B A
S E

Biotechnol. Agron. Soc. Environ. 2003 **7** (2), 79–85

An assessment methodology for determining pesticides adsorption on granulated activated carbon

Marie-Catherine Gérard, Jean-Paul Barthélemy

Unité de Chimie analytique et Phytopharmacie. Faculté universitaire des Sciences agronomiques de Gembloux. Passage des Déportés, 2. B–5030 Gembloux (Belgique). E-mail : barthelemy.jp@fsagx.ac.be

Received 3 February 2003, accepted 28 April 2003.

In many countries, water suppliers add granular activated carbon reactor in the drinking water treatment notably in order to remove pesticides residues. In Europe, their concentrations must lie below the values imposed by the EU directives (98/83/EC). A couple of years ago, some mini-column tests were developed to improve the use of the activated carbon reactor in relation with lab experiments. Modelling, which was elaborated to predict the lifetime of reactors, did not bring validated results. Nevertheless, this kind of experiment allows us to assess the adsorption performances of an activated carbon for different pesticides. Because of the lack of comparable available results, we have developed a standardized methodology based on the experiment in mini-column of granular activated carbon. The main experimental conditions are activated carbon: Filtrasorb 400 (Chemviron Carbon); water: mineral and organic reconstituted water (humic acid concentration: 0,5 mg/l); influent concentration 500 $\mu g \cdot l^{-1}$; activated carbon weight: 200 mg; EBCT (Empty Bed Contact Time): 0.16 min.; linear speed: 0.15 $m \cdot s^{-1}$. In these conditions, it appears that diuron is highly adsorbed in comparison with other active substances like chloridazon, atrazine or MCPA. From the ratio of effluent volume for the breakthrough point with respect to diuron, it is suggested that products of which the difference factor ratio is – (a) below 0.40: may be reckoned as weakly adsorbed (MCPA); (b) from 0.41 to 0.80: may be reckoned as moderately adsorbed (chloridazon and atrazine); (c) above 0.80: as highly adsorbed on granular activated carbon. Active substances that are weakly adsorbed and have to be removed from drinking water, may highly reduce the lifetime of an activated carbon bed. This kind of information is particularly useful for water suppliers and for regulatory authorities.
Keywords. Activated carbon, adsorption, herbicides, drinking water process, pesticides.

Une méthodologie d'évaluation pour la détermination de l'adsorption de pesticides sur le charbon actif en grains. Dans plusieurs pays, les producteurs d'eau ajoutent un réacteur de charbon actif en grains dans leur chaîne de production d'eau potable. Le but est d'éliminer notamment les résidus de produits phytosanitaires. En Europe, leur concentration doit se situer en dessous des normes légales décrites dans les directives de l'UE (98/83/CE). Il y a quelques années, des tests en mini-colonnes ont été développés afin d'améliorer l'utilisation des réacteurs de charbon actif à partir d'expériences menées à l'échelle du laboratoire. Les modèles mathématiques, qui avaient été élaborés pour prévoir le temps d'utilisation des réacteurs, n'ont pas pu livrer de résultats validés. Néanmoins, ce type d'expérience permet d'estimer les performances d'adsorption d'un charbon actif pour différents pesticides. En fonction du manque de résultats disponibles comparables, nous avons développé une méthodologie standardisée basée sur l'expérience en mini-colonne de charbon actif en grains. Les conditions expérimentales principales sont : charbon actif Filtrasorb 400 (Chemviron Carbon) ; eau minérale et organique reconstituée (concentration en acide humique : 0,5 mg/l) ; concentration de l'influent 500 $\mu g \cdot l^{-1}$; masse de charbon actif 200 mg ; EBCT (temps de contact en lit vide) 0,16 min. ; vitesse linéaire 0,15 $m \cdot s^{-1}$. Dans ces conditions, il apparaît que le diuron est fortement adsorbé en comparaison avec d'autres matières actives, comme le chloridazon, l'atrazine ou encore le MCPA. En faisant le rapport du temps de percée d'un produit à celui du diuron, il est suggéré de classer les substances comme suit – rapport inférieur à 0,40 : peuvent être reconnues comme peu adsorbées (MCPA) ; rapport de 0,41 à 0,80 : peuvent être reconnues comme moyennement adsorbées (chloridazon et atrazine) ; rapport supérieur à 0,80 : substances fortement adsorbées sur le charbon actif en grains. Les matières actives qui sont peu adsorbées et qui doivent être éliminées de l'eau potabilisable, peuvent fortement réduire le temps d'utilisation du lit de charbon actif. Ce type d'information est particulièrement utile pour les producteurs d'eau et pour les autorités d'agréation des produits phytosanitaires.
Mots-clés. Charbon actif, adsorption, herbicide, potabilisation des eaux, pestcide.

