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Inffluence of the Activated Carbon Nature and the Aqueous Matrix on the Pesticides Adsorption

Natividad Miguel, María P. Ormad, Rosa Mosteo,
Jorge Rodríguez and José L. Ovelleiro
Department of Chemical Engineering and Environmental Technologies
University of Zaragoza. Pedro Cerbuna, 12. 50009. Zaragoza
Spain

1. Introduction

Water flowing through surface and/or subsoil acquires a chemical composition due to its dissolution effect on soluble minerals of rocks and organic compounds deriving from the degradation of organic matter. This natural composition of water is basically altered by four pollution sources: domestic wastewaters, industrial wastewaters, uncontrolled wastewaters and run-off pollution in agricultural areas. The latter can result in the presence of pesticides in natural waters, because these compounds can pass through the soil and subsoil and pollute surface and groundwaters which are supplies sources for water intended for human consumption.

Pesticides are a group of artificially synthesized substances used to fight pests and improve agricultural production. However, they are generally toxic for living organisms and are very difficult to degrade, being toxic agents with persistent and bioaccumulative effects. In spite of their benefits in the agriculture, they have undesirable effects due to its toxicity, carcinogenesis and mutagenesis (Becker & Wilson, 1980; Kouras et al., 1998).

In Europe, pesticides are considered Hazardous Pollutants in accordance with current legislation relating to water (Directive 2000/60/CE; Directive 2006/11/CE). In the Ebro River Basin (Spain), these substances are controlled via a Pesticides Control Network, which systematically analyzes 44 organic pesticides in surface waters. These pesticides were selected in accordance with their appearance in lists of hazardous substances and/or their high level of use in Spanish agriculture (Claver et al., 2006). Among these substances, there are a big variety of pesticides, such as triazines, urea derivates, drins, etc.

Although the concentration of these substances detected in natural waters is generally very low, the maximum permissible concentration in human drinking waters in Spain is often exceeded (ROYAL DECREE 140/2003), which establishes a limit of 0.5 μg L^{-1} as the total amount of pesticides and 0.1 μg L^{-1} for any single pesticide. Consequently, the treatment used to produce drinking water must guarantee the removal of these types of substances or at least reduce their concentration below the limits established in current legislation.

Systems of drinking water production consist of different stages depending on the initial water quality. Actually, a lot of drinking water plants use an adsorption stage onto activated

carbon in their treatments systems (Ormad et al., 2008). The aim of this stage is the removal of organic compounds, micropollutants such as volatile organic compounds, pesticides, PCBs and phenolic compounds, and some heavy metals with trace concentrations in water. In general, any organic compound with a molecular weight greater than 45 can be adsorbed onto activated carbon (Kenneth et al., 1992). For this purpose, the activated carbon can be used with two shapes: granular activated carbon (GAC) or powered activated carbon (PAC). The adsorption is a superficial phenomenon which is influenced by a lot of factors. These factors are related both the activated carbon (specific surface, particle and pore size, pore distribution, etc.), both the environmental conditions (pH, temperature, chemical composition of the solution, etc.) (Smith & Weber, 1985; Kilduff et al., 1998; Matsui et al., 2003; Gun'ko et al., 2008). The activated carbon is produced from different carbonic substances, of vegetal or mineral origin, by an activation process by which particles with specific surfaces about 10^3 m^2 g^{-1} are achieved. The final properties of activated carbon depend on both the used raw, both the activation method applied (Gun'ko et al., 2008).
The aim of this work is to study the effectiveness of the adsorption process with activated carbon in order to remove the 44 organic pesticides detected systematically in the Ebro river. Moreover, the influence of the activated carbon nature and the aqueous matrix in the treatment is studied. For this, two types of PAC are used: one of mineral origin and other of vegetal one; and the treatment is carried out with two types of solutions, in distilled and natural water. Finally, the influence of the contact time in the removal of the studied pesticides is studied.

2. Materials and methods

2.1 Samples

The adsorption treatment onto PAC is applied on solutions of pesticides dissolved in distilled water (pH = 5.5, dissolved organic carbon (DOC) = 0 mg C L^{-1}) and in natural water coming from Ebro river (Spain) (pH = 8, DOC = 3 mg C L^{-1}). Each sample is fortified with 500 ng L^{-1} of each studied pesticide in order to ensure their presence and to study their possible removal (Miguel et al., 2008). The studied pesticides and their classification according their biological activity, chemical nature and toxicity are shown in table 1.

PESTICIDE	BIOLOGICAL ACTIVITY	CHEMICAL NATURE	TOXICITY
Alachlor	Herbicide	Organic-chlorinated	Moderately toxic
Aldrin	Insecticide	Organic-chlorinated	Very toxic
Ametryn	Herbicide	Heterociclic compound	Moderately toxic
Atrazine	Herbicide	Heterociclic compound	Moderately toxic
Chlorpiryfos	Insecticide	Organic-phosphorated	Very toxic
Chlorfenvinfos	Insecticide	Organic-phosphorated	Extremely toxic
pp'-DDD	Insecticide	Organic-chlorinated	Moderately toxic
pp'-DDE	Insecticide	Organic-chlorinated	Moderately toxic
op'-DDT	Insecticide	Organic-chlorinated	Very toxic
pp'-DDT	Insecticide	Organic-chlorinated	Very toxic
Desethylatrazine	Herbicide	Heterociclic compound	Moderately toxic
3,4-Dichloroaniline	Herbicide	Organic-chlorinated	Moderately toxic

Table 1. Studied pesticides and their characteristics

PESTICIDE	BIOLOGICAL ACTIVITY	CHEMICAL NATURE	TOXICITY
4,4′-Dichlorobenzophenone	Acaricide	Organic-chlorinated	Moderately toxic
Dicofol	Acaricide	Organic-chlorinated	Moderately toxic
Dieldrin	Insecticide	Organic-chlorinated	Extremely toxic
Dimethoate	Insecticide	Organic-chlorinated	Very toxic
Diuron	Herbicide	Urea derivate	Moderately toxic
α-Endosulphan	Insecticide	Organic-chlorinated	Very toxic
Endosulphan-sulphate	Insecticide	Organic-chlorinated	Very toxic
Endrin	Insecticide	Organic-chlorinated	Extremely toxic
α-HCH	Insecticide	Organic-chlorinated	Very toxic
β-HCH	Insecticide	Organic-chlorinated	Moderately toxic
χ-HCH	Insecticide	Organic-chlorinated	Very toxic
δ-HCH	Insecticide	Organic-chlorinated	Moderately toxic
Heptachlor	Insecticide	Organic-chlorinated	Very toxic
Heptachlor epoxide A	Insecticide	Organic-chlorinated	Very toxic
Heptachlor epoxide B	Insecticide	Organic-chlorinated	Very toxic
Hexachlorobenzene	Fungicide	Organic-chlorinated	Very toxic
Isodrin	Insecticide	Organic-chlorinated	Extremely toxic
4-Isopropylaniline	Herbicide	Heterociclic compound	Moderately toxic
Isoproturon	Herbicide	Urea derivate	Moderately toxic
Metholachlor	Herbicide	Organic-chlorinated	Moderately toxic
Methoxychlor	Insecticide	Organic-chlorinated	Slightly toxic
Molinate	Herbicide	Carbamate	Very toxic
Parathion methyl	Acaricide/ Insecticide	Organic-phosphorated	Extremely toxic
Parathion ethyl	Acaricide/ Insecticide	Organic-phosphorated	Extremely toxic
Prometon	Herbicide	Heterociclic compound	Moderately toxic
Prometryn	Herbicide	Heterociclic compound	Slightly toxic
Propazine	Herbicide	Heterociclic compound	Slightly toxic
Simazine	Herbicide	Heterociclic compound	Moderately toxic
Terbuthylazine	Herbicide	Heterociclic compound	Moderately toxic
Terbutryn	Herbicide	Heterociclic compound	Moderately toxic
Tetradiphon	Insecticide/ Acaricide	Organic-chlorinated	Slightly toxic
Trifluralyn	Herbicide	Heterociclic compound	Slightly toxic

Table 1. Studied pesticides and their characteristics (continuation)

2.2 Analytical methodology

The EPA Method 525.2 is used in order to determine the pesticides in samples (EPA Method 525.2). This methods is based on the analysis by gas chromatography together with mass spectrometry (GC/MS), with a previous solid-liquid extraction. An Autotrace Workstation (Zymark) automatic extractor was used for the extraction. The chromatographic conditions

and equipment used are shown in table 2 and results of the methodology validation in table 3. The results were obtained using the Xcalibur POLARIS 1.2 version program (ThermoQuest).

