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Organochlorine Pesticides Removal by Pinus Bark Sorption

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Pesticides belong to a chemical family that calls our attention because of its hazardous effects in the environment. The organochlorine pesticides were strongly used in the past, but their persistency and bioaccumulation make them an actual problem. Common wastewater treatment methods, like activated carbon sorption, mean expensive investment and operating costs. Pine bark is a wood industry byproduct and has a high affinity with hydrophobic compounds because of its organic composition. The aim of this work is to test the capability of this material to remove organochlorine pesticides from water solutions. This capability was quantified by studying the best operating conditions for pine bark fixed bed mini-columns, the yield of removal from spiked water solutions, and the saturation parameters. The yield of removal from spiked organochlorine water solutions ranging from 1 to 10 μg/L, was 97% on average, for heptachlor, aldrin, endrin, dieldrin, DDD, DDT, and DDE. Lindane could not be efficiently adsorbed by this methodology (38% for yield of removal). Saturation studies, performed until 60.00 L of spiked solution/g of adsorbent was reached, did not reveal system rupture. When compared with activated carbon, pine bark displays analogous response, suggesting that for compounds with similar physicochemical characteristics pine bark will play a significant role.

Introduction

In the last years, governments, industries, and the public have become increasingly aware of the hazardous vestigial compounds in water whose characteristics of high toxicity and persistency make them one of the greatest environmental problems. Pesticides belong to this group of chemicals often detected in the environment, rivers, soils, atmosphere, or even in milk or human tissues (*1–5*). The utilization of organochlorine pesticides, like DDT, was generalized in the past, but they are still persistent because of the long degradation period in soils. Less than 0.1% of the applied pesticides is estimated to effectively reach pests, and therefore excessive amounts are contaminating soil and water resources (*6*). Pesticides, as other organic pollutants, are strongly hydrophobic and when in contact with organic materials, in soil or sediments, tend to be adsorbed in particles producing aggregates. These natural products play a significant role in managing the fate of these organic pollutants in aquatic environments, even if it takes long periods (*7*).

Biological processes, activated carbon adsorption, or ionic exchange with synthetic resins are commonly used to remove trace amounts of toxic compounds from water (*8, 9*). These

materials have been efficient but are rather expensive. Bearing this in mind, the possibility of using alternative materials easily available at a low cost has been studied. A considerable number of natural materials are successfully used in water treatment such as wood, peat, rice straw, and flyash (*10–14*). Despite the scarse information available, pine bark, a spare material from sawmills, can be an effective sorbent for a large number of vestigial compounds and have an important role in wastewater treatments overcoming activated carbon systems. Being an organic material with only 0.5% of ashes, it has a highly complex structure with 39.3% of soluble materials in polar solvents, mainly dye compounds, and 59.7% of aromatic contents among others (*15*). Vasconcelos (*16*) performed a detailed characterization of the same pine bark used in the present experiments, describing a complex chemical structure that includes fatty matter, carbohydrates, starch, lignin, and aromatic compounds. It also presents phenolic structures, pectines, suberin, and hydrolyzable tannins. Inorganic material includes metallic elements, with calcium being the most representative one, at levels of 0.759 mg of Ca/g of pine bark. Potassium, magnesium, and sodium are in lower concentration, with 0.460, 0.353, and 0.216 mg/g, respectively. This large variety of functional groups motivated some research in the past for chromium removal from industrial wastewater, showing good results when the bark is pretreated with sodium or calcium salts, hydroxides, and formaldehyde (*17*).

The significant percentage of organic contents in pine bark that probably could interact with organochlorine pesticides motivated this study. As a preliminary study, special attention was dedicated to the adsorption capacity in fixed bed columns as an indicator of the viability to future implementation of a full-scale process. The working methodology can be described by three main steps: **validation** of the chromatographic method for organochlorine pesticides analysis, **factorial experiments** to optimize the best operating conditions with pine bark columns, and **sorption studies** on the yield of pesticides removed from spiked water solutions, a preliminary study of saturation, and comparative behavior with activated carbon.

