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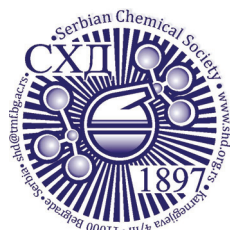
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Original scientific paper

On the removal of s-triazine herbicides from waters using commercial low-cost granular carbons

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Abstract: The adsorption capacities of three low-cost granular active carbons, used in a water treatment facility for the removal of the triazine herbicides propazine, prometryn and prometon, was evaluated. Kinetic studies showed that the three carbon samples used could be suitable in practice for the treatment of moderate contents of the herbicides in contaminated waters. The apparent adsorption rate constants were 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 depend mainly on the adsorbate molecules rather than the nature or distribution of the adsorption sites. Such lateral interactions seem to be established mainly between the isopropyl groups of adjacent molecules, being of the same order for the three molecules.

Keywords: granular carbon; adsorption; triazine herbicides; herbicide removal; propazine; prometryn; prometon.

INTRODUCTION

For several decades, active granular carbon has been used in water treatment in the filtration units of landfills because of their known adsorbent properties.¹ There are several parameters on which the efficiency of the different types of granular carbon assets depend: the adsorbent properties of the type of carbon used, grain size and distribution, filter bed depth, treatment applied to the water

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before arriving at the coal filters and finally, but very important, on the concrete compound (or compounds) to be eliminated from the treated water.²

The adsorbent properties of carbons depend on the type of carbon itself, its origin (either vegetable, such as coconut, wood or rabble, or mineral, both in mineral form or coke), and on the exact thermal and/or chemical activation. These properties are standardized according to the adsorption of iodine, of Methylene Blue or of more specific substances, such as atrazine, toluene or trichloroethylene.³ In addition, the practical performance is determined not only by the granulometry (mean particle diameter, effective size, coefficient of uniformity and abrasion) and the depth of the employed filter bed, but also by the purely filtering capacity.⁴

The purely adsorbent activity of an activated carbon (granular or as powder) is related to the presence of “pores” in its surface, which are responsible of the adsorptive process. Although active carbon is an amorphous substance and is essentially apolar, it has surface functional groups (mainly carboxyl-, carbonyl- and phenol-) that are responsible for the adsorption capacity.⁵

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 for human consumption.

The *s*-triazine herbicides are continuously accessing the environment due to their persistence in soils and hydric sediments, caused by their low solubilities in water, and their strong sorption on carbonous materials and clays.⁶

Wood charcoal was used as an effective low-cost adsorbent for the removal of contaminants, such as endosulfan,⁷ from waters. Other waste activated carbons (granular and powder) were studied for the removal of atrazine.⁸

In a previous paper, the adsorption capacities of three low-cost granular active carbons used in a water treatment facility were evaluated for the removal of simetryn, a triazine herbicide.⁹

The aim of this work was to compare the adsorption capacities of such low-cost granular active carbons for the removal of propazine, prometryn and prometon, three triazine herbicides having the same basic chemical structure but with different substituents, as shown in Fig. 1.

EXPERIMENTAL

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

Commercial active carbons used were provided by Aguas de LevanteTM, GalaquimTM and KemiraTM, having the characteristics given in Table I.

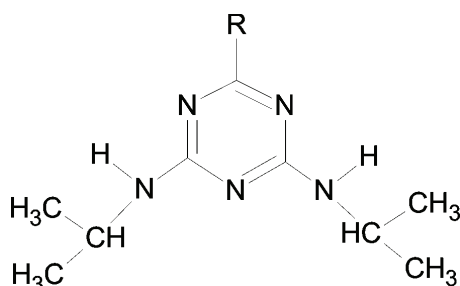


Fig. 1. Chemical structures of the investigated herbicides. Propazine, R = -Cl; prometryn, R = -SCH₃; prometon, R = -OCH₃.

The analyses were made 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 to 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 hexane, 3 mL ethyl acetate and 2 mL deionized 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 hexane. The solvent was evaporated from the 4 mL of eluted samples with dry nitrogen and the residual was dissolved in 500 μ L 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, the initial samples were diluted with deionized water to suitable volumes.