Gas Chromatographer TRACE GC 2000 (TermoFinnigan)	
Column	DB5-MS (J&W, 30 m, 0,25 mm, 0,25 µm)
Temperature program	90 ^{o}C (1 min) – 20 ^{o}C min^{-1} – 180 ^{o}C (1 min) – 2 ^{o}C min^{-1} – 240 ^{o}C (1 min) – 20 ^{o}C min^{-1} – 310 ^{o}C (10 min)
Injector temperature	250^{o}C
Injection volume	1 µL, splitless 0.8 min
Carrier gas	He (N55), 1mL min^{-1}
Mass Spectrometer POLARIS (ThermoFinnigan)	
Ionization energy	70 eV
Acquisition mode	Full scan
Mass array	50-450 amu
Screener speed	1 scan s^{-1}
Acquisition time	32.5 min

Table 2. Pesticides analysis conditions

Pesticide	Quantification limit (µgL^{-1})		Calibration interval (µgL^{-1})	Validity interval (µgL^{-1})	Recovery interval (%)	
	Instrumental step	Full method			Instrumental step	Full method
Isoproturon	20	0.030	20-500	0.030-300	75-130	63-110
Diuron	20	0.030	20-500	0.030-300	82-128	70-123
3.4-Dichloroaniline	20	0.030	20-500	0.030-300	88-130	47-106
4-Isopropylaniline	20	0.030	20-500	0.030-300	80-130	60-125
Desethylatrazine	20	0.030	20-500	0.030-300	76-130	80-129
Trifluralyn	20	0.015	20-500	0.030-300	70-130	70-127
Dimethoate	20	0.030	50-500	0.030-300	66-124	54-137
Simazine	50	0.030	20-500	0.030-600	75-135	64-127
Prometon	20	0.030	20-500	0.030-300	76-124	0-125
Atrazine	200	0.100	200-5000	0.100-300	78-130	75-127
Propazine	20	0.015	20-500	0.015-300	86-130	73-127
Terbuthylazine	20	0.015	20-500	0.015-300	79-130	83-128
Parathion methyl	50	0.030	50-500	0.030-300	78-139	72-130
Parathion ethyl	20	0.030	20-500	0.030-300	74-122	64-128
Alachlor	20	0.015	20-500	0.015-300	75-125	70-124
Ametryn	20	0.030	20-500	0.030-300	78-130	0-116
Prometryn	20	0.030	20-500	0.030-300	80-120	17-116
Terbutryn	20	0.030	20-500	0.030-300	80-120	13-114
Chlorpyrifos	20	0.015	20-500	0.015-300	75-120	73-116
Chlorfenvinfos	20	0.015	20-500	0.015-300	76-130	70-126
HCHs	20	0.015	20-500	0.015-300	84-124	70-120
Hexachlorobenzene	20	0.030	20-500	0.030-300	70-130	74-136
Heptachlor	20	0.015	20-500	0.015-300	75-130	58-113

Table 3. Results of the validation of the pesticides analysis methodology

Pesticide	Quantification limit (μgL^{-1})		Calibration interval (μgL^{-1})	Validity interval (μgL^{-1})	Recovery interval (%)	
	Instrumental step	Full method			Instrumental step	Full method
Heptachlor epoxide A	20	0.015	20-500	0.015-300	85-125	62-112
Heptachlor epoxide B	20	0.015	20-500	0.015-300	84-130	58-113
Aldrin	20	0.015	20-500	0.015-300	85-125	64-126
4,4′-Dichlorobenzophenone	20	0.015	20-500	0.015-300	75-120	68-126
Isodrin	20	0.015	20-500	0.015-300	85-125	66-120
α-Endosulphan	20	0.015	20-500	0.015-300	70-125	70-93
pp′-DDE	20	0.015	20-500	0.015-300	89-122	64-107
Dieldrin	20	0.015	20-500	0.015-300	70-125	62-120
Endrin	20	0.015	20-500	0.015-300	80-125	74-122
pp′-DDD + op′-DDT	40	0.030	40-1000	0.030-600	79-125	66-139
Endosulphan-sulphate	20	0.015	20-500	0.015-300	83-125	73-126
pp′-DDT	20	0.030	20-500	0.030-300	76-130	50-120
Dicofol	50	0.030	50-500	0.030-300	80-148	63-136
Methoxychlor	20	0.015	20-500	0.015-300	77-126	75-130
Metholachlor	20	0.015	20-500	0.015–300	76-115	73-128
Molinate	20	0.015	20-500	0.015–300	91-130	75-113
Tetradifon	20	0.015	20-500	0.015-300	85-130	70-116

Table 3. Results of the validation of the pesticides analysis methodology (continuation)

2.3 Activated carbon characterization

The characterization of used PACs is carried out with analysis by screener electronic microscopy (SEM) and by the method Brunauer-Emmet-Teller (BET). This characterization is carried out before and after each applied treatment.

The BET method is used in order to determine the specific surface by the measurement of the gas adsorption at low termperature. The equipment used is a Micromeritic Instruments Co., Pulse Chemisorb 2700.

The SEM analysis is carried out with a screener electronic microscope (JEOL JSM 6400) which can generates images of secondary and retrodispersed electrons accelerated with tensions between 0.2 and 40 KV. This microscope allow observations up to 3.5 nm of resolution and has coupled a computerized system of dispersed X rays energy (INCA 300 X-Sight, Oxford Instruments) with a resolution of 133 eV to 5.9 KeV. Moreover, it has coupled a computerized system to register and analizar difraction diagrams of retrodispersed electrons (Electron Back Scatter Diffraction).

2.4 Experimental procedure

The treatment of PAC adsorption is applied with distilled and natural water fortified with studied pesticides and the PAC concentration used is 10 mg L^{-1} (in a similar way than in drinking water plants in Spain). The PAC is put into de sample and it is softly stirred during 10 min. in a Jar-Test (SBS).

Two types of PAC are used: BM8 (CHIEMIVALL), of mineral origin and coming from bitominous mineral; and VPlus (CHIEMIVALL), of vegetal origin and coming from wood. Two PACs are activated with vapour and obey with the norm EN-12903 to their application in drinking water. Their characteristics are shown in the table 4.

Specifications	BM8	VPlus
Iodine number (mg g^{-1})	800	950
Ashes content (%)	< 10	3
pH of the aqueous extract	9.0 - 10.0	9.0 - 10.0
Humidity (%)	< 8	5
Particle size	< 0.044 mm (90%)	< 0.044 mm (90%)
Origin	Mineral	Vegetal

Table 4. Characteristics of PAC BM8 and VPlus (CHIEMIVALL)

The concentrations of each pesticide before and after applying the treatment are analysed by GC/MS and the removal yields are calculated according to the equation 1:

$$\eta_{removal\ i} = \left[\frac{C_{i\ \ initial-solution} - C_{i\ \ final-solution}}{C_{i\ \ initial-solution}} \right] * 100 \quad (1)$$

where $\eta_{removal\ i}$ is the removal yield of each pesticide, $Ci_{initial\text{-}solution}$ is the concentration of each pesticide in the sample before the treatment, $Ci_{final\text{-}solution}$ is the concentration of each pesticide in the sample after the treatment, and i each studied pesticide.

Moreover, the average removal yield of all pesticides is calculated according to the equation 2:

$$\eta_{average-removal} = \left[\frac{\sum_i \eta_{removal_i}}{n} \right] \quad (2)$$

where $\eta_{average\text{-}removal}$ is the average removal yield of all studied pesticides, $\eta_{removal\ i}$ is the removal yield of each pesticide and n is the number of pesticides (n=44).

The study of the influence of the treatment time is carried out by experiments at different contact times: 10 min., 30 min., 1 h., 2 h. and 4 h..

3. Results

3.1 Pesticides removal

Pesticides removal percentages achieved after the application of the PAC adsorption treatment, with two types of used PACs and in two studied aqueous matrix, are shown in the table 5.

Average removal percentages achieved in the solution of distilled water are: 34% with mineral PAC and 46% with vegetal PAC. All pesticides in distilled water are better remove by vegetal PAC adsorption, except for the endosulphan-sulphate which is lightly better removed with mineral PAC. It is due to the fact that, in general, the adsorption equilibrium is reached faster with vegetal PAC tan with mineral (Matsui et al., 2003).

With respect to the pesticides solution in natural water, the average removal percentages achieved are: 33% with mineral PAC and 26% with vegetal PAC. In this case, all pesticides are better removed with mineral PAC, with the exception of triazines (simazine, atrazine, propazine, terbuthylazine, prometon, ametryn, prometryn, terbutryn and desethylatrazine) which are removed equal or lightly better with vegetal PAC. It is due to the influence of the organic matter contained in natural water and pore size of the used PACs. Although *a priori* the adsorption onto vegetal PAC is faster, this PAC has a higher pore size, therefore the competition for its occupation between the organic matter of natural water and pesticides increases, decreasing in this way the adsorption (Matsui et al., 2003).