1. INTRODUCTION

For many years, monitoring surveys carried out in Europe as well as in United States, have pointed out that using agricultural and non agricultural pesticides leads to residues in surface and ground waters (Hopman *et al.*, 1992; Bouland *et al.*, 1998; Chauveheid *et al.*, 1999; Duguet, d'Arras, 1999; Phytophar-Belgaqua, 1997, 1999).

According to the 80/778/EEC directive (CE, 1980), the 97/57/EEC directive (CE, 1997), which states the annex VI of the 91/414 directive regarding the setting on the market of pesticides, and the 98/83/EC directive (CE, 1998), the maximal admitted concentration is 0.1 $\mu g \cdot l^{-1}$ for each pesticide and 0.5 $\mu g \cdot l^{-1}$ for the whole in drinking water.

In order to manage this environmental issue, different mathematical prediction models were elaborated, as PESTLA, GLEAMS, PELMO, etc. (Cornejo *et al.*, 2000) and different possibilities to remove pesticides from waters were developed, as adsorption on activated carbon, ozone treatment, etc. (Camel, Bermond, 1998, Beltran *et al.*, 1999, Chiron *et al.*, 2000, Ince, Apikyan, 2000, Rositano *et al.*, 2001).

The insertion of activated carbon in the drinking water process allows removing by adsorption substances like dissolved natural organic matter, micro-pollutants, etc. Activated carbon may be used in powder and in granules. Powdered activated carbon is added in coagulation-flocculation tanks and taken off in the filtration steps. The reactor of granular activated carbon is inserted in the filtration steps in the drinking water process. Thus, these reactors also work as a bacterial bed. Adsorption on activated carbon and microbial breakdown process occur in the granular activated carbon bed.

Experiments in mini-column, which are led on lab scale, were developed in order to assess the adsorption performances of granular activated carbons for different substances. The results obtained in laboratory could be adapted on a pilot or industrial scale by modelling, for example by Rapid Small Scale Column Test (Crittenden *et al.*, 1991; Le Bec *et al.*, 1994; Hopman *et al.*, 1994). However, the application in industrial conditions, as for instance in surface waters whose composition and bacterial charge vary from a river to another, has brought to the fore that the experiment in mini-column cannot be used to assess the lifetime of activated carbon reactors (Heijman, Hopman, 1999). In the opposite, this experiment allows comparing the adsorption performances of different activated carbons, or the adsorption performances of one activated carbon for different substances (Gérard, 2002).

Determining the adsorption performances of activated carbon for pesticides has already been studied by experiments in mini-column (Matsui *et al.*, 1994; Gérard *et al.*, 1998; Paune *et al.*, 1998; Griffini *et al.*, 1999). Unfortunately, the experimental conditions used by each of them appear to be so different that it is impossible to compare the results or to get a global view of adsorption performances for the studied substances.

The setting of a standardized experiment to assess the adsorption performances on granular activated carbon is warranted by the pesticide issue management in the drinking water treatment and by the demands of regulatory authorities. Therefore, we developed a methodology able to demonstrate the differences of adsorption performances of a granular activated carbon for herbicides, which are characterized by different physico-chemical properties, and mainly in a short time experiment (maximum 15 days).

