

Evaluation of Commercial Active Carbons for the Removal of s-Triazine Herbicides from Waters

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Abstract: The adsorption capacity of powdered 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 some of the carbon samples used could be suitable in the practice for the treatment of moderate contents of the herbicides in contaminated waters. 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. Such lateral interactions seem to be established mainly between the isopropyl groups of adjacent molecules, being of the same order for the three molecules. The effectiveness of the active carbons was evaluated by determining the percentage of reduction achieved by each product.

Key words: Active carbon, adsorption, triazine herbicides, herbicides removal, propazine, prometryn, prometon.

1. Introduction

Active carbon has been used for decades in water treatment as landfill or filtration units due to their well-known adsorbent properties [1]. There are several parameters that depend upon the efficiency of different types of active carbon: adsorbent properties, grain size and distribution, filter bed depth, treatment applied to the water before incoming in the filters, and finally, but very important, the concrete compound (or compounds) to be eliminated from the treated water [2].

The type of carbon includes its origin, and the specific type of activation, thermal and/or chemical,

and determination of the absorptive properties, which are standardised with testing for absorption of iodine, of methylene blue, or of more specific substances like atrazine, toluene, or trichloroethylene. In addition, the practical performance is determined by the granulometry (mean particle diameter, effective size, coefficient of uniformity), abrasion, and the depth of the used filtering bed, but also by the purely filtering capacity [3]. Although the active carbon is an amorphous substance and it is essentially apolar, it has surfacial functional groups (mainly carboxyl-, carbonyl- and phenol-) responsible for the adsorbent capacity [4].

The minimization of synthetic organic compounds that appear with increasing frequency in waters used as

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resource for human consumption, is one important activity in water treatment, in which the use of active carbon is increasingly demanded. Wood charcoal has been used as an effective low-cost adsorbent for the removal contaminants from waters [5]. Other wasted activated carbons (granular and powder) have been studied for the removal of atrazine [6].

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 [7]. In a previous paper, the adsorption capacity of three low-cost granular active carbons, used in a water treatment facility, was evaluated for the removal of simetryn, a triazine herbicide [8].

The aim of this work was to evaluate the adsorption capacity of various commercial active carbons for the removal of three triazine herbicides having the same chemical structure except for a substituent, such as propazine, prometryn, and prometon, whose structures are shown in Fig. 1.

2. Experiment

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

Commercial active carbons used were provided by several manufacturers and have the characteristics given in Table 1.

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 hexane, 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

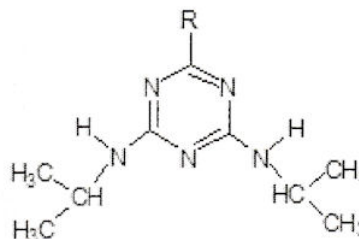


Fig. 1 Chemical structures of the investigated herbicides. Propazine, R = -Cl; Prometryn, R = -SCH₃; Prometon, R = -OCH₃

through the cartridges. The elution was performed with the 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 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 each herbicide were introduced in such bottles and placed in a thermostated linear bath shaker (from OVAN mod. Ovantherm100). Samples of 1 mL were taken at intervals of 1-2 min. The filtrates of such samples were stored in darkness at 4 °C 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 4 °C and analyzed for residual herbicide concentration. Blank samples consisting of the same solutions excepting the herbicide were treated in the same manner.

Table 1 Characteristics of active carbons.

	AC1	AC2	AC3	AC4	AC5	AC6	AC7	AC8	AC9	AC10	AC11
Apparent density ($\text{g}\cdot\text{L}^{-1}$) ¹	650	500	330	450	320	400-500	350	400-500	500	450	440
Humidity (%)	8	10	5	-	-	< 3	2	< 3	6.1	8	6.8
Ash contents (%)	12	-	3	10	8	-	12	-	9.2	11	4
Iodine index ($\text{mg}\cdot\text{g}^{-1}$)	650	800	950	850	800	1000	1000	850	1000	850	1100
BET Superficial area ($\text{m}^2\cdot\text{g}^{-1}$)	-	750	-	-	-	1000	1100	900	1000	900	1100
Particle size, weight (%)	< 400-60	65	< 325	-	-	> 40	100	85	93.5	90	80
pH	2-4	-	9-10	-	-	9	8	9	-	-	-

AC1: Kemisorb 046 PW, from Kemira Ibérica S.A.

AC2: Chemviron Pulsorb PWX-HA from Aguas de Levante S.A.

