium per adsorbent g or kg; q_0 is maximum amount of solute adsorbed per adsorbent g or kg, i.e., the adsorption capacity; and K_L is the Langmuir constant, which is related to the adsorption equilibrium involving several factors, including physical, chemical and energetic characteristics [22,23]. Freundlich model is represented in (2), where K_F is an empirical constant which provides an indication of the adsorption capacity and *1/n* indicates the energetic heterogeneity of the adsorption sites [24]; *q* and *C* are defined as above.

$$\log q = \log K_F + \frac{1}{n} \cdot \log C \qquad (2)$$

Table 2 depicts the parameters corresponding to each model.

Table 2: Adsorption parameters obtained from Langmuir and Freundlich models linear fitting.

Langmuir Model		Freundlich Model	
q_0 (mg/kg)	17±2	n	1.99±0.02
K_L (L/mg)	0.8±0.2	K_F (mg/kg)	7.2±0.4
r^2	0.977	r^2	0.937

The values of r^2 indicate that Langmuir model is more suitable for this isotherm.

C. Effect of pH

Fig.4 shows the isotherms obtained at different pH conditions (2.5, 4.5 and 7.0), remaining constant temperature (25ºC) and ionic strength (30mM). Langmuir-fitting values are tabulated in Table 3.

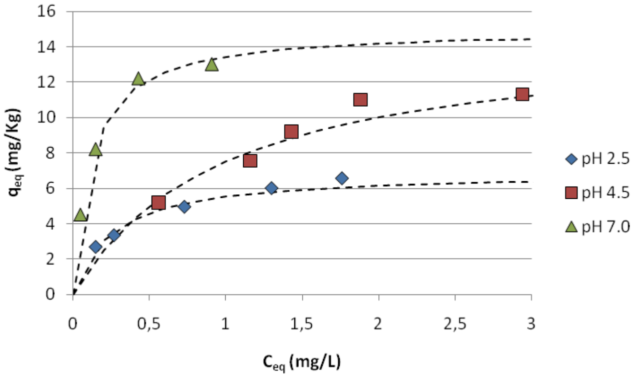

Fig.4: Carbendazim adsorption isotherms on silica at different pH values (25ºC, I= 30mM). Langmuir fittings are given in dashed lines.

Table 3: Langmuir parameters at different pH values (25ºC, I= 30mM).

	pH 2.5	pH 4.5	pH 7.0
q_0 (mg/kg)	6.9±0.5	17±1	15±1
K_L (L/mg)	2±1	0.8±0.2	8±1
r^2	0.9750	0.9924	0.9981

The adsorption efficiency of silica is evidently increased with an increment in pH, being silica and carbendazim gradually deprotonated as pH increases. It is noticeable that at ambient conditions (pH 7.0, I 30 mM and 25ºC), more than 85% of carbendazim is retained by silica when initial concentrations do not exceed 3 ppm.

Considering this fact, two different equilibria can be proposed:

- *Eq.A:* $SiO^-_{(s)} + CBZH^+_{(aq)} \longrightarrow SiO \bullet CBZH_{(s)}$
- *Eq.B:* $SiOH_{(s)} + CBZ_{(aq)} \longrightarrow SiOH \bullet CBZ_{(s)}$

where CBZ represents carbendazim, SiOH and SiO^- represent protonated and deprotonated unoccupied sites in silica (respectively), and SiO•CBZH and SiOH•CBZ stand for occupied (adsorbed) sites. Clearly, equilibrium between protonated carbendazim and protonated silica is discarded (given that it should lead to an increment in adsorption at lower pH values).

The corresponding thermodynamic equilibrium constants for Equilibria A and B would be (3) and (4).

$$K_{ads} = \frac{\theta_{ads}}{\theta_{SiO} \cdot a_{CBZH}} \qquad \text{Eq.A (3)}$$

$$K_{ads} = \frac{\theta_{ads}}{\theta_{SiOH} \cdot a_{CBZ}} \qquad \text{Eq.B (4)}$$

where a_{CBZ} and a_{CBZH} are the activities of carbendazim species; and θ_{SiOH}, θ_{SiO} and θ_{ads} are the fractions of protonted, deprotonated and occupied sites in silica, respectively.

