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EVALUATION OF THREE LOW-COST GRANULAR CARBONS ON SIMETRYN REMOVAL FROM WATERS

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Evaluation of Three Low-Cost Granular Carbons on Simetryn Removal from Waters

(Evaluación de tres carbones activos de bajo costo en la remoción de simetrina presente en aguas)

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Abstract

The adsorption capacity of three low-cost commercial granular active carbons, used in a water treatment facility, for the removal of simetryn, an s-triazine herbicide, was evaluated. Kinetic studies showed that the three carbon samples used could be suitable in the practice for the treatment of moderate contents of the herbicide in contaminated waters. Apparent rate adsorption constants have been calculated. Equilibrium studies showed that the data fit the Frumkin isotherm. The results show that in the adsorption process there are repulsive lateral interactions that could depend mainly of the adsorbate molecules rather than the nature or distribution of adsorption sites, or that the differences between the characteristics of the adsorption sites of the carbons are low.

Keywords: granular carbon, adsorption, simetryn removal, wastewater, Frumkin isotherm.

Resumen

Se ha estudiado la capacidad de adsorción de tres carbones activos comerciales de bajo coste que han sido empleados para eliminación de simetrina presente en un agua. Este herbicida de la familia de las s-triazinas puede ser un buen referente para el resto de compuestos de la familia, que podrían encontrarse habitualmente en aguas naturales empleadas como fuente de captación en potabilización de aguas de consumo. El estudio cinético concluye que los tres carbones pueden ser empleados para la eliminación de simetrina en aguas moderadamente contaminadas con aquél. También se han obtenido las constantes aparentes de adsorción. El estudió también arrojó que el equilibrio se ajusta a la isoterma de Frumkin. Finalmente, en el proceso adsortivo se comprueban interacciones laterales repulsivas que podrían depender mayoritariamente de las moléculas del adsorbato más que de la naturaleza y distribución de los sitios de adsorción del propio carbón activo, o bien que las diferencias entre las características de los sitios de adsorción de los carbones son pequeñas.

Palabras clave: carbón granular, carbón activado, adsorción, eliminación de simetrina, aguas residuales, isoterma de Frumkin.

1. Introduction

The utilization of active granular carbon in water treatment as landfill of filtration units on the basis of their known adsorbent properties is a technology used for several decades (Marín-Galvín, 1990). The efficiency of the different types of granular carbon assets depends on several circumstances: concrete adsorbent properties of the type of carbon used, grain, depth of the filter bed, previous treatment applied to the water before the incoming in the coal filters, and finally, of the compound (or compounds) to eliminate of the treated water (Lemarchand *et al.*, 1981).

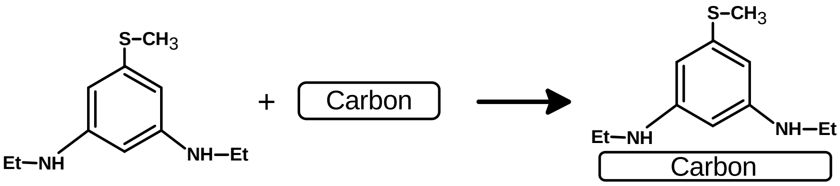
The adsorbent properties of the carbons will depend on the type of carbon itself, his origin (vegetable as coconut, wood or rabble, or mineral, both as mineral form or coke), and the concrete of thermal and/or chemical activation. These properties are standardized according to the essays of adsorption of iodine, of methylene blue, or of more specific substances like atrazine, toluene, or trichloroethylene (Commercial information, 2006). In addition, the practical performance will be determined by not only the granulometry (mean particle diameter, effective size, coefficient of uniformity, abrasion) and the depth of the used filtering bed, but by the purely filtering capacity (Marín-Galvín, 1995).

The purely adsorbent activity of an activated carbon (granulated or as powder) is tied to the presence of "pores" in its surface, which carry out the adsortive process. Though the active carbon is an amorphous substance and essentially apolar, it has surfacial functional groups (mainly carboxylic, carbonyl- and phenol-) that are the responsible of the adsorbent capacity (Ives, 1976).

On the other hand, the main field of activity in water treatment in which the use of active carbon is increasingly demanded is that of the minimization of synthetic organic compounds, which are difficult to remove by conventional treatments, and that appear with increasing frequency in the waters habitually used as resource for human consumption.

The s-triazine herbicides are continuously accessing to the environment due to its persistence in soils and hydric sediments, caused by the low solubilities in water, and their strong sorption on carbonous materials and clays (Ayele *et al.*, 1996).

Wood charcoal has been used as an effective low-cost adsorbent for the removal contaminants as endosulfan (Sudhakar and Diksit, 1999), from waters. Other wasted activated carbons (granular and powder) have been studied for the removal of atrazine (Gosh and Philip, 2005). The aim of this work was to evaluate the adsorption capacity of three low-cost granular active carbons, used in a water treatment facility, for the removal of simetryn, a triazine herbicide.