TABLE I. Characteristics of the studied active carbons

Material	AC1	AC2	AC3
	Coconut	Vegetable	Mineral
Superficial area, m ² g ⁻¹	1000	950	900
Iodine index, mg g ⁻¹	1000	900	950
Methylene Blue index, mg g ⁻¹	260	265	255
Atrazine adsorption (1 μ g L ⁻¹), mg g ⁻¹	40	35	30
Toluene adsorption (1 mg L ⁻¹), mg g ⁻¹	100	110	90
Trichloroethylene adsorption (50 μ g L ⁻¹), mg g ⁻¹	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

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 into such bottles and placed in a thermostated linear bath shaker (from Ovan model Ovantherm 100). Samples of 1 mL were taken at intervals of 15 min. The filtrates of such samples were stored in the dark at 4 °C and analyzed for the residual herbicide concentration as described above. Blank samples consisting of the same solutions but without 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 in the kinetic experiment to be sufficient for

equilibrium to be attained. The filtrates of the samples were stored in the dark at 4 °C and analyzed for residual herbicide concentration. Blank samples consisting of the same solutions but without the herbicide were treated in the same manner.

RESULTS AND DISCUSSION

Typical decreasing curves of the residual herbicide concentration with time were obtained for the three studied samples of carbon. The kinetics of herbicides adsorption by one of the assayed activated carbons is given in Fig. 2 as an example. It can be seen that the equilibrium was attained faster for propazine than for the other two herbicides. In all cases, around a 75 % was removed after 3 h 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 increase in the removal was obtained, although on some occasions, a very slight decrease in the removal was observed. Since the industrial filters have residence times of 1.5 to 2 h, the use of two filtration units mounted in series (or even using only one unit) could be suitable in the practice for the treatment of moderate contents of herbicide in contaminated waters, this being the case for the three studied carbon samples as well as for the three investigated herbicides.

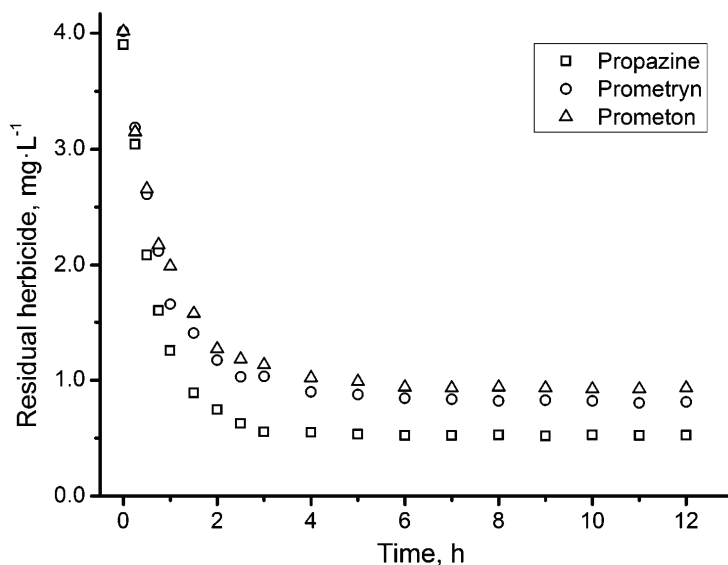


Fig. 2. Adsorption kinetics on carbon AC3 as the residual herbicide concentration vs. time at 25 °C. Initial herbicide concentration, 4 mg mL⁻¹.

Though 12 h seem enough to reach equilibrium conditions, the equilibrium study was performed, as stated above, for 36 h.

Adsorption kinetics can be attributed to the occupation of the available adsorbent sites by the adsorbate molecules. Although the adsorption process could

be complex due to the non-equivalence of the adsorption sites arising from the pore and particle size distributions and differences in the chemical affinities, a simple model can be assumed to compare the adsorption kinetics of the herbicides onto the samples. At infinite time, it could be supposed that all the available sites had 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:

$$\ln \frac{c - c_{\infty}}{c} = \ln \frac{c_0}{c_0 - c_{\infty}} - kt$$

where c_0 , c and c_{∞} are the initial and residual herbicide concentration at the instant and at infinite time, respectively, and k is the apparent rate constant.

Plots corresponding to the studied three carbons are shown in Fig. 3. As can be seen, the plots are linear, indicating that the above equation can be considered as a good approximation for the adsorption process.