In this case, we have to use as initial concentrations very high values that are not representative of the concentrations measured in natural waters. Therefore, the comparison of the results to the reference value of 0.1 $\mu g \cdot l^{-1}$ does not make sense. Other reference values will be taken into account.

2. MATERIALS AND METHODS

2.1. Materials

Apparatus. LC analyses were performed with a high pressure liquid chromatograph (HPLC) Beckman with GOLD System, including a Programmable Solvent Module 126 and a Diode Array Module 168 Detector. The injection loop is 50 µl.

Stationary phases columns and Solid Phase Extraction (SPE) cartridges. The HPLC analytical column is 25 cm, 4 mm I.D. packed with 5-µm Nucleosil 100-5 C18 HD (Machery-Nagel).

The SPE cartridges are used for water extraction. To the cartridge Oasis 3cc (60 mg) we have added 500 mg bulk C18 (Waters).

Chemicals. All organic solvents were purchased "chromatographic grade" (Acros). LC-quality water was prepared by purifying distilled water in a Milli-Q filtration system (Millipore). Other chemicals were obtained from Merck.

The pesticides were supplied by Dr. Ehrenstorfer. The main physico-chemical properties are presented in **table 1**.

We used the humic acids Fluka n°53680 (Riedel-de-Haën).

The activated carbon is Filtrasorb 400 (Chemviron Carbon), of which the specific surface is 1100 $m^2 \cdot g^{-1}$. The granulometry of the activated carbon lies between 0.075 and 0.150 mm.

Table 1. The main physico-chemical properties of pesticides — *Principales propriétés physico-chimiques des pesticides* (*Pesticide Manual*, 1999).

Parameter	Atrazine	Diuron	MCPA	Chloridazon
Formule	$C_8H_{14}ClN_5$	$C_9H_{10}Cl_2N_2O$	$C_9H_9ClO_3$	$C_{10}H_8ClN_3O$
Molecular weight (Da)	215.7	233.1	200.6	221.6
Solubility in water (mg·l^{-1})	33 at 22°C	36,4 at 25°C	734 at 25°C	340 at 20°C
pKa	1.7	-	3.07	-
DT50	86 days at pH 5 5 days at pH 13	90–180 days	< 7 days to 1 month*	150 hours at pH 7
Kow	2.5	2.85	2.75	1.19

- = no data ; * = in relation with microbial activity, moisture content and the concentration of organic matter in soil; DT50 = degradation time 50%; Kow = Octanol water ratio.

The mineral and organic reconstituted waters correspond to mineral reconstituted water (these data were kindly communicated by the water supplier in Belgium CIBE (Compagnie Intercommunale Bruxelloise des Eaux), to which humic acids are added. Since humic acids are responsible for a large part of the competitor effect of the natural organic matter against pesticides, they are added to the mineral reconstituted water in order to have a standardized global reconstituted water.

The Meuse water is characterized by a Total Organic Carbon (TOC) of 2.47 mg C·l^{-1}, pH of 8.21 and conductivity of 471 µS·cm^{-1}.

2.2. Methods

Analytical method of diuron, atrazine, chloridazon and MCPAin water. The analytical methods of diuron, atrazine, chloridazon and MCPA are based on SPE (off-line)-HPLC-DAD (Diode Array Detector) methods which are described elsewhere (Gérard *et al.*, 2001). The recoveries correspond to the European demands of the 91/414/EEC-guideline on residue analytical method, that set SPE (Solid Phase Extraction) recovery values between 70 and 110 % with RSD (Relative Standard Deviation) below or equal to 20 %. These methods make it possible to reach the quantification limit of 0.03 µg·l^{-1} for diuron, atrazine, chloridazon and 0.06 µg·l^{-1} for MCPA in distilled water.

Experiment in mini-column with granular activated carbon. The features of the experiment are based on the Accelerated Column Test (ACT) (Van Santfoort, 1990). They are made of an influent solution (volume : 5 l), an HPLC pump (flow rate: 3 ml·min^{-1}), the granular activated carbon column, and of the effluent solution (**Figure 1**). The influent and effluent solutions and the granular activated carbon column lie in a cooling bath at the temperature of 10 °C ± 1 °C.