In general, it can be observed that the aqueous matrix doesn't influence in the adsorption treatment with mineral PAC for the group of studied pesticides since the average removal percentages achieved are similar to solutions in distilled and natural water. It is due to the fact that the pore size of the mineral PAC is smaller than the particle size of the organic matter and then their interaction and influence is prevented. However, the adsorption treatment with vegetal PAC is influenced by the used aqueous matrix since to the pesticides solution in distilled water the removal percentages achieved are higher than to the pesticides solution in natural water. This is because the pore size of vegetal PAC is greater and the presence of organic matter in natural water competes with pesticides for the occupation of PAC pores or blocks them getting worse the adsorption capacity (Gillogly et al., 1998; Knappe et al., 1999; Pelekani et al., 1999; Newcombe et al., 2002; Matsui et al., 2003). Moerover, the quantity of pollutants that can be adsorbed in a PAC is lower as the pH of the solution is greater. For this, the adsorption is more effective in distilled water than in natural water (Hu et al., 1998).

Therefore, according to achieved results, the adsorption with vegetal PAC is more effective in order to remove the studied pesticides when they are in distilled water and the adsorption with mineral PAC is more effective, when pesticides are in natural water.

Triazines (simazine, atrazine, propazine, terbuthylazine, prometon, ametryn, prometryn, terbutryn and desethylatrazine) are heterociclic compounds used as herbicides. The adsorption of these substances is more effective with mineral PAC both in natural and distilled water. In distilled water the removal is about 40% and about 20% in natural water.

With respect to organic-phosphorated insecticides (parathion methyl, parathion ethyl, chlorpiryfos, chlorfenvinfos and dimethoate), they are removed in a similar way in distilled and natural water, although their removal in distilled water is more effective using vegetal PAC (45%) and in natural water using mineral PAC (45%).

Hexachlorocilohexanes pesticides (HCHs), which are organic-chlorinated insecticides, are removed in a similar way with mineral PAC both in distilled and natural water. However, the removal of theses pesticides is greater in distilled water with vegetal PAC (40-45%) than with mineral PAC in natural water (30%).

Hexachlorobezene, organic-chlorinated compound used as insecticide, is removed in a similar way with two PACs in distilled water, about 65%. However, it is removed 60% with mineral PAC and 50% with vegetal PAC in natural water.

PESTICIDE	η removal (%) DISTILLED WARTER		η removal (%) NATURAL WATER	
	MINERAL PAC	VEGETAL PAC	MINERAL PAC	VEGETAL PAC
Simazine	30	40	15	25
Atrazine	30	50	15	15
Propazine	30	50	15	20
Terbuthylazine	30	50	25	25
Prometon	20	40	10	10
Ametryn	30	50	25	30
Prometryn	35	50	20	20
Terbutryn	30	45	25	25
Desethylatrazine	25	25	25	25
Parathion methyl	35	55	45	40
Parathion ethyl	40	55	55	45
Chlorpiryfos	35	45	45	30
Chlorfenvinfos	25	30	45	35
Dimethoate	30	40	45	35
α-HCH	30	45	30	30
β-HCH	25	40	30	20
χ-HCH	25	40	30	20
δ-HCH	30	45	30	20
Hexachlorobenzene	65	65	60	50
Heptachlor	20	30	30	15
Heptachlor epoxide A	25	40	25	15
Heptachlor epoxide B	30	40	25	15
α-endosulphan	30	20	20	10
Endosulphan sulphate	40	30	20	10
Endrin	20	35	25	15
Dieldrin	40	50	25	10
Isodrin	30	45	30	15
Aldrin	20	35	25	10
pp´-DDE	20	30	15	10
pp´-DDD+op´-DDT	20	35	30	20
pp´-DDT	20	35	20	10
Isoproturon	15	40	10	15
4-isopropylaniline	90	100	60	60
Diuron	100	100	100	100
3,4-dichloroaniline	80	85	70	65
Molinate	30	50	15	10
Trifluralyn	20	30	35	20
Alachlor	30	45	35	25
Metholachlor	30	45	35	30

Table 5. Removal yields of studied pesticides

PESTICIDE	η removal (%) DISTILLED WARTER		η removal (%) NATURAL WATER	
	MINERAL PAC	VEGETAL PAC	MINERAL PAC	VEGETAL PAC
Methoxychlor	20	40	35	20
Tetradiphon	40	50	35	25
Dicofol	25	50	40	35
4,4´-dichlorobenzophenone	65	75	55	50
η average-removal (%)	**34**	**46**	**33**	**26**

Table 5. Removal yields of studied pesticides (continuation)

Heptachlor, organic-chlorinated insecticides, are removed equal in distilled and natural water with mineral PAC, about 30%. Their removal increases when these pesticides are in distilled water with vegetal PAC achieving removal percentages about 40%.

With respect to drins (aldrin, isodrin, dieldrin and endrin), all of them organic-chlorinated compounds used as insecticides, the vegetal PAC is more effective when they are in distilled water (40%) and the mineral PAC is more effective in order to remove them in natural water (25%).

Regarding to endosulphans, organic-chlorinated insecticides too, they are better removed with mineral PAC both in distilled and natural water.

With respect to DDTs, organic-chlorinated insecticides, the mineral PAC is more effective in order to remove them in natural water achieving removal percentages about 20%, and the vegetal PAC is more effective in distilled water, increasing their removal up to 35%.

Finally, for the rest of studied pesticides, they are better removed with vegetal PAC in distilled water and with mineral PAC in natural water. It's worth noting that diuron, urea derivate pesticide, which is complete removed with two PACs and in both solutions, and anilines (4-isopropylaniline and 3,4-dichloroaniline) for which the removal percentages achieved are very high in all cases.

Since in natural water the more effective PAC is the mineral PAC in order to adsorb the studied pesticides, the study of the influence of the contact time is carried out with mineral PAC and solutions of pesticides in natural water at different contact times (10 min., 30 min., 1 h., 2 h. and 4 h.). Average removal yields of the group studied pesticides at different treatment times are shown in figure 1.

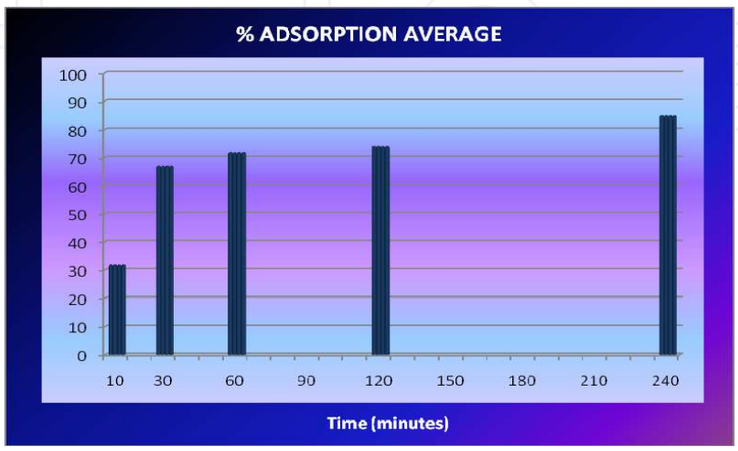

Fig. 1. Average yields of pesticides adsorption with mineral PAC in natural water

Average yields of the pesticides adsorption at different contact times are: 32% in 10 min., 67% in 30 min., 71% in 1 h., 74% in 2 h. and 85% in 4 h. In accordance with these results, it can be observed that the adsorption of pesticides is produced mainly in the first 30 minutes. Since this moment and up to 2 hours of treatment the adsorption continues but lesser. Finally, between 2 and 4 hours of treatment the adsorption lightly increases and the group of studied pesticides is adsorbed 85%.

The evolution of the pesticides adsorption in the time is the typically observed in multi-component mixtures: the main adsorption happens in the first minutes of the treatment, after the adsorption is lower, and finally the adsorption lightly increases (Noll et al., 1992). In the concrete case of the studied pesticides, the main adsorption occurs in the first 30 minutes of treatment, time which coincides with the recommendations given by the WEF-ASCE (WEF-ASCE, 1998) regarding to the contact time in the activated carbon adsorption.

Results about the adsorption of different groups of studied pesticides in natural water with mineral PAC at different contact times are shown in figures 2 to 12.

Triazines adsorption is shown in figure 2.