Experimental Section

Reagents. Chlorinated pesticides used were obtained from PolyScience (Kit 510CX), and those tested were as follows: lindane (LIN), purity 99%; heptachlor (HEP), purity 99%; aldrin (ALD), purity 99%; dieldrin (DIE), purity 99%; endrin (END), purity 99%; endosulfan (ENS), purity 96%; DDE, purity 99%; DDD, purity 70%; and DDT, purity 99%. Solvents used were *n*-hexane, SupraSol (Merck); dichloromethane, p.a. (Pronolab); and ethyl acetate, p.a. (Merck).

Apparatus. To prepare the pine bark, a mill, a Roscht sieve, and an Heraeus stove to dry the bark were used. To extract standards and samples for chromatographic analysis, a Whatman vacuum system with 12 entries equipped with a vacuum pump from KNF Neuberger D-70112 Freibeug were used. The cartridges for solid-phase extraction (SPE) containing 500 mg of octadecylsilica (C-18), 43−60 μm, and the adapters were obtained from Merck. The chromatograph was an HP5890 equipped with a [63]Ni electron capture detector and a HP3392A registrator.

Procedure. *Pine Bark Preparation*. Experiments were conducted with *Pinus pinaster* bark collected in a sawmill in the Porto region, North Portugal, dried at 105 $\pm$ 5 °C until constant weight. After being ground, the bark was sieved in different fractions, with only one of them selected for the appropriate analysis.

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TABLE 1. Validation Parameters for the Analytical Method[a]

	LIN	HEP	DIE	ENS	ALD	END	DDD	DDE	DDT
linearity range (mg/L)	0.05−0.56	0.05−0.65	0.11−0.95	0.06−0.51	0.14−0.90	0.18−1.18	0.02−0.61	0.14−1.14	0.14−0.83
sample detection limits (μg/L)	0.50	0.10	0.22	0.12	0.14	0.36	0.04	0.28	0.28
reproducibility (CV %)	11.6	10.9	8.8	11.0	13.3	30.0	11.6	12.6	30.3
% SPE	80.1 ± 10.5	48.6 ± 8.0	84.3 ± 10.5	83.3 ± 8.1	42.7 ± 5.0	150.3 ± 40.4	59.4 ± 7.9	44.3 ± 6.0	59.9 ± 6.1
N	11	16	15	16	15	16	14	15	14

[a] CV %, coefficient of variation; % SPE, yield of extraction; N, number of replicates.

TABLE 2. Operating Conditions Used in Factorial Planing Experiments (Results Are Expressed in μg of Pesticide Adsorbed/g of Pine Bark)

	factor levels[a]	LIN	HEP	ALD	DDE	DIE	END	DDD	DDT	ENS
1	(500, 125−300, 8)	1.266	2.391	2.500	2.467	2.451	2.649	3.043	2.400	2.504
2	(1000, 125−300, 8)	2.399	2.400	2.500	2.494	2.488	2.787	3.037	2.400	2.546
3	(500, 710−850, 8)	1.034	2.346	2.472	2.473	2.061	0.624	2.979	2.400	1.906
4	(500, 125−300, 30)	0.491	2.374	2.489	2.456	2.209	1.387	2.957	2.305	2.226
5	(1000, 710−850, 8)		2.216	2.439	2.361	2.025	1.199	2.719	2.400	1.957
7	(500, 710−850, 30)	1.277	2.443	2.485	2.468	2.110	1.558	2.943	2.400	1.935
8	(1000, 710−850, 30)	1.403	2.376	2.490	2.486	2.319	2.073	3.076	2.400	2.261

[a] The factor levels column indicates the pine bark amount, particle size, and superficial velocity (mg, μm, cm/min, respectively).

SPE Extraction for Pesticides Analysis. Samples and standards were extracted and preconcentrated by SPE prior to chromatographic analysis. Conditioning of the C-18 cartridge was performed with 10 mL of dichloromethane. Five hundred milliliters of solution was then adsorbed, at 10 mL/min, by means of vacuum control. After the system was dried for about 30 min, organochlorine pesticides were eluted with 5 mL of ethyl acetate and evaporated to dryness by a rotary evaporator operated at 40 °C. The extract was then diluted with *n*-hexane (0.5 mL) for gas chromatographic analysis.