In the influent solution, 1 g NaN_3 l^{-1} is added in order to avoid any microbial development on the activated carbon in the mini-column. The objective of this experiment is to assess the adsorption of pesticides on granular activated carbon, without taking into account the microbial contribution in pesticides removal in the column.

Two different pesticide concentrations in the influent solutions are tested: on the one hand 500 µg·l^{-1}, and on the other hand 100 µg·l^{-1}. Although these concentrations are 1000 times higher than what may be analyzed in surface water in Belgium, the influent concentration has to be adapted to a feasible experiment on lab scale. Since the objective is to compare the adsorption performances of an activated carbon for different pesticides, the choice of the influent concentration has to be made so as to illustrate significant different adsorption performances between pesticides and to classify them.

The experimental conditions are :
- activated carbon weight: 200 ± 5 mg, density: 425 kg·m^{-3},
- column design: length: 25 cm, diameter: 0.5 cm, carbon bed height: ± 2.4 cm,
- flow rate: 3 ml·min^{-1} (± 10 %).

The column is conditioned by going through milliQ water during 15 hours.

At each 10 l·g^{-1} , the influent solution is renewed.

The principle of the experiment is to measure the concentration evolution of pesticides in the effluent in relation with the water volume that goes through the column. The results allow plotting the breakthrough curve of a substance, and therefore illustrating the water volume that may go through the activated carbon bed up to reaching the breakthrough point in the effluent.

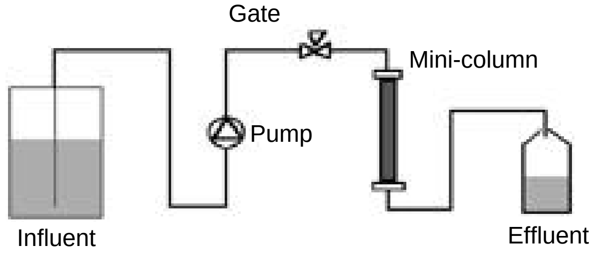

Figure 1. Experiment in mini-column of granular activated carbon — *Expérience en mini-colonne de charbon actif en grains.*

3. RESULTS

3.1. Experimental parameters

The experimental parameters are presented in **table 2**.

According to these data and results, it appears that the measured influent concentrations are in agreement with the Directive 91/414 guideline on residue analytical method (CE, 1991), that set up the recoveries between 70 and 110 %. Finally, these data and results reveal that the experimental conditions are similar.

3.2. Experiments in mini-column of granular activated carbon : influent concentration 500 µg·l^{-1}

The results of the breakthrough curves of the different substances are presented in **figure 2**.

The four herbicides that are characterized by mere different physico-chemical properties (**Table 1**) show very different results.

3.3. Experiments in mini-column of granular activated carbon: influent concentration of 100 and 500 µg·l^{-1}

Experiments in mini-column of granular activated carbon are also carried out with an influent concentration of 100 µg·l^{-1}, for diuron and MCPA, the most and the less adsorbed substances in our scale (**Figure 2**).

The objective of these experiments is to highlight the most effective influent concentration to determine significant adsorption differences between the substances and especially in a short time (maximum 15 days).

Breakthrough curves of diuron and MCPA in mineral and organic reconstituted water (humic acids: 0.5 mg·l^{-1}) at the influent concentrations of 100 and 500 µg·l^{-1} are presented in **figure 3**.

Table 2. Influent concentration and hydrodynamic parameters of the experiments — *Concentration de l'influent et paramètres hydrodynamiques des expériences.*

Pesticide	Influent concentration (µg·l^{-1})		Activated carbon weight (mg)	EBCT* (min)	Linear speed (m·s^{-1})
	theoretical	measured			
Atrazine	508	482.3	200.1	0.16	0.15
Diuron	504	472.2	200.5	0.15	0.15
	107	95.1	200.7	0.16	0.15
Chloridazon	500	467.2	200.3	0.16	0.15
MCPA	505	479.0	200.5	0.16	0.15
	101	109.2	200.2	0.16	0.15

* EBCT = empty bed contact time.