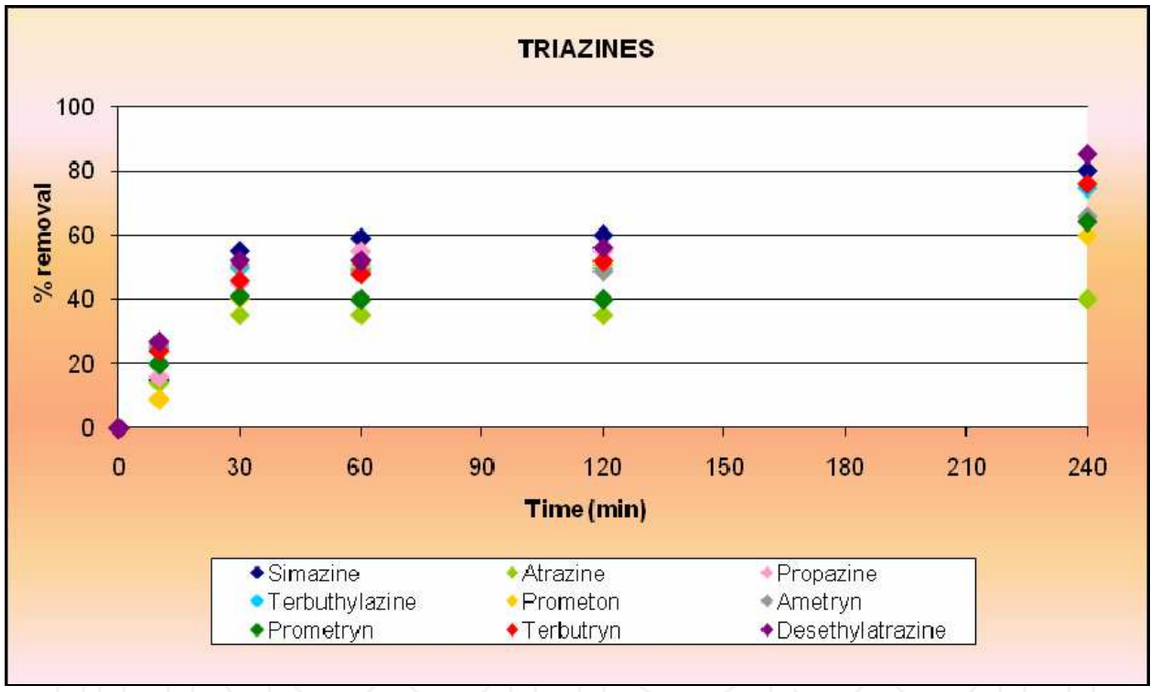

Fig. 2. Triazines adsorption

In accordance with achieved results, and as it is showed in the figure 2, at 10 minutes of contact time the triazines adsorption is between 10 and 25%. This percentage considerably increases up to 35-55% in 30 minutes of treatment. Next, until 2 hours of treatment adsorption isn't observed, and it increases up to 60-85% at 4 hours of treatment for all triazines, with the exception of atrazine which is adsorbed 40% in 4 hours.

With respect to organic-phosphorated pesticides, in the figure 3 it can be observed that the removal at 10 minutes of treatment is about 50%. The adsorption is complete at 30 minutes for all of these pesticides except to chlorpiryfos which is adsorbed 80% in 30 minutes and it requires 4 hours of treatment to remove it completely.

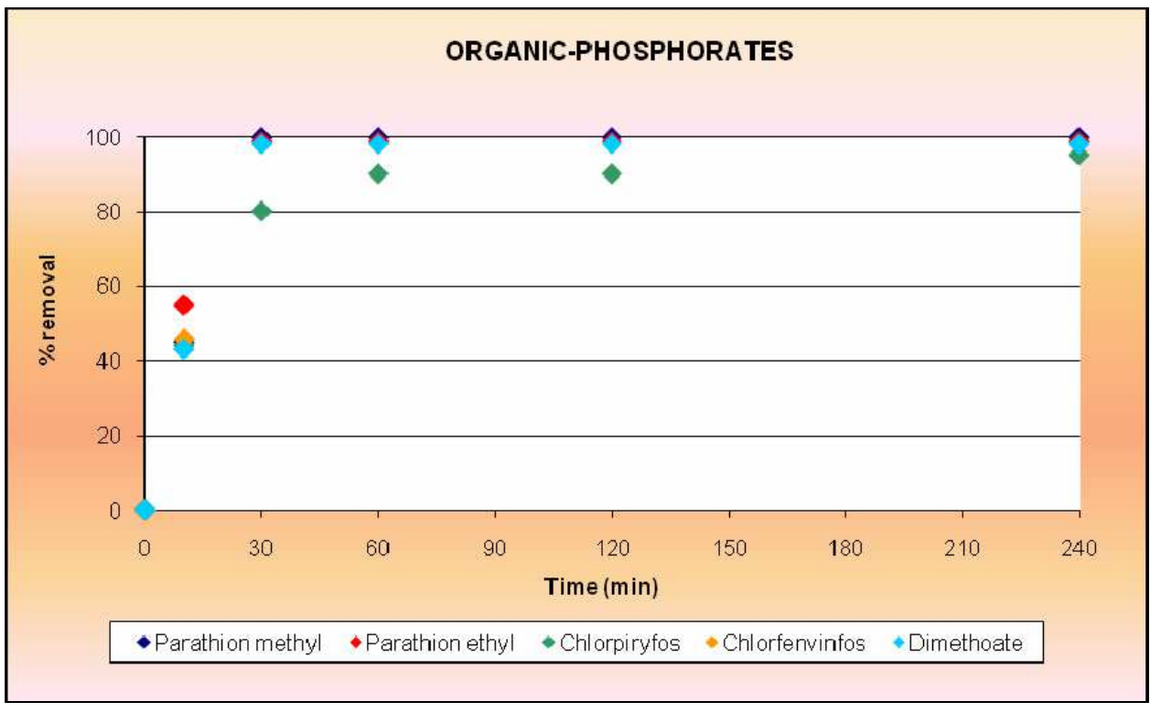

Fig. 3. Organic-phosphorated pesticides adsorption

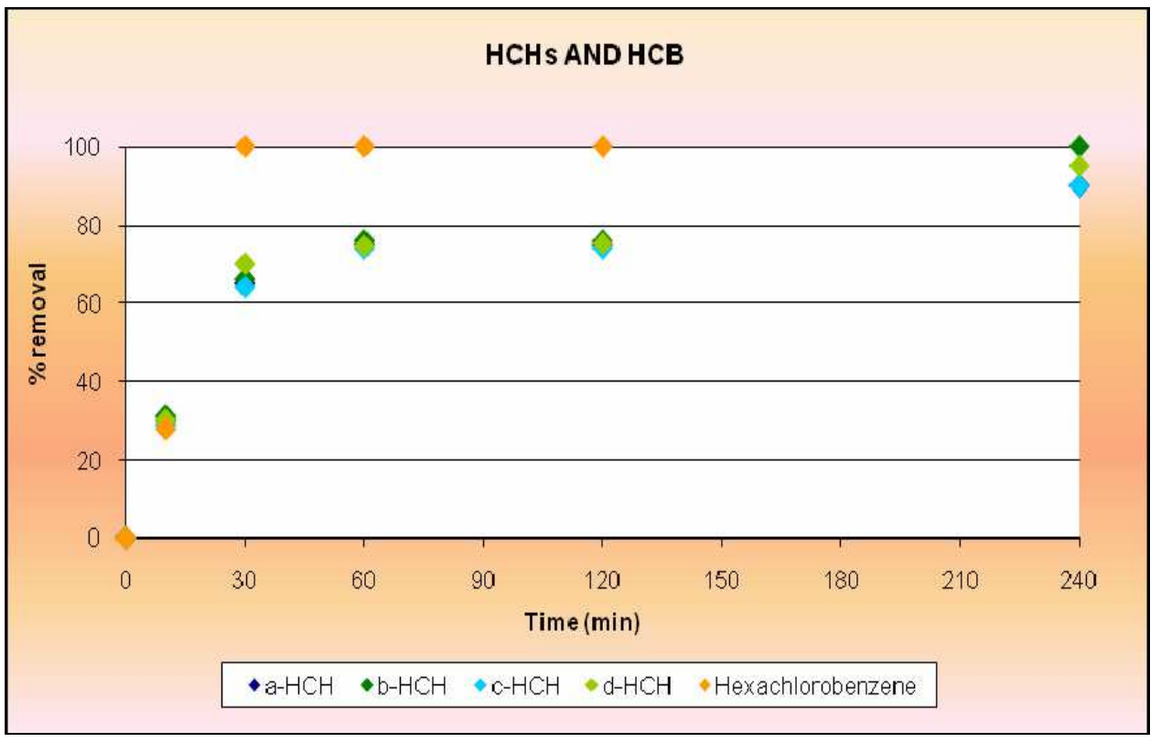

Fig. 4. HCHs and HCB adsorption

Regarding to HCHs (figure 4), it can be observed the same behavior. The adsorption yield at 10 minutes is 30%. This percentage notably increases up to 65% in 30 minutes of treatment and next, practically there isn't adsorption until 2 hours. The adsorption increases up to the complete removal of HCHs at 4 hours of treatment.
The adsorption of hexachlorobenzene (HCB, figure 4) is faster since at 10 minutes of treatment the adsorption is 60% and it is complete removed at 30 minutes.
With respect to heptachlors (figure 5) it can be observed that three heptachlor are adsorbed about 25% in 10 minutes. The adsorption increases, mainly for heptachlor, until 30 minutes. At this time the removal of heptachlor is 90% and of heptachlors epoxide is 60%. Until 2 hours the adsorption doesn't increase and it lightly increases at 4 hours. The complete removal of heptachlor is achieved at 2 hours and after 4 hours of treatment the removal of heptachlors epoxide is about 70%.