Defining the acidic constant of silica as $K_{aSi} = \theta_{SiO}\cdot[H^+]/\theta_{SiOH}$, supposing that $\theta_{ads}=k\cdot q$ (i.e., the fraction of adsorbed sites is proportional the mass adsorbed), assuming that $\theta_{SiOH} + \theta_{SiO} + \theta_{ads} = 1$, defining the acidic constant and mass balances for carbendazim species as usual, and replacing in (3) and (4); then (5) and (6) can be deduced.

$$\left(\frac{K_{ads}\cdot K_{aSi}[H^+]}{(K_{aSi}+[H^+])\cdot(K_{aCBZ}+[H^+])}\right)\cdot C=\frac{k\cdot q}{1-k\cdot q} \qquad \text{Eq.}A\ (5)$$

$$\left(\frac{K_{ads}\cdot K_{aCBZ}[H^+]}{(K_{aSi}+[H^+])\cdot(K_{aCBZ}+[H^+])}\right)\cdot C=\frac{k\cdot q}{1-k\cdot q} \qquad \text{Eq.}B\ (6)$$

Equations (5) and (6) lead to Langmuir-type isotherms, being the factors in brackets equal to the Langmuir constant K_L. Given that $K_{aSi} \approx 2.10^{-10} <<< [H^+]$, then $K_{aSi} + [H+] \approx [H+]$ and K_L reduces to the expressions shown in (7) and (8) [25].

$$K_L=\frac{K_{ads}\cdot K_{aSi}}{K_{aCBZ}+[H^+]} \qquad \text{Eq.}A\ (7)$$

$$K_L=\frac{K_{ads}\cdot K_{aCBZ}}{K_{aCBZ}+[H^+]} \qquad \text{Eq.B (8)}$$

Both models clearly support the fact that K_L and q_0 are increased at higher pH values, so they cannot be differentiated by pH effect experiments.

It is important to make clear that a third equilibrium could have been proposed:

- *Eq.C:* $SiO^-_{(s)} + CBZ_{(aq)} \longrightarrow SiO{\bullet}CBZ^-_{(s)}$

but it would have led to a Langmuir constant $K_L=K_{ads}.K_{aSi}.K_{aCBZ}.[H^+]^{-1}.(K_{aCBZ}+[H^+])$, which is proportional to $[H^+]^{-1}$ and which should have shown an exponential increment with pH, not agreeing with the experimental K_L values.

D. *Effect of ionic strength*

Fig.5 shows the isotherms obtained at different ionic strength conditions (3, 30 and 300 mM), remaining constant temperature (25ºC) and pH (4.5). Langmuir-fitting parameters for each one of the isotherms are given in Table 4.

Table 4: Langmuir parameters at different ionic strengths (25ºC, pH= 4.5).

	I 3mM	I 30mM	I 300mM
q_0 (mg/kg)	17±2	17±1	11.4±0.5
K_L (L/mg)	0.9±0.1	0.8±0.2	4.7±0.3
r^2	0.9937	0.9924	0.9933

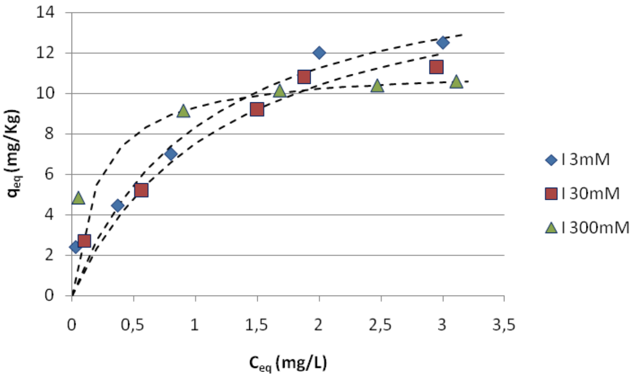

Fig.5: Carbendazim adsorption isotherms on silica at different ionic strengths (25ºC, pH= 4.5). Langmuir fittings are given in dashed lines.

In order to understand these facts, activity coefficients (γ) have to be included in (3) to (8). It will be assumed that only the activity coefficients corresponding to charged species and sites ($CBZH^+$ (γ_{CBZH}) and SiO^- (γ_{Si})) are affected by ionic strength. Then (9) and (10) can be withdrawn for the corresponding Langmuir constants.

$$K_L=\frac{K_{ads}\cdot K_{aSi}\cdot\gamma_{CBZH}}{(\gamma_{CBZH}\cdot K_{aCBZ}+[H^+])\cdot\gamma_{Si}} \qquad \text{Eq.}A\ (9)$$

$$K_L=\frac{K_{ads}\cdot K_{aCBZ}\cdot\gamma_{CBZH}}{\gamma_{CBZH}\cdot K_{aCBZ}+[H^+]} \qquad \text{Eq.B (10)}$$

Assuming that the activity coefficients decrease when ionic strength increases, it can be seen that Equlibrium A predicts an increase in K_L when ionic strength rises, while Equilibrium B predicts the contrary.