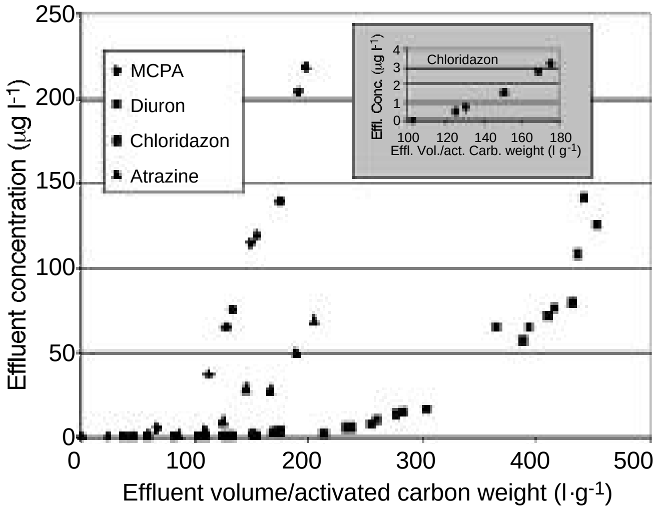

Figure 2. Breakthrough curves of atrazine, chloridazon, diuron and MCPA (influent concentration: 500 µg·l^{-1}) in mineral and organic reconstituted water (humic acid concentration: 0.5 mg·l^{-1}) — *Courbes de percée de l'atrazine, du chloridazon, du diuron et du MCPA (concentration de l'influent : 500 µg·l^{-1}) en eau minérale et organique reconstituée (concentration des acides humiques : 0.5 mg·l^{-1}).*

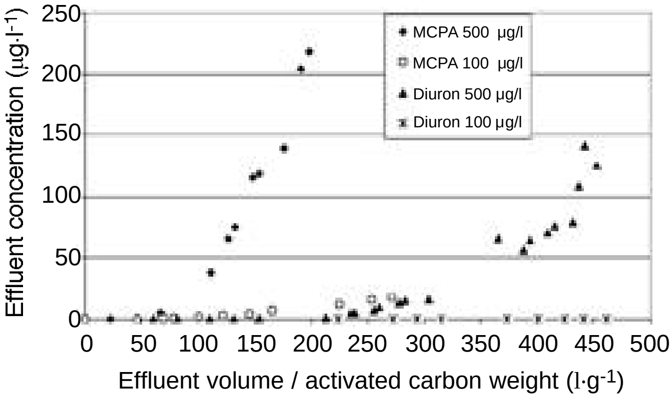

Figure 3. Breakthrough curves of diuron and MCPA in mineral and organic reconstituted water (humic acids: 0.5 mg·l^{-1}) at the influent concentrations of 100 and 500 µg·l^{-1} — *Courbes de percée du diuron et du MCPA en eau minérale et organique reconstituée (concentration en acides humiques : 0.5 mg·l^{-1}) aux concentrations des influents de 100 et 500 µg·l^{-1}.*

4. DISCUSSION

4.1 Experiments in mini-column of granular activated carbon: influent concentration 500 µg·l^{-1}

Our previous works (Gérard, 2002) demonstrated that adsorption performances on activated carbon could not only refer to mere physico-chemical characteristics, as octanol-water ratio (K_{ow}) or pKa. Nonetheless, they may be reckoned as signs of the diversity of the physico-chemical characteristics of the tested molecules that will belong to the comparison scale of adsorption performances on granular activated carbon.

The data of effluent volume/activated carbon weight for a breakthrough point of 1.5 $\mu g \cdot l^{-1}$ for each substance are presented in **table 3**.

The concentration of 1.5 $\mu g \cdot l^{-1}$ is chosen firstly because it belongs to the rank below 1% of the initial concentration (1.5 $\mu g \cdot l^{-1}$ = 0.3% of 500 $\mu g \cdot l^{-1}$) and secondly in order to possess data around the target value of 1.5 $\mu g \cdot l^{-1}$.