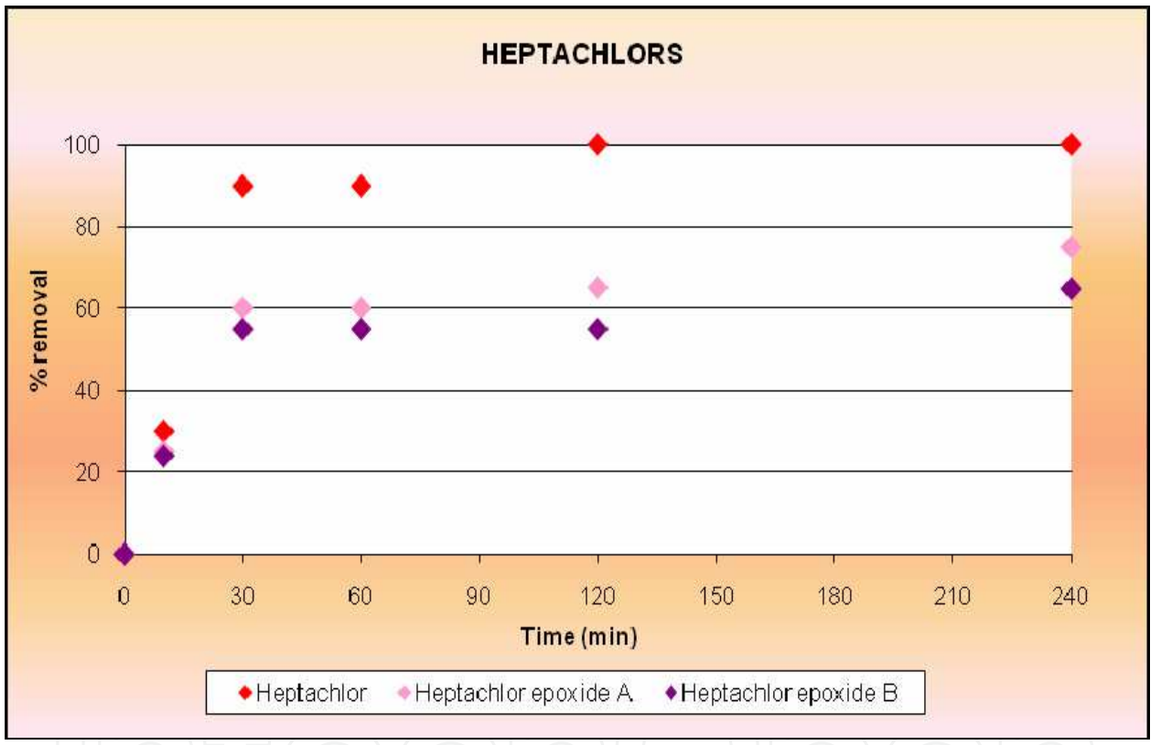

Fig. 5. Heptachlors adsorption

The behavior of two studied endosulphans is completely different, as can be observed in figure 6. Two of them are adsorbed 20% at 10 minutes, but α-endosulphan is complete removed at 30 minutes meanwhile endosulphan sulphate is adsorbed 70% after 4 hours of treatment.
With respect to drins (figure 7), all of them are removed about 30% in 10 minutes of treatment. At this time, the aldrin and isodrin (isomers between them) adsorption increases with the time, achieving adsorption yields about 85-100% in 4 hours. In the case of endrin and dieldrin (isomers between them), the adsorption is lower and after 4 hours their removal yields are about 60%.
In accordance with results obtained for DDTs (figure 8), their adsorptions are similar until 1 hour of treatment (50-60%). After and until 4 hours, the adsorption of pp'-DDE and pp'-DDD+op'-DDT lightly increases up to 65-85%. On the contrary, the adsorption of pp'-DDT notably increases at 2 hours or treatment achieving its complete removal.