2. Experimental

In all cases, Merck analytical grade reagents were used with the exception of simetryn, which was from Polyscience (HPLC standard quality). All reactants were used without further purification.

Active carbons used were provided by Aguas de Levante™, Galaquim™ and Kemira™, having the characteristics given in Table I.

Table I. Characteristics of active carbons (commercial information)

	AC1 (1)	AC2 (2)	AC3 (3)
Material	Coconut	Vegetable	Mineral
Superficial area, $m^2 \cdot g^{-1}$	1000	950	900
Iodine index, $mg \cdot g^{-1}$	1000	900	950
Methylene blue index, $mg \cdot g^{-1}$	260	265	255
Atrazine adsorption ($1 \mu g \cdot L^{-1}$), $mg \cdot g^{-1}$	40	35	30
Toluene adsorption ($1 mg \cdot L^{-1}$), $mg \cdot g^{-1}$	100	110	90
Trichloroethylene adsorption ($50 \mu g \cdot L^{-1}$), mg/g	20	25	25
Abrasion minimum coefficient	75	75	70
Effective size, mm	0.9-1.1	0.9-1.1	0.9-1.1

Particle mean diameter, mm	1.4	1.4	1.35
Uniformity coefficient	1.4	1.3	1.4

(1) Aguas de Levante^{TM}; (2) Galaquim^{TM}; (3) Kemira^{TM}.

Source: Of authors' own (2008)

The analyses were made by using a Varian GC 3800 gas chromatograph coupled with an Autodrive 8200 autosampler. The pH of the samples was adjusted to 6.5 by adding HCl or NaOH prior the preconcentration using C18 packed cartridges (Supelco 505471). Such cartridges were connected to a vacuum generator (Supelco 57030-U) equipped with a pump (Millipore XX 55 220 50) and activated by the successive addition of 3 mL hexan, 3 mL ethyl acetate and 2 mL deionised water. The samples were then slowly passed through the cartridges. Dry argon was passed during 20 min through the cartridges. The elution was performed with 2 mL ethyl acetate and 2 mL hexan. The solvent was evaporated from the 4 mL of eluted samples with dry nitrogen and the residual was dissolved in 500 µL hexane. Then, the samples were processed in the gas chromatograph. The calibration of the method was made with standards of the herbicide. When the concentrations of herbicide were very high (higher than 1 $mg \cdot mL^{-1}$) the initial samples were diluted with deionised water to suitable volumes.

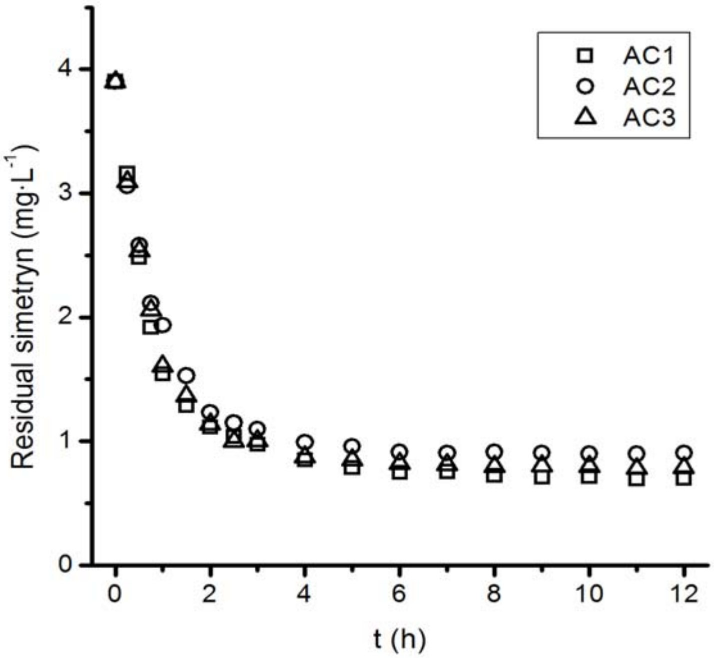
For kinetic studies, glass bottles (Schott Duran GL45) of 100 mL capacity were used. A suitable adsorbent dose and 75 mL of solution of simetryn were introduced in such bottles and placed in a thermostated linear bath shaker (from OVAN mod. Ovantherm 100) Samples of 1 mL were taken at intervals of 15 min. The operating temperature was 25ºC in all the experiences. The filtrates of such samples were stored in darkness at 4ºC and analyzed for residual herbicide concentration as described above. Blank samples consisting of the same solutions excepting the herbicide were treated in the same manner.