Difference factors in relation with the more adsorbed substance (diuron), are presented in **table 4**.

According to these results and taking into account the adsorption performances of these pesticides in different studies (Gérard *et al.*, 1998, Gérard, 2002), our suggestion is that a substance which has, in these experimental conditions, a difference factor in comparison to diuron:

– below 0.40: may be reckoned as weakly adsorbed,
– from 0.41 to 0.80: may be reckoned as moderately adsorbed,
– above 0.80: as highly adsorbed on granular activated carbon.

From these previous works, it appears that diuron is highly adsorbed in relation with the other pesticides, like atrazine, lenacil or MCPA. Indeed, the results of the experiments in mini-column in mineral and organic reconstituted water (humic acid concentration: 0.5 $mg \cdot l^{-1}$) presented a difference factor of 0.40 between atrazine and diuron, and of 0.23 between MCPA and diuron. The experimental conditions were similar to those of this paper with the following modifications: activated carbon weight: 400 mg, Empty Bed Contact Time (EBCT): 0.32 min and influent concentration: 100 $\mu g \cdot l^{-1}$. The huge disadvantage of this kind of experiment is the too long experimental time (from 3 to 6 months).

Table 3. Effluent volume/activated carbon weight for a breakthrough point at the concentration of 1.5 $\mu g \cdot l^{-1}$ — *Volume d'effluent/masse de charbon actif pour un point de percée à la concentration de 1.5 $\mu g \cdot l^{-1}$.*

Pesticide (at 500mg·l-1)	**Effluent volume/activated carbon weight (l·g-1) for a breakthrough point at the concentration of 1.5 µg·l-1**
MCP	« 50.3 »
Atrazine	85.4
Chloridazon	151.1
Diuron	213.6

« x » = data achieved by linear assessment between two measured values in order to determine the value corresponding to 1.5 $\mu g \cdot l^{-1}$.

Table 4. Difference factors of pesticides in comparison with diuron — *Facteurs de différence des pesticides en comparaison avec le diuron*.

Pesticide	**Difference factor in relation with diuron**
MCPA	0.23
Atrazine	0.40
Chloridazon	0.65
Diuron	**1**

4.2 Experiments in mini-column of granular activated carbon: influent concentration of 100 and 500 $\mu g \cdot l^{-1}$

The comparison of effluent volumes for a breakthrough point of 0.3 $\mu g \cdot l^{-1}$ (**Table 5**), for MCPAand for diuron at the two influent concentrations shows that:

– the decrease in influent concentration by a factor 5 causes an increase in effluent volume/weight of activated carbon by a factor 2.2 for diuron and 1.5 for MCPA;
– the discussion covers a rank of effluent volume/weight of activated carbon of 300 $l \cdot g^{-1}$ with an influent concentration of 100 $\mu g \cdot l^{-1}$ and of 215 $l \cdot g^{-1}$ with an influent concentration of 500 $\mu g \cdot l^{-1}$.

The concentration of 0.3 $\mu g \cdot l^{-1}$ is not only chosen because it belongs to the rank below 1% of the initial concentration (0.3 µg/l = 0.3% of 100 $\mu g \cdot l^{-1}$), but also in order to possess data around the target value of 0.3 $\mu g \cdot l^{-1}$.

Following the results, it appears to be more interesting to use as influent concentration 500 $\mu g \cdot l^{-1}$. The main advantage is to reduce the experimental time from 25 to 10 days.

Table 5. Effluent volume/activated carbon weight for a breakthrough point of 0.3 $\mu g \cdot l^{-1}$ for MCPA and diuron — *Volumes d'effluent/masse de charbon actif pour un point de percée de 0.3 $\mu g \cdot l^{-1}$ pour le MCPA et le diuron*.

Pesticide	**Effluent volume for a breakthrough point 0.3 µg·l-1**
MCPA 100	« 50.8 »
MCPA 500	« 34.1 »
Diuron 100	« 303.9 »
Diuron 500	« 136.5 »

« x » = data achieved by linear assessment between two measured values in order to determine the value corresponding to 0.3 $\mu g \cdot l^{-1}$.