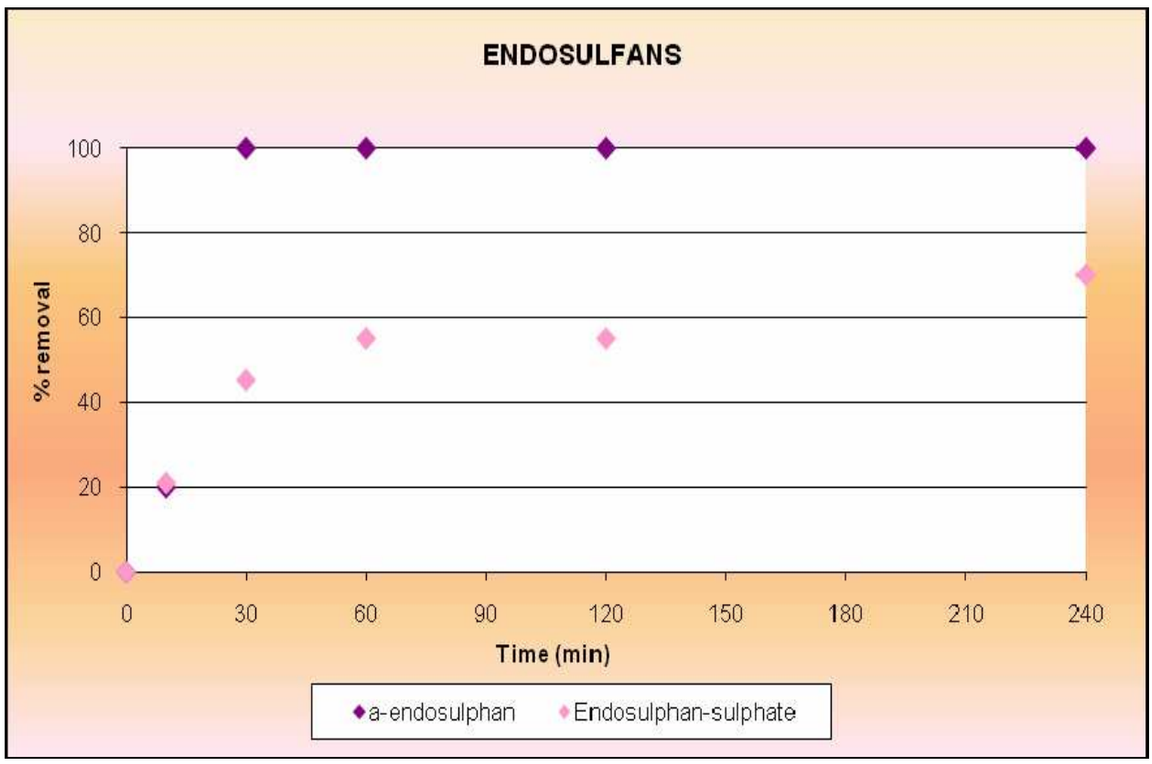

Fig. 6. Endosulphans adsorption

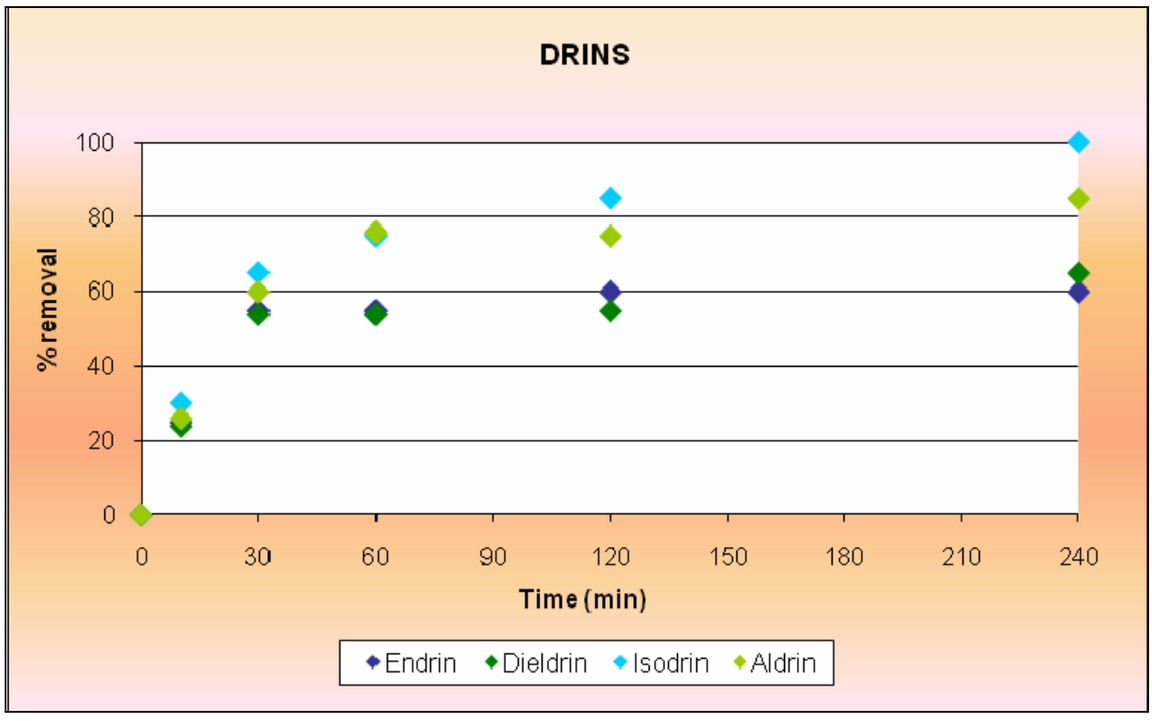

Fig. 7. Drins adsorption

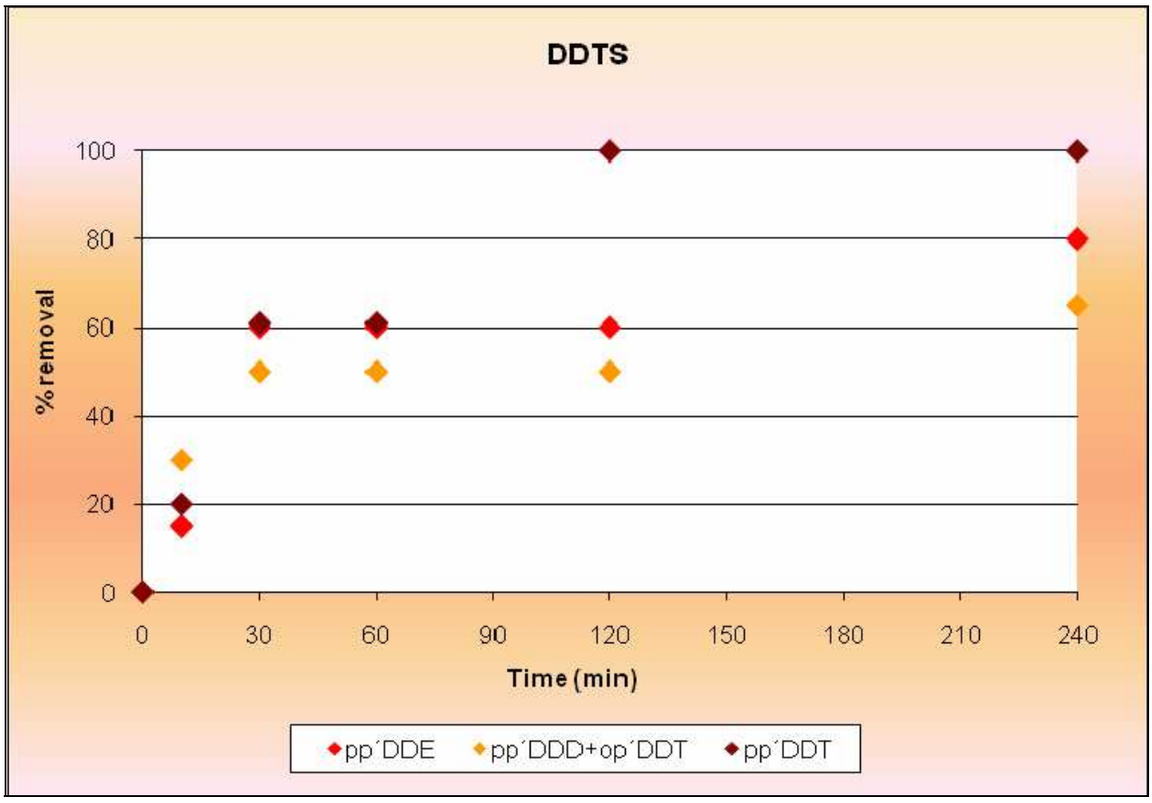

Fig. 8. DDTs adsorption

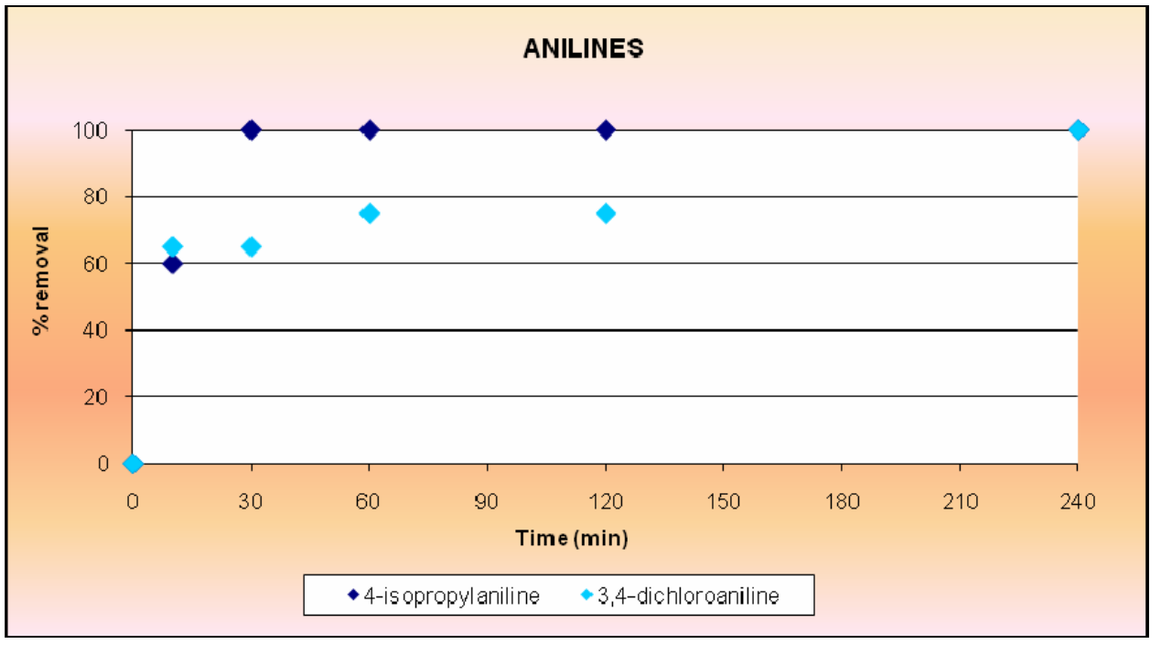

Fig. 9. Anilines adsorption

With respect to anilines (figure 9), it can be observed their different behavior to the adsorption versus the time. Two anilines are removed about 70% at 10 minutes of treatment. However, 4-isopropylaniline is complete adsorbed at 30 minutes meanwhile 3,4-dichloroaniline requires 4 hours of treatment for its total adsorption.
Regarding urea derivates pesticides (figure 10), their behavior is complete different too. At 10 minutes the diuron removal is very high, 65%. Its removal increases up to 95% after 4 hours of treatment. On the contrary, isoproturon is adsorbed 10% in 10 minutes although after 4 hours the same adsorption than diuron is achieved (95%).