Regarding these facts, it can be proposed that carbendazim is adsorbed as a protonated molecule on deprotonated silica sites. These hypotheses will be further supported by the analysis of silica after adsorption (Section III.G).

At high ionic strengths, the adsorption capacity of silica decreases, suggesting that ions in solution (e.g. Ca^{+2}) compete with carbendazim for the adsorption sites.

E. *Effect of temperature*

Fig.6 shows the isotherms obtained at three different temperatures (25ºC, 30ºC and 40ºC), remaining constant pH (4.5) and ionic strength (30mM). In order to obtain the isotherms initial slopes, concentrations of the initial solutions were kept below 1.5mg/L.

From the initial slope values obtained, enthalpy and entropy adsorption values can be determined by plotting lnK vs 1/T. The slope and y-intercept of this plot indicate that the adsorption enthalpy ΔH is -4.7±0.8 $kcal.mol^{-1}$ and that the adsorption entropy ΔS is -11±3 $cal.mol^{-1}.K^{-1}$. These values are typical for a physisortive process, and they imply that the adsorption is exothermic and that it increases the order of the system, as expected.

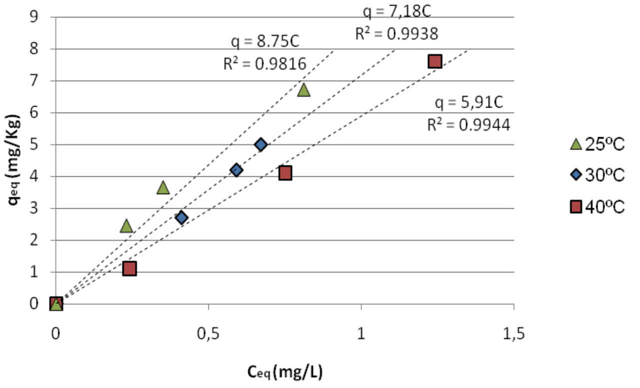

Fig.6: Carbendazim adsorption isotherms on silica at different temperatures (pH= 4.5, I=30mM). Linear regression parameters are given within the plot.

F. Solids Analysis

In order to confirm the presence and nature of carbendazim adsorbed on silica surface, IR spectra were recorded for the solid samples after adsorption. The spectra were compared with that corresponding to pure carbendazim and protonated carbendazim (as the hydrochloride adduct). Moreover, the spectrum obtained for the commercial silica was used as a reference.

The IR spectrum of the solid after adsorption differs from the one of pure silica. Fig.7 shows the four IR spectra described above (silica, silica after adsorption, carbendazim and protonated carbendazim) in the range 1500-2000cm^{-1}, where the C=O stretching vibration is expected to appear. Indeed, when the infrared spectrum of carbendazim is analyzed, the absorption band at ca. 1711 cm^{-1} was assigned to this mode, and the broad and intense absorptions at 1640 and 1580 cm^{-1} can be assigned to C=C stretching mode of the benzimidazole ring.

The spectrum obtained after 24 h adsorption of carbendazim over silica shows the νC=O shifted toward higher wavenumbers, as a medium intensity band at 1753 cm^{-1}. Interestingly, a similar shift is observed for carbendazim hydrochloride derivative, as showed in Fig.7. It is likely that the protonation of carbendazim at the benzimidazole group [26] prevents the resonance interaction between the C=O and the ring, leading to the blue shift observed for the νC=O stretching mode.

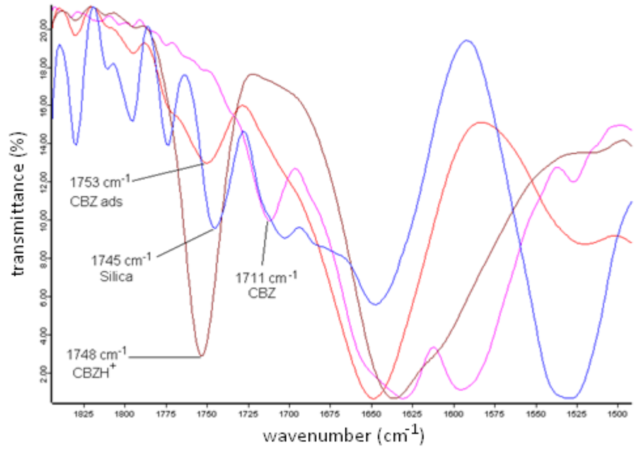

Fig.7: IR spectrum of silica, solid carbendazim (CBZ), solid carbendazim-HCl adduct (CBZH^{+}) and adsorbed carbendazim (CBZ ads) in the 1500-1850 cm^{-1} region.