Chromatographic Analysis. Chromatographic separation of organochlorine pesticides was performed at a PAS 1701 capillary column (25 m × 0.32 mm i.d. × 25 μm film) with a splitless injection volume of 1 μL. Both carrier and makeup gas were argon/methane (95/5) at 1.5 and 50 mL/min, respectively. The injector and detector temperatures were 250 and 300 °C, respectively. The initial oven temperature was kept at 80 °C for 1 min; then was programmed to 205 °C at a rate of 35 °C/min, held for 30 s; then it was raised to 250 °C at 5 °C/min, and finally held for 5 min. The organochlorine pesticides quantification was performed by the external standard method.

Sorption Tests with Pine Bark. Sorption tests were performed with vertical fixed bed columns filled with the bark. Columns of 8.75 × 17.1 mm (diameter × height) packed with 500 mg of pine bark (125−300 μm) were previously washed with 50 mL of distilled water. Then 500 mL of a known standard solution of organochlorine pesticides was passed through the columns with a superficial velocity of 8 cm/min (average flow rate of 5 mL/min).

Results and Discussion

A special interest in the reduction of laboratory chemical hazardous residues motivated the selection of both the extraction procedure, by using mini-column SPE instead of a liquid−liquid one, and the design of the sorption tests in similar mini-columns. This methodology reduces the volume of organic solvents used and the contents of pesticides in standards that needed to be discarded.

Validation Parameters of the Analytical Method. Calibration curves were obtained with seven points, ranging from 50 to 1180 pg/L of each pesticide. Detection limits (Table 1)

were calculated from the calibration curve (*18*). Precision of the chromatographic analysis was evaluated by the standard deviation of 23 injections of a standard solution prepared in different days. Reproducibility was 10%, on average, expressed by means of the coefficient of variation (CV %). Endrin and DDT presented lower reproducibility (Table 1). Recovery was determined to evaluate the performance of the SPE method by means of 15 extractions of a standard. Results revealed 80% of recovery, on average, with poorer performance for heptachlor, aldrin, endrin, DDD, DDT, and DDE. Recovery data was used as a correction factor in the quantification of samples. This methodology of analysis can be characterized by a high capacity of detection of traces and an acceptable reproducibility and accuracy when compared with other similar methods.

Optimization of Operating Conditions for Pine Bark Sorption. To optimize operating conditions, an experimental factorial planning (*18*) was used, by means of 16 experiments, studying the relationship $N = n^m$ where N is the number of experiments, m is the number of factors to study, and n is the factor levels. Three factors were studied—pine bark particle size, amount of pine bark, and superficial sample velocity. The factor levels considered were two: the upper and the lower limits (Table 2).

As expected, the optimal conditions were those corresponding to both lower particle size (limited by head pressure loss and bed compacting problems) and sample velocity (traducing higher contact time), as shown in Table 2. The increase in the adsorbent amount did not significantly improve the yield of removal, meaning that the conditions that require the least costs and labor can be recommended. Only three pesticides of the group (dieldrin, endrin, and endosulfan) reflected slight effects in the yield of removal due to variations of the operating conditions. The operating conditions used in subsequent assays were 500 mg of 125−300 μm pine bark at 8 cm/min. The global bed porosity measured by mercury porosimetry (attending to interparticle and intraparticle porosity) was 74%.

Variability of Pine Bark Pesticides Removal. The yield and the reproducibility of the removal of a spiked organochlorine water solution (individual concentration ranging from 2 to 5 μg/L) was measured for eight independent experiments (Table 3). The yield of removal, calculated by

TABLE 3. Yield of Pesticides Removal and Its Variability for a Set of Eight Experiments

	LIN	HEP	ALD	DDE	DIE	END	DDD	DDT	ENS
C_{in} (μg/L)	2.80	2.70	4.76	2.80	2.96	4.40	3.20	4.16	5.06
yield of removal (%)	37.56	92.98	98.85	97.35	98.32	96.86	97.28	99.36	97.08
reproducibility (CV %)	57.14	5.47	0.81	1.43	0.79	4.91	1.94	1.24	1.63