5. CONCLUSIONS

The experiment in mini-column of granular activated carbon enables us to point out the differences of adsorption performances of pesticides in relation with their physico-chemical properties. The experiment, adapted from the Accelerated Column Test (Van Santfoort, 1990), allows conserving a significant sensitivity of adsorption performances differences and reducing the experimental time below 15 days.

The standardized reconstituted water we used may be reckoned as representative of a surface water in Belgium. The main experimental conditions are:

- activated carbon: Filtrasorb 400 (Chemviron Carbon)
- influent concentration: 500 $\mu g \cdot l^{-1}$
- activated carbon weight: 200 mg
- EBCT: 0.16 min.
- linear speed: 0.15 $m \cdot s^{-1}$.

Among the studied pesticides of different physico-chemical properties, diuron is the most adsorbed on activated carbon. From the comparison to this substance, it is suggested that products of which the difference factor is:

- below 0.40: may be reckoned as weakly adsorbed
- from 0.41 to 0.80: may be reckoned as moderately adsorbed, and
- above 0.80: as highly adsorbed on granular activated carbon.

Therefore, herbicides like chloridazon and atrazine are considered as moderately adsorbed and MCPA as weakly adsorbed.

In relation with mere physico-chemical properties, as solubility in water, or K_{ow}, it is not possible to establish direct relations between the results and these data. More specific physico-chemical properties, as molecular flatness, etc. may influence the adsorption result.

Active substances, which are weakly adsorbed and have to be removed from drinking water, may highly reduce the lifetime of an activated carbon bed. The active, moderately adsorbed substances will be responsible for a weaker decrease in lifetime.

These considerations come from a standardized experiment whose results may be changed in relation with the real conditions of a surface water, and notably because the real pesticide concentrations in natural waters are much lower than in the test. Therefore, these results can not be directly implemented on industrial scale in drinking water plants. The results constitute a basis on which an assessment of the adsorption performances of pesticides on granular activated carbon may be carried out and on which their influence on the lifetime of the activated carbon reactor in the drinking water process may be studied in real conditions.

Acknowledgements

The authors are grateful to the “Fonds budgétaire des matières premières” of the DG4 in the Ministry of Agriculture, for its financial support (Belgium).

Bibliography

Beltran FJ., Rivas J., Acedo B. (1999). Atrazine removal by ozonation processes in surface waters. *J. Environ. Sci. Health* **34** (3), p. 449–468.

Bouland S., Royer S., Montiel A., Welté B. (1998). Analyse en ligne de pesticides et de leurs métabolites dans la Seine et étude de leur dégradation au cours du traitement. *J. Eur. Hydrol.* **29** (1), p. 79–87.

Camel V, Bermond A. (1998). The use of ozone and associated oxidation processes in drinking water treatment. *Water Res.* **32** (11), p. 3208–3222.

CE (1980). Directive 80/778/CEE du Conseil relative à la qualité des eaux destinées à la consommation humaine J.O. n° L-229/11 du 30/08/80.

CE (1991). Directives pour les méthodes d’analyse de résidus. In Directive 91/414/CEE du Conseil concernant la mise sur le marché des produits phytopharmaceutiques (J.O. n° L230 du 19.08.1991).

CE (1997). Directive 95/57 CE du Conseil du 22 septembre 1997 établissant l’annexe VI de la directive 91/414/CEE. J.O. n° L-265-87 du 27/09/97.

CE (1998). Directive 98/83/CE du Conseil du 3 novembre 1998 relative à la qualité des eaux destinée à la consommation humaine J.O. n° L-330 du 05/12/98.

Chauveheid E., Bertinchamps C., Savoir R. (1999). Évolution des teneurs en micropolluants organiques dans les captages de la CIBE. *Trib. Eau* **600–601** (4-5), p. 75–83.

Chiron S., Fernandez-alba A., Rodriguez A., Garcia-Calvo E. (2000). Pesticide chemical oxidation: state-of-the-art. *Water Res.* **34** (2), p. 366–377.