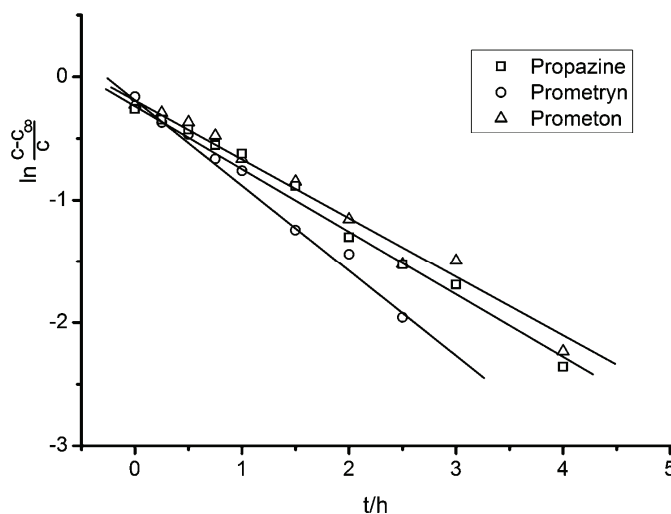


Fig. 3. Plots corresponding to the kinetic model; Carbon AC2.

The apparent rate constants for the three carbons used are given in Table II. As can be seen, although the AC1 carbon leads in all cases to the maximum removal, the other carbons reached equilibrium more rapidly. In general, the AC3 carbon approached equilibrium with an apparent rate constant similar to that of AC2 but giving a maximum removal similar to that of AC1. In addition, the adsorption of propazine occurred faster than the adsorptions of the two other compounds and equilibrium was reached at *c.a.* 45 min, 1 h prior that for propazine.

TABLE II. Apparent rate constants ($k / \text{mg g}^{-1} \text{h}^{-1}$) for the adsorption processes

Sample	Propazine	Prometryn	Prometon
AC1	0.66	0.47	0.46
AC2	0.78	0.63	0.61
AC3	0.76	0.59	0.56

The adsorption of the herbicides onto granular active carbons from solutions in distilled water does not fit the Langmuir isotherm. Nevertheless, it fit well with the Freundlich isotherm, as is shown by the fact that the plots of $\ln q$ vs. $\ln c$ were linear (q being the amount of adsorbed herbicide). This isotherm is useful for practical work with the herbicide-adsorbent system.

In addition, if it is assumed that at the tested concentrations the maximum adsorption was not reached (which seems logical because the maximum concentration of the herbicide samples is limited by the low solubility of these substances in water), the fitting with the Frumkin isotherm is good. Hence, using the data obtained at the lowest concentrations, the values of q_{max} , K and a/q_{max} can be estimated from the intercept and the slope of the plot of $\ln(q/c)$ vs. q , respectively, as shown in Fig. 4. Thus, q_{max} was obtained using the higher concentrations and the estimated parameters, and fitting the experimental data to the Frumkin equation.

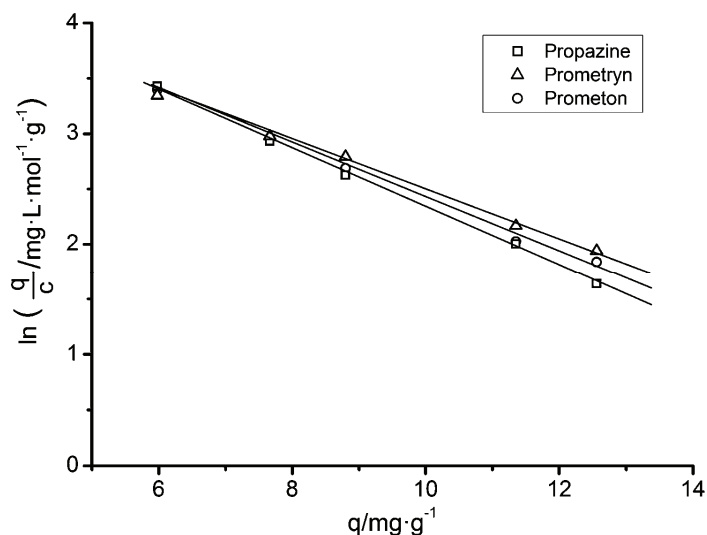


Fig. 4. Plot of the linearized Frumkin isotherm for AC1 carbon.

The results show that in the adsorption process there are repulsive lateral interactions, because the exponential parameters of the isotherm are negative. The results obtained for the three carbons and the three herbicides investigated are given in Table III.