The equilibrium studies were performed at constant temperature using the data obtained in the previous kinetic study. The same type of samples were placed on the shaker and agitated for a period of 36 h, which was found to be enough to reach the equilibrium in the kinetic experiment. The filtrates of the samples were stored in darkness at 4ºC and analyzed for residual herbicide concentration. Blank samples consisting of the same solutions excepting the herbicide were treated in the same manner.

3. Results and discussion

Kinetics of simetryn adsorption by the three activated carbons essayed is given in Figure 1. Typical decreasing curves of residual simetryn with time were obtained for the three samples of carbon studied. In all cases around a 75% was removed after 3h and the maximum removal was reached after 8-12 h, being around 80%. The extension of the experiments to 36 h showed that a very slight increment in the removal was reached, though in occasions a very slight decrease in the removal was observed. So, though 12 h seem enough to reach the equilibrium conditions, the equilibrium study was performed, as stated above, after 36 h.

Figure 1: Adsorption kinetics as residual simetryn concentration vs. time at 25ºC. Initial simetryn concentration, 4 mg·mL^{-1}.



Source: Of authors' own (2008)

The industrial filters have residence times of 1.5 to 2 hours. So, the use of two filtration units in series (or even using one only unit) could be suitable in the practice for the treatment of moderate contents of the herbicide in contaminated waters ($\leq 0{,}80\ \mu g \cdot L^{-1}$), this being true for the three carbon samples used.

Adsorption kinetics can be attributed to the occupation of the available adsorbent sites by the adsorbate molecules. Though the adsorption process could be complex due to the non-equivalence of the adsorption sites arising from the pore and particle distribution and differences in the chemical affinities, a simple model can be assumed to compare the adsorption kinetics of simetryn on the samples. At infinite time it could be supposed that all the available sites have been occupied and the number of available sites must be proportional to the difference between the initial and the residual concentrations of adsorbent. If a second-order adsorption kinetics is assumed (first-order in both the adsorbate and the sites of adsorption), it is easy to show that the following equation is fulfilled:

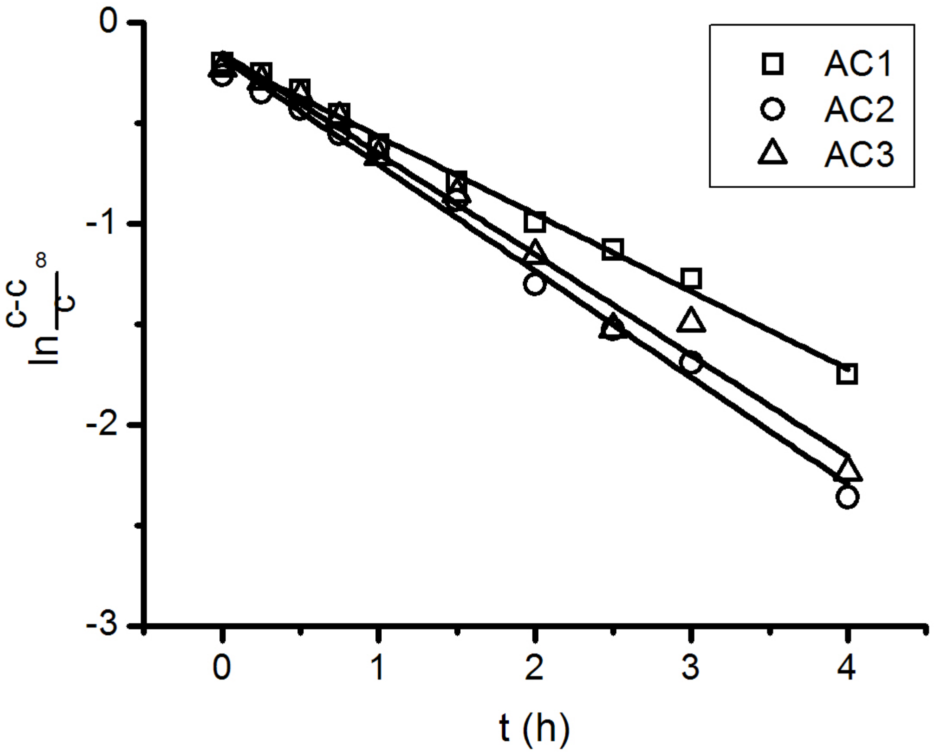
$$\ln \frac{c - c_\infty}{c} = \ln \frac{c_0}{c_0 - c_\infty} - kt \qquad \text{(Eq. 1)}$$

where c_0, c and c_∞ are the initial and residual simetryn concentration at each instant and at infinite time, respectively, and k the apparent rate constant.

Figure 2 shows the plots corresponding to the three carbons studied. As can be seen, the plots are roughly linear and the above equation appears as a well approximation for the adsorption process.