AC3: Chiemivall K plus from Chiemivall S.L.

AC4: Picahidro SP19 from PICA Italy S.p.A.

AC5: Picahidro MP21 from PICA Italy S.p.A.

AC6: CPL Carbon Link Filtracarb WP7 from Brenntag.

AC7: CPL Carbon Link Filtracarb SK1-P75 from Brenntag.

AC8: CPL Carbon Link Filtracarb SK8-P75 from Brenntag.

AC9: PMI 1000C from Galaquim. S.L.

AC10: PMI IC from Galaquim. S.L.

AC11: PMI I 1000S from Galaquim. S.L.

For studies of effectiveness two rounds of testing have been carried out, by preparing aliquots of 1 L of raw water from the Guadalmellato reservoir that reached the facility of Villa Azul (Córdoba, Spain), and fortified with two concentrations of each herbicide. To each 1 L beaker with herbicide was added the same dose of activated carbon, while a glass was maintained as blank without the addition of activated carbon. The testing procedure is described below.

Dispersions in ultrapure water of $10 \text{ g}\cdot\text{L}^{-1}$ of each active carbon to be tested and solutions of $10 \text{ g}\cdot\text{L}^{-1}$ of PAX-10 polychloride aluminum in ultrapure water were used as stock.

The procedure starts with the addition of $0.9 \text{ mg}\cdot\text{L}^{-1}$ herbicide to a sample of 12 L of raw water from Villa Azul facility. With this raw water 12 beakers of 1 L are filled. 11 glasses are treated with a dose of $15 \text{ g}\cdot\text{m}^{-3}$ for each carbon tested. The glasses were then subjected to a quick agitation during 15 minutes, followed by the addition of $25 \text{ g}\cdot\text{m}^{-3}$ of PAX-10 for each solution, and a quick stirring during 2 minutes. After a slow shaking over 10 minutes and a repose of 1 hour, test samples of 500 mL of supernatant of each beaker were taken and filtered in Whatman filters. Then the herbicide concentration was determined in each case.

A second test as the previous one was also made, but with a herbicide concentration of $1.5 \text{ mg}\cdot\text{L}^{-1}$ and a dose

of $15 \text{ g}\cdot\text{m}^{-3}$ for each carbon tested.

3. Results and Discussion

Typical decreasing curves of residual herbicides with time were obtained for all the samples of carbon studied. Kinetics of herbicides absorption by activated carbon AC11 is given in Fig. 2 as an example. The equilibrium is reached faster for propazine than for the other two herbicides. For the three herbicides around a 75% was removed after 25 min and the maximum removal was reached after 60-80 min, being around 85%. The extension of the experiments to 4 h showed a very slight increment in the removal, though in occasions a very slight decrease in the removal was observed. Since the industrial filters have residence times of 1.5 to 2 hours, the use of only one filtration unit could be suitable in the practice for the treatment of moderate contents of the herbicide in contaminated waters, this being true for the three herbicides. In other cases, the times and the amounts of removal were different, but the kinetics was essentially the same.

Though 80 min seem enough to reach the equilibrium conditions, the equilibrium study was performed, as stated above, after 24 h.

Adsorption kinetics can be attributed to the occupation of the available adsorbent sites by the adsorbate