Cornejo J., Jamet P. (coord.) (2000). *Pesticide/soil interactions. Some current research methods*. Versailles, France : INRAéditions, 490 p.

Crittenden JC., Reddy PS., Arora H., Trynoski J., Hand DW., Perram DL., Summers RS. (1991). Predicting of GAC performance with rapid small scale column tests. *J. AWWA* **January**, p. 77–87.

Duguet JP., d’Arras D. (1999). Surveillance et contrôle des pesticides. Le point de vue d’un exploitant : Lyonnaise des Eaux. *Tech. Sci. Méthodes* **2**, p. 51–53.

Gérard MC., Barthélemy JP., Copin A. (1998). Characterisation of adsorption behaviours of pesticides on activated carbon in drinking water treatment. *Med. Fac. Landbouwwet Univ. Gent* 63/2a, p. 231–242.

Gérard MC., Barthélemy JP., Copin A. (2001). Special solid phase extraction (SPE) two layers cartridge for simultaneous analysis of medium and most polar pesticides in waters. *Int. J. Environ. Anal. Chem.* **80** (4), p. 281–294.

Gérard M. (2002). *Étude de l’adsorption sur le charbon actif et de l’ozonation des eaux sur l’élimination de différents herbicides des eaux potabilisables*. Thèse de doctorat. Faculté universitaire des Sciences agronomiques de Gembloux, 280 p.

Griffini O., Bao ML., Burrini D., Santianni D., Barbierei C., Pantani F. (1999). Removal of pesticides during the drinking water treatment process at Florence water supply, Italy. *J. Water SRT-Aqua* **48** (5), p. 177–198.

Heijman SGJ., Hopman R. (1999). Activated carbon filtration in drinking water production: model prediction and new concepts. *Colloids Surf.* **151**, p. 303–310.

Hopman R., van Beek CG., Janssen HM., Puijker LM. (1992). Speurtocht naar bestrijdingsmiddelen in de bronnen voor de drinkwaterbereiding. *H_2O* **7**, p. 176–185.

Hopman R., Meerbeek MA., Siegers WG., Kruithof JC. (1994). Mini-column tests for evaluation of pesticide removal by adsorption. *Water Supply* **14**, p. 49–60.

Ince NH., Apikyan IG. (2000). Combination of activated carbon adsorption with light-enhanced chemical oxidation via hydrogen peroxide. *Water Res.* **34** (17), p. 4169–4176.

Le Bec R., Mandon F., Sorrento LJ., Labouyrie L., Merlet N. (1994) Development of rapid tests for the evaluation of dynamic adsorption and biological activity of granular activated carbons. *Water Supply* **14**, p. 71–84.

Matsui Y., Kamei T., Yuasa A., Tambo N. (1994) Adsorption capacity of organic pesticides on granular activated carbon. *Water Supply* **14**, p. 31–41.

Paune F., Caixach J., Espadaler I., Om J., Rivera J. (1998). Assessment on the removal of organic chemicals from raw and drinking water at a Llobregat river water works plant using GAC. *Water Res.* **32** (11), p. 3313–3324.

Phytophar-Belgaqua (Ed) (1997). *Phytophar-Belgaqua. Le Livre Vert*; Bruxelles : Phytophar-Belgaqua, 44 p.

Phytophar-Belgaqua (Ed) (1999). *Phytophar-Belgaqua. Le Livre Vert*. Bruxelles : Phytophar-Belgaqua, 48 p.

Rositano J., Newcombe G., Nicholson B., Sztajnbok P. (2001). Ozonation of N.O.M. and algal toxins in four treated waters. *Water Res*. **35** (1), p. 23–32.

Tomlin CDS. (Ed) (2000). The Pesticide Manual. A world compendium. 12th ed. Croydon, United Kingdom: The British Crop Protection Council. ISBN 1-901396-12-6, 1250 p.

Van Santfoort F. (1990). Élimination des micropolluants dans l’eau potable. *Trib. Eau* **544** (2), p. 39–43.

(28 réf.)