In Table 2 the apparent rate constants for the three carbons used are shown. As can be seen, though AC1 carbon leads to the maximum removal (see Figure 1) the other carbons reach the equilibrium more rapidly. In fact, AC3 carbon approaches to the equilibrium with an apparent rate constant similar to AC2 but giving a maximum removal similar to AC1.

Figure 2: Plots corresponding to the kinetic model.



Source: Of authors' own (2.008)

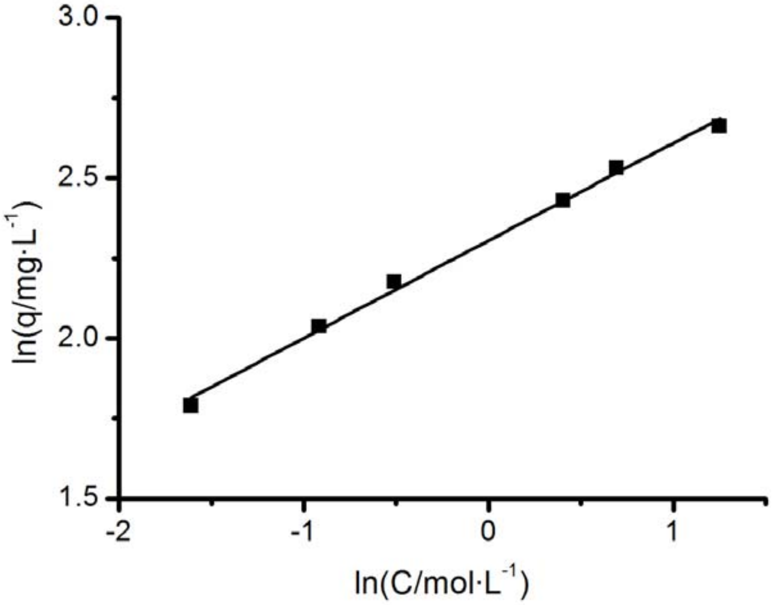
Table 2: Apparent rate constants for the adsorption process on the three carbons

Sample	k ($mg \cdot g^{-1} \cdot h^{-1}$)
AC1	0.46±0.02
AC2	0.64±0.02
AC3	0.60±0.02

Source: Of authors' own (2008)

Simetryn adsorption onto AC from simetryn solutions in distilled water fit well with Freundlich isotherm but not with Langmuir isotherm and is shown in Figure 3 for the AC1 samples.

Figure 3: Plot of the linearized Frumkin isotherm for AC1 carbon.



Source: Of authors' own (2008)

Frumkin isotherm is an extension of Langmuir isotherm (Bockris *et al.*, 2000). It states that adsorbed molecules do interact and affect further adsorption by either repulsion or attraction of molecules. The fitting with the Frumkin isotherm is well and the results show that in the adsorption process there are repulsive lateral interactions (the exponential parameter of the isotherm is negative). The calculated maximum specific adsorption capacity was 26.10 mg·g^{-1}. Table 3 shows the results obtained for the three carbons.

Table 3: Isotherm parameters. q: adsorbed simetryn, K: adsorption constant, *a:* adsorption parameter, q_{max}: maximum specific adsorption capacity (mg·g^{-1})

Sample	$K_{Freundlich}$	$a_{Freundlich}$	$K_{Frumkin}$	$a_{Frumkin}$	q_{max}
AC1	9.97±0.05	0.30±0.05	119.9±0.5	–3.10±0.05	26.10±0.2
AC2	8.76±0.05	0.38±0.05	108.4±0.5	–3.23±0.05	23.72±0.2
AC3	8.92±0.05	0.36±0.05	112.1±0.5	–3.32±0.05	24.55±0.2

Freundlich: $q = K \cdot c^{a}$ (Eq. 2)

Frumkin: $$\frac{q}{q_{\max} - q} \exp(-2aq / q_{\max}) = K \cdot c$$ (Eq. 3)

Source: Of authors' own (2008)

As can be seen, the calculated maximum specific adsorption capacity was similar for the three carbons although slightly greater for AC1. On the other hand, the repulsive lateral interactions arising from the exponential parameter of the Frumkin isotherm are very close for the three samples. This indicates either that these repulsive lateral interactions depend mainly of the adsorbate molecules rather than the nature or distribution of adsorption sites, or that the differences between the characteristics of the adsorption sites of the carbons used are low.

4. Conclusions

1. Kinetic studies showed that the three carbon samples used could be suitable in the practice for the treatment of moderate contents of the herbicide in contaminated waters.
2. Apparent rate adsorption constants have been calculated, under the assumption that the adsorption kinetics is first-order in both the herbicide and the adsorption sites.
3. Equilibrium studies showed that the data fit the Frumkin isotherm. The results show that in the adsorption process there are repulsive lateral interactions that depend mainly of the adsorbate molecules rather than the nature or distribution of adsorption sites.

5. Acknowledgements

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