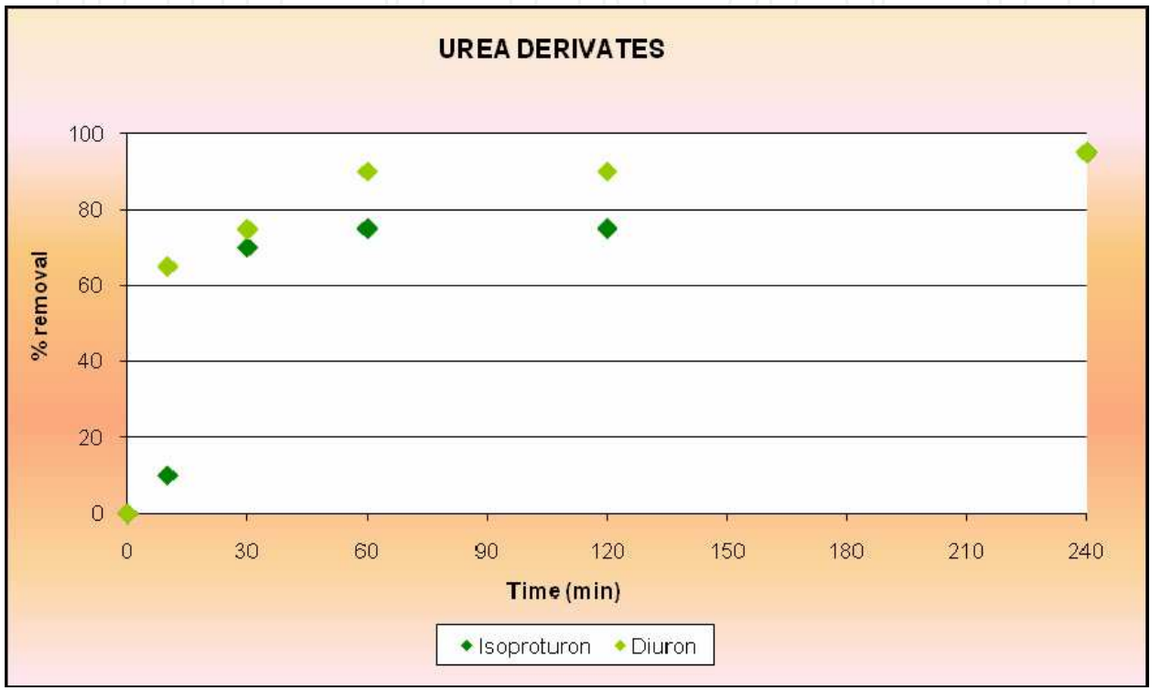

Fig. 10. Urea derivates adsorption

In accordance with the results obtained to anilides (figure 11), it can be observed the same behavior for alachlor and metholaclor, and different one for methoxychlor. The three pesticides are adsorbed 35% in 10 minutes. However, alachlor and metholachlor increase their adsorption gradually with the time, achieving a removal about 70% in 4 hours of treatment, while the methoxychlor adsorption is 90% in 30 minutes and total in 4 hours.
With respect to the rest of studied pesticides (figure 12), dicofol and 4,4'-dichlorobenzophenone are quickly adsorbed achieving their complete adsorption in 30 minutes of treatment. Molinate and trifluralyn are mainly adsorbed in the first 30 minutes of treatment and after 4 hours, the adsorption is total, like a lot of studied pesticides. Finally, the tetradiphon adsorption is progressive in the time and its complete adsorption is achieved in 2 hours of treatment.
As it has been mentioned before, the adsorption of studied pesticides shows the typical tendency of a multicomponent mixture. Moreover, the main adsorption of the group of pesticides happens in the first 30 minutes of treatment. In this time, the removal of each individual studied pesticide presents a pseudo-first order kinetic, that is corresponded with the next equation:

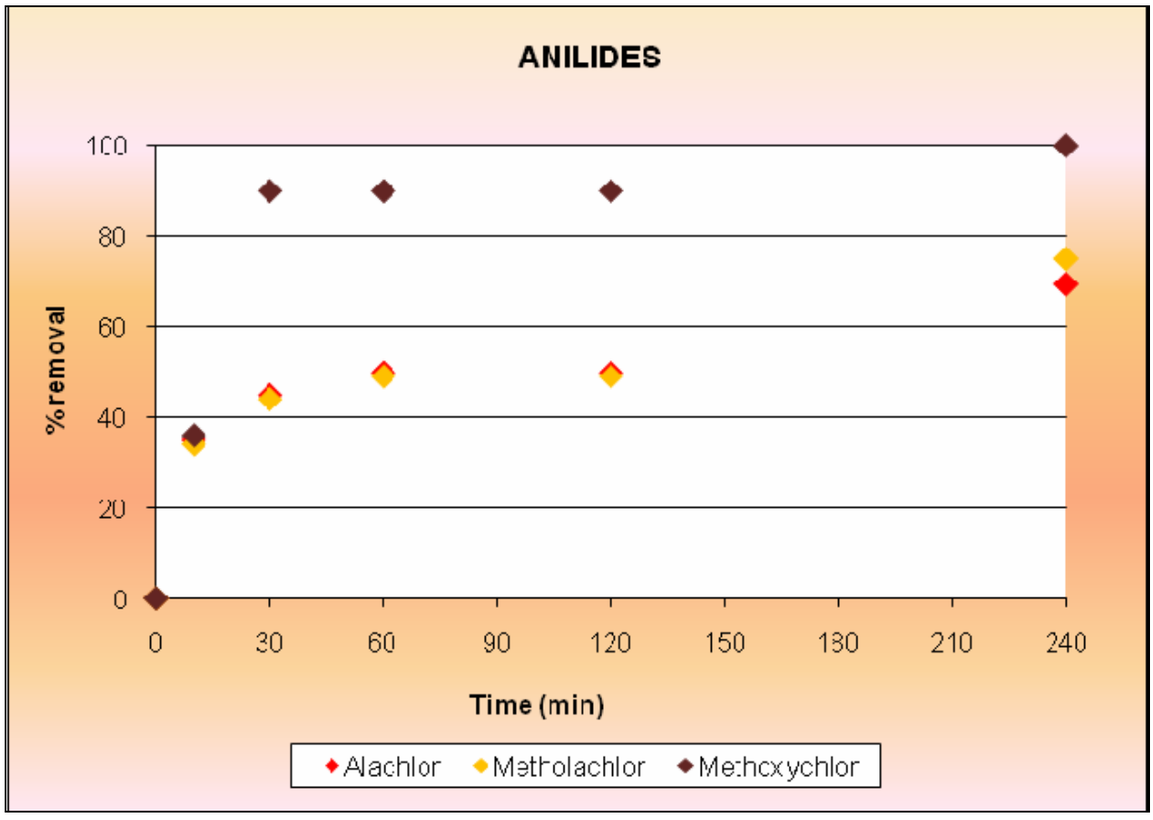

Fig. 11. Anilides adsorption

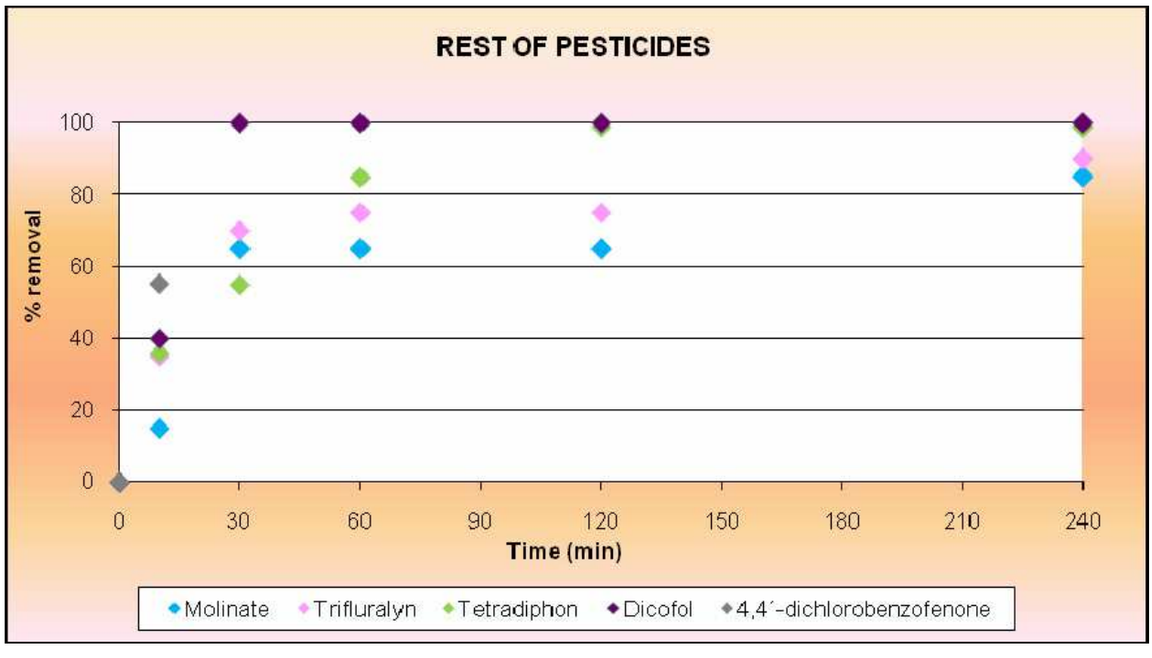

Fig. 12. Rest of studied pesticides adsorption

$$\log \frac{C}{C_0} = k * t \tag{3}$$

Where C is the pesticide adsorbed concentration, C_0 is the pesticide initial concentration, t is the time of treatment and k is a constant which represents the adsorption rate of each pesticide. Rate constants, k, of each studied pesticide and regression coefficients, R^2, obtained for each lineal equation are shown in table 6.