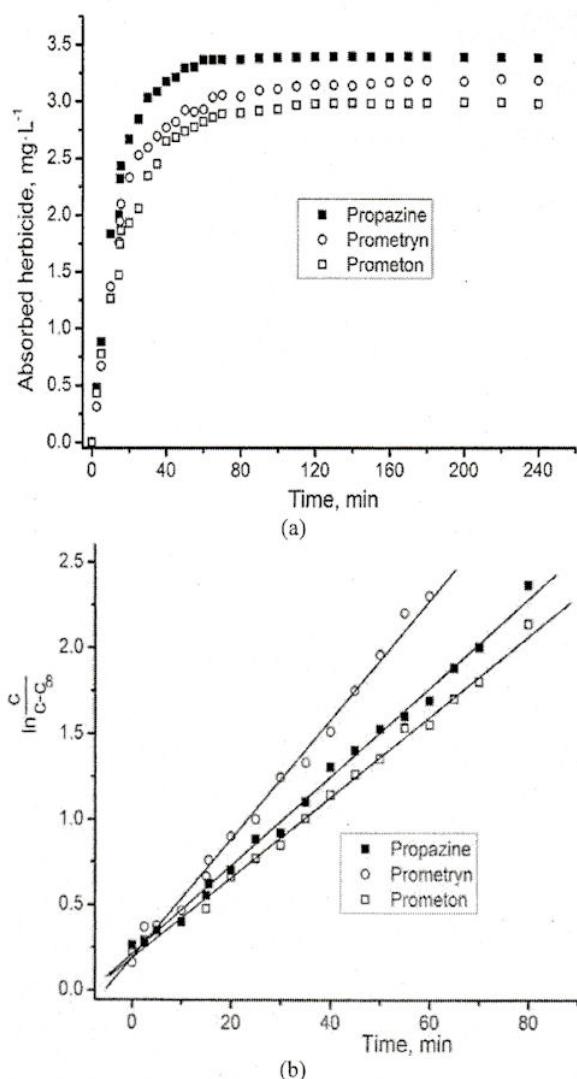


Fig. 2 (a) Adsorption kinetics on the carbon AC11 as absorbed herbicide concentration vs. time at 25 °C. Initial herbicide concentration, 4 mg·mL⁻¹. (b) Plots corresponding to the kinetic model. Carbon AC11.

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 the herbicides 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:

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

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

Fig. 2b shows the plots corresponding to the three carbons studied. As can be seen, the plots are linear, this indicated that the above equation can be considered as a well approximation for the adsorption process.

Though AC11 carbon leads in all cases to the maximum removal, all carbons reach the equilibrium in similar times (ranging from 60 to 100 minutes). In addition, the adsorption of propazine takes place faster (in general) than the adsorptions of the two other compounds.

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

In addition, if it is assumed that at the tested concentrations the maximum adsorption is 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. The results show that in the adsorption process there are repulsive lateral interactions, because the exponential parameter of the isotherm is negative. These repulsive lateral interactions are similar for the majority of the samples, this indicated that they depend mainly of the adsorbate molecules rather than the nature or distribution of 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 takes place with the triazine ring parallel to the carbon surface, as occurs on mercury

electrodes [9-11]. So, 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.

To determine the effectiveness of different active carbons, the results obtained can be evaluated from two viewpoints. First, checking the residual quantities of simazine found in each sample after treatment with activated carbon and, second, evaluating the percentage of reduction achieved by each product.

The results obtained with both doses of herbicides are essentially similar for each type of carbon and herbicide. Thus, the lowest residual was obtained with samples AC6, AC11, and AC5 for the lower dose of herbicide, and samples AC11, AC5 and AC6 for the highest dose.

If now the average yields for the two doses of herbicide are evaluated as a whole with all samples obtained from active carbons, it can be concluded that the highest effectiveness was achieved with the sample AC11, followed by samples AC5 and AC6, which is seen in Fig. 3.

Finally it can be noted that as the practical view point to decide in a treatment facility which carbon must be used against a specific herbicide, the economical aspect of the cost of each carbon should be taken into account, almost of the dose of carbon and yielding of removing obtained.

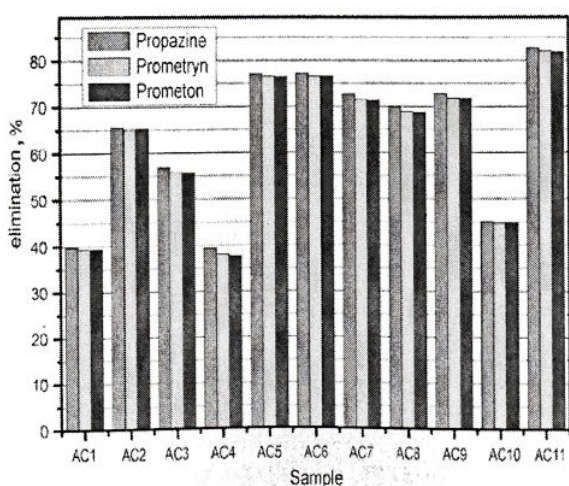


Fig. 3 Effectiveness of the different active carbons.

4. Conclusions

- Kinetic studies showed that the some of the active carbon samples used could be suitable in the practice for the treatment of moderate contents of the herbicides herbicides propazine, prometryn and prometon in contaminated waters.
- Equilibrium studies showed that the data fit the Frumkin isotherm, and that the adsorption involves repulsive lateral interactions depending mainly of the adsorbate molecules rather than the adsorption sites. These lateral interactions (mainly between the isopropyl groups of adjacent molecule) are of the same order for the three molecules.
- The effectiveness of the active carbons was evaluated by determining the percentage of reduction achieved by each product.

Acknowledgments

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