Table III. Isotherm parameters; q – adsorbed herbicide (mg g^{-1}), K – adsorption constant, a – adsorption parameter, q_{max} – maximum specific adsorption capacity (mg g^{-1}); Freundlich: $q = Kca$; Frumkin: $(q/(q_{\text{max}} - q))\exp(-2aq/q_{\text{max}}) = Kc$

Herbicide	Sample	$K_{\text{Freundlich}}$	$a_{\text{Freundlich}}$	K_{Frumkin}	a_{Frumkin}	q_{max}
Propazine	AC1	10.21	0.31	122.2	-3.13	27.15
	AC2	9.32	0.39	109.7	-3.27	25.62
	AC3	9.12	0.37	115.3	-3.37	25.05
Prometryn	AC1	9.87	0.30	121.9	-3.09	26.32
	AC2	8.66	0.38	108.9	-3.21	23.92
	AC3	8.82	0.36	114.1	-3.34	24.75
Prometon	AC1	9.82	0.30	120.9	-3.09	26.02
	AC2	8.63	0.37	108.6	-3.20	23.51
	AC3	8.79	0.35	112.3	-3.31	24.58

As can be seen, the calculated maximum specific adsorption capacity was similar for the three investigated carbons, although it was slightly higher for AC1. On the other hand, the repulsive lateral interactions arising from the exponential parameter of the Frumkin isotherm are very similar for the three samples. This indicates that these repulsive lateral interactions depend mainly of the adsorbate molecules rather than the nature or distribution of the adsorption sites. Moreover, such lateral interactions are very similar for the three herbicides. This could easily be explained if it is assumed that the adsorption of the three compounds occurs with the triazine ring parallel to the carbon surface, as is the case on mercury electrodes.^{10–12} Hence, the main lateral interactions must be established mainly between the isopropyl groups of adjacent molecules, and these interactions must be of the same order for the three molecules.

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ИЗВОД

УКЛАЊАЊЕ *s*-ТРИАЗИНСКИХ ХЕРБИЦИДА ИЗ ВОДА ПОМОЋУ КОМЕРЦИЈАЛНИХ ГРАНУЛИСАНИХ УГЉЕВА

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Испитиван је адсорпциони капацитет три комерцијална гранулисана активна угља. Они су коришћени у третману вода за уклањање триазинских хербицида, пропазина, прометрина и прометона. Кинетичка испитивања су показала да три употребљена узорка активних угљева могу бити корисни у пракси за третман вода са умереним садржајем хербицида.

Израчунате су константе брзине адсорпције. Добијени резултати су у сагласности са Фрум-киновом изотермом. Резултати показују да током адсорпције постоје одбојне бочне интеракције које знатно више зависе од карактеристика адсорбата, а мање од расподеле и типа активних места на адсорбенсу. Таква бочна интеракција се остварује углавном између изо-пропил група суседних молекула који су истом положају код сва три испитивана хербицида.

(Примљено 7. марта 2009)

REFERENCES

1. R. Marín Galvín, *Equipamientos y Servicios Municipales* **34** (1990) 65
2. D. Lemarchand, A. Le Marechal, G. Martin. *TSM-L'eau* **11** (1981) 561
3. *Commercial information from Aguas de Levante™, Galaquim™ and Kemira™*, 2006
4. R. Marín Galvín, *Análisis de Aguas y Ensayos de Tratamiento: Principios y Aplicaciones*, Ed. G. P. E., S.A., Barcelona, Spain, 1995
5. P. Y. Divet. *Ingeniería Química*, octubre 1976, 123
6. J. Ayele, P. Levavasseur, M. Mazet, *J. Water-SRT Aqua* **45** (1996) 28
7. Y. Sudhakar, A. Dikshit, *J. Environ. Sci. Health* **34** (1999) 587
8. P. K. Gosh, L. Philip, *J. Environ. Sci. Health* **40** (2005) 425
9. L. Alonso, M. González Jiménez, J. M. Cardenete López, R. Marín Galvín, J. M. Rodríguez Mellado, *VirtualPro* **86** (2009)1
10. M. J. Higuera, M. Ruiz Montoya, R. Marín Galvín, J. M. Rodríguez Mellado, *J. Electroanal. Chem.* **474** (1999) 174
11. M. J. Higuera, M. Ruiz Montoya, R. Marín Galvín, J. M. Rodríguez Mellado, *Bull. Electrochem.* **19** (2003) 513
12. J. M. Rodríguez Mellado, R. Marín Galvín, M. Ruiz Montoya, in *New trends in electrochemistry research*, M. Núñez, Ed., Nova Science Publishers Inc., New York, 2007, p. 187.