As it can be observed, with a contact time of 30 minutes, the most of studied pesticides follows a kinetic of pseudo-first order, just like in studies carried out by other authors (Ayranci and Hoda, 2005; Salman and Hameed, 2010). Moreover, rate constants obtained haven't any direct relation neither solubility nor molecular weight of studied pesticides (Ayranci and Hoda, 2005).

With respect to individual pesticides, parathion methyl and ethyl, chlorfenvinfos, dimethoate, hexachlorobenzene, α-endosulphan, 4-isopropylaniline, dicofol and 4,4'-dichlorobenzophenone are the pesticides that are adsorbed faster.

Three times slower than these pesticides, are adsorbed heptaclor and methoxyclor, and about a half of these, chlorpiryfos, molinate, HCHs, diuron and isoproturon are adsorbed.

PESTICIDE	k (h^{-1})	R^2	PESTICIDE	k (h^{-1})	R^2
Simazine	0,712	0,985	Heptachlor epoxide B	0,687	0,998
Atrazine	0,369	0,996	α-endosulphan	5,703	0,920
Propazine	0,525	0,997	Endosulphan sulphate	0,517	0,997
Terbuthylazine	0,589	0,989	Endrin	0,687	0,998
Prometon	0,462	0,984	Dieldrin	0,687	0,998
Ametryn	0,589	0,989	Isodrin	0,908	1,000
Prometryn	0,432	0,983	Aldrin	0,797	1,000
Terbutryn	0,496	0,965	pp´-DDE	0,822	0,977
Desethylatrazine	0,595	0,989	pp´-DDD+op´-DDT	0,575	0,952
Parathion methyl	5,649	0,960	pp´-DDT	0,810	0,993
Parathion ethyl	5,691	0,947	Isoproturon	1,102	0,944
Chlorpiryfos	1,381	0,997	4-isopropylaniline	5,634	0,967
Chlorfenvinfos	5,661	0,948	Diuron*	1,075	0,771
Dimethoate	5,858	0,946	3,4-dichloroaniline*	0,769	0,557
α-HCH	0,908	1,000	Molinate	0,947	0,970
β-HCH	0,908	1,000	Trifluralyn	1,037	0,998
χ-HCH	0,908	1,000	Alachlor*	0,471*	0,807
δ-HCH	1,052	0,999	Metholachlor*	0,479*	0,815
Hexachlorobenzene	5,618	0,967	Methoxychlor	2,061	0,980
Heptachlor	2,076	0,970	Tetradiphon	0,659	0,939
Heptachlor epoxide A	0,797	1,000	Dicofol	5,812	0,941
			4,4´-dichlorobenzophenone	5,671	0,960

*In the case of diuron, 3,4-dichloroaniline, alachlor and metholachlor, the regression coefficiente obtained are lower than for the rest of pesticides. It is due to the fact that the main adsorption of these pesticides happens in the first 10 minutes of treatment

Table 6. Rate constants and regression coefficients of studied pesticides

Finally, pesticides wich are adsorbed slowest onto activated carbon are triazines, heptachlors epoxide, endosulphan-sulphate, drins, DDTs, 3,4-dichloroaniline, alachlor, metholachlor and tetradiphon.

3.2 Results of activated carbon characterization

Results corresponding to the chemical analysis by SEM of used PACs (vegetal and mineral), before and after applying treatments in distilled and natural water, are shown in table 7.
In accordance with the comparison of the SEM analysis before and after the treatments, the main variations produced are the following:

- Oxygen percentage lightly increases after the treatment in natural water for both PACs, vegetal and mineral.
- A little quantity of calcium appears after the treament in natural water for both PACs.
- For the rest of elements, the variations produced after applying treatments aren't significants.

Results corresponding to the characterization of vegetal and mineral PAC after the treatment in distilled and natural water by the BET method are shown in table 8.
In accordance with the results obtained about BET surfaces, it can be said that:

- The treatment in distilled water doesn't cause the reduction of the surface are in both used PACs.
- The treatment in natural water causes a reduction of the surface are in both PACs, about 10%. This decrease is due to the adsorption of organic matter contained in natural water onto activated carbon.

VEGETAL PAC			
ELEMENT	**% WEIGHT BEFORE THE TREATMENT**	**% WEIGHT AFTER TREATMENT IN DISTILLED WATER**	**% WEIGHT AFTER TREATMENT IN NATURAL WATER**
O	1.41	1.57	4.44
Si	-	0.30	0.49
Ca	-	-	0.41
Al	-	-	-
S	-	-	-
Fe	-	-	-
MINERAL PAC			
ELEMENT	**% WEIGHT BEFORE THE TREATMENT**	**% WEIGHT AFTER TREATMENT IN DISTILLED WATER**	**% WEIGHT AFTER TREATMENT IN NATURAL WATER**
O	2.93	3.01	3.47
Si	0.69	1.03	1.03
Ca	-	-	0.26
Al	0.35	0.33	0.38
S	0.24	0.37	0.16
Fe	0.24	0.32	0.37

Table 7. Results about the chemical analysis by SEM of used PACs

PAC	BET SURFACE ($m^2 g^{-1}$)		
	Before the treatments	After the treatments in distilled water	After the treatment in natural water
VEGETAL	555.2±10.9	563.2±12.0	497.6±9.9
MINERAL	745.4±14.5	746.7±14.3	676.9±13.0

Table 8. BET surfaces of used PACs

4. Conclusions

In accordance with the study of the activated carbon nature and aqueous matrix influence it can be said that:

- Removal percentages of studied pesticides achieved in a contact time of 10 minutes are: 34% with mineral PAC and 46% with vegetal PAC to the solution in distilled water; 33% with mineral PAC and 26% with vegetal PAC to the solution in natural water.
- In general, the adsorption with vegetal PAC is more effective in order to remove the studied pesticides in distilled water, and the adsorption with mineral PAC is more effective in order to remove the studied pesticides in natural water.
- In the solution of distilled water, all pesticides are better removed by the treatment with vegetal PAC, with the exception of endosulphan-sulphate which is lightly better removed with mineral PAC.
- With respect to the solution in natural water, all studied pesticides have greater removal percentages by the adsorption with mineral PAC, with the exception of some triazines which are lightly better removed with vegetal PAC.
- In general, the adsorption treatment with mineral PAC isn't influenced by the aqueous matrix since the average removal percentages obtained are similar both distilled and natural water. However, the use of vegetal PAC is influenced by the aqueous matrix since the average removal percentages achieved in natural water are considerably lower that the percentages achieved in distilled water.
- The treatment of activated carbon adsorption in distilled water doesn't cause the surface are reduction in any used PAC. However, the treatment in natural water causes a reduction about 10% of two PACs. This reduction is due to the adsorption of organic matter of the natural water onto the activated carbon.

According to the study of the influence of the contact time it can be said that:

- The adsorption with mineral PAC in natural water achieves a partial removal of the studied pesticides.
- Average adsorption percentages of studied pesticides in natural water in different contact times using mineral PAC are: 32% in 10 minutes, 67% in 30 minutes, 71% in 1 hour, 74% in 2 hours and 85% in 4 hours.
- The main adsorption of studied pesticides is achieved in the first 30 minutes of treatmen with mineral PAC. This time coincides with the recommendations given by the WEF-ASCE (WEF-ASCE, 1998) regarding to the contact time in the activated carbon adsorption.

- The most of studied pesticides have a pseudo-first order kinetic in the first 30 minutes of contact time.
- Organic-phosphorated pesticides, hexachlorobenzene, heptachlor, α-endosulphan, 4-isopropylaniline, methoxychlor and 4,4'-dichlorobenzophenone are the pesticides which are fastest adsorbed. Triazines, heptachlors epoxide, drins, DDTs, endosulphan-sulphate, 3,4-dichloroaniline, alachlor, metholachlor and tetradiphon are the pesticides which are slowest adsorbed.

Therefore, the treatment of adsorption with PAC is an effective technique in order to remove pesticides in water.

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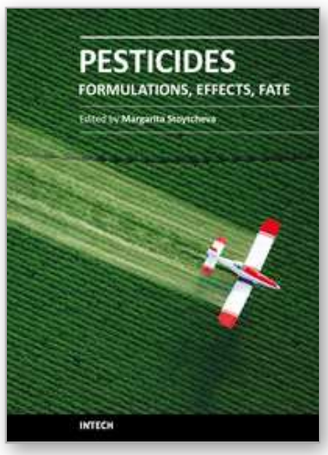

Pesticides - Formulations, Effects, Fate
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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
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