Based on these considerations, the adsorption of carbendazim in its protonated form over silica is suggested.

As a confirmation of the adsorption of carbendazim on silica, thermogravimetric analyses (TGA) were done on the four solids described in the previous section (silica, carbendazim, carbendazim-HCl adduct and adsorbed carbendazim). Fig.8 shows the thermograms obtained from the samples, and Table 5 summarizes the temperature ranges, mass percentages and assignations for each loss.

When considering silica after adsorption, it can be observed that it shows two additional losses (respecting to pure silica) at 120-230ºC and 230-340ºC. These additional losses support the fact that carbendazim was effectively adsorbed on silica. The mass loss of 45.49% at 120-230ºC can be assigned to H_2O, CO, CH_3OH and HCl (theoretical value: 46.69%), while the loss of 54.51% at 230-340ºC corresponds to the rest of the compound $C_7H_5N_3$ (theoretical value 53.31%).

Table 5: Temperature ranges, mass losses (theoretical and experimental) and assignations for TGA of carbendazim, carbendazim-HCl adduct and adsorbed carbendazim (*) in the range 50-600ºC.

(*)In the case of adsorbed carbendazim, the losses were normalized to 100% after subtraction of the losses observed in silica (within the same ranges).

Sample	Temperature range (ºC)	Mass loss (%)		Assignation
		Obs.	Theor.	
carbendazim	185-245	25.45%	23.02%	CO_2
	245-380	74.55%	76.98%	$C_8H_9N_3$
carbendazim-HCl adduct	95-160	24.75%	24.84%	CO_2 , H_2O
	160-220	15.12%	14.84%	HCl
	280-360	60.13%	60.32%	$C_8H_9N_3$
adsorbed carbendazim	120-230	45.49%	46.62%	H_2O , CO , CH_3OH , HCl
	230-340	54.51%	53.38%	$C_7H_5N_3$

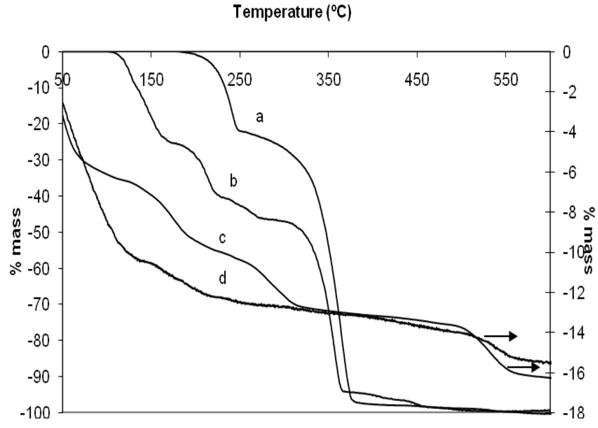

Fig.8: Thermograms obtained for carbendazim (a), carbendazim-HCl adduct (b), adsorbed carbendazim (c) and silica (d) in the range 50-600ºC.

Moreover, the position of these losses on the thermogram, when compared to the ones observed for carbendazim and carbendazim-HCl, suggest that carbendazim is adsorbed as a protonated molecule, as was drawn out from the IR spectra.

IV. CONCLUSION

Pesticide carbendazim is adsorbed by silica from aqueous solutions, adsorption being favored at neutral pH and not being affected considerably by ionic strength (except at high I values). This substance is adsorbed as protonated species rather than as neutral carbendazim on deprotonated sites of silica surface, being this observation supported by IR and TGA analysis of silica after adsorption, and by pH and I effects on adsorption isotherms as well.

The isotherms obtained are Langmuir-type (type I), suggesting that adsorption is, in this case, a physical process. Adsorption ΔH and ΔS values clearly support this hypothesis.

In summary, our results indicate that silica appears to be a good adsorbent for carbendazim at environment conditions (20°C, I= 30 mM, pH= 7), since approximately 90% of the pesticide is adsorbed from solutions 1-3 ppm.

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