TABLE 4. Pine Bark Removal Capability (Adsorbed Amount of Pesticide/Mass of Adsorbent, μg/g)

av individual C_{in} (μg/L)	HEP	ALD	DDE	DIE	END	DDD	DDT	ENS
1.31	1.21	1.25	1.23	1.22	1.40	1.53	1.20	1.20
2.61	2.46	2.47	2.43	2.46	2.76	3.02	2.38	2.48
5.23	4.94	4.98	4.92	4.94	5.67	6.09	4.76	4.97
7.84	7.42	7.47	7.34	7.19	8.35	9.00	6.76	7.50
10.45	9.66	9.88	9.64	9.63	10.97	11.77	8.81	9.69

TABLE 5. Pine Bark Removal Capability (Yield of Removal, %)

av individual C_{in} (μg/L)	HEP	ALD	DDE	DIE	END	DDD	DDT	ENS
1.31	97.07	100.00	98.75	97.41	98.24	99.00	85.77	95.02
2.61	92.89	98.85	97.35	98.32	96.86	97.28	99.36	97.08
5.23	99.29	99.52	98.50	98.87	99.50	99.79	99.15	97.33
7.84	98.98	97.73	97.84	95.90	97.72	96.80	93.92	98.01
10.45	96.63	98.79	96.41	96.32	96.22	94.92	91.80	94.89

eq 1, was 97.3% ± 1.5% on average, excluding lindane.

$$\text{yield of removal} = 100\% \left([C_{in} - C_{out}]/C_{in} \right) \qquad (1)$$

where C_{in} and C_{out} are the influent and effluent concentrations of the pesticide.

The results obtained revealed a higher affinity of pine bark to the most hydrophobic and less polar compounds of the group. Probably, the pine bark role can be similar to that of an organic solvent in liquid−liquid extraction. The distribution of a neutral organic compound between pine bark and water can be correlated with the octanol−water partition coefficient (K_{ow}). Log K_{ow} for this group of organochlorines ranges from 5.982 (DDT) to 4.817 (lindane) (Table 6). Probably the poorer capacity of adsorption obtained for lindane can be explained by its smallest log K_{ow} of the group

and/or the fact that at such small feed concentrations the outer surface of the adsorbent plays the dominant role in the adsorption.

Sorption Studies. To study the sorption capability of pine bark, five standard solutions with individual concentrations (C_{in}) ranging from 1 to 10 μg/L were percolated through pine bark columns. The choice of this range of concentration was influenced by the information provided by the literature, where the expected levels in agriculture and urban effluents do not normally exceed 1.5 and 2.5 μg/L, respectively (21). Results shown in Table 4 did not conduct the expected linear response between equilibrium concentrations and the respective adsorbed amount of pesticide/mass of adsorbent. Probably the reproducibility of the analytical methodology, within the small effluent concentrations (some of them lower than detection limits), could be influencing this conclusion. Despite the lack of information extracted from these experiments, in order to judge the dominant sorption mechanisms, the results in Table 5 clearly show an excellent capability of pine bark to adsorb these kinds of compounds. Subsequent studies performed will clarify the sorption mechanisms involved in the process.

Pine Bark Saturation. The breakthrough occurs when all the sites of the adsorbent are occupied and the mass transfer zone is at the bottom of the column. The mass transfer zone is the area of the adsorbent bed where the sorption takes place (22). The definition of the breakthrough curve is very important for the prevision of the adsorbent saturation and its regeneration needs. The tests performed with minicolumns were based on the assumption that the breakthrough curve obtained is similar to the breakthrough curve under practical conditions (23). A standard solution of pesticides, whose feed individual concentrations (C_{in}) ranged from 2.5 to 5 μg/L, was continuously passed through the column until a treated amount of 60.00 L of solution/g of adsorbent was reached. Only endosulfan, dieldrin, and endrin achieved the breakthrough (Figure 1) if the breakthrough point is considered 0.5 μg/L. For the other compounds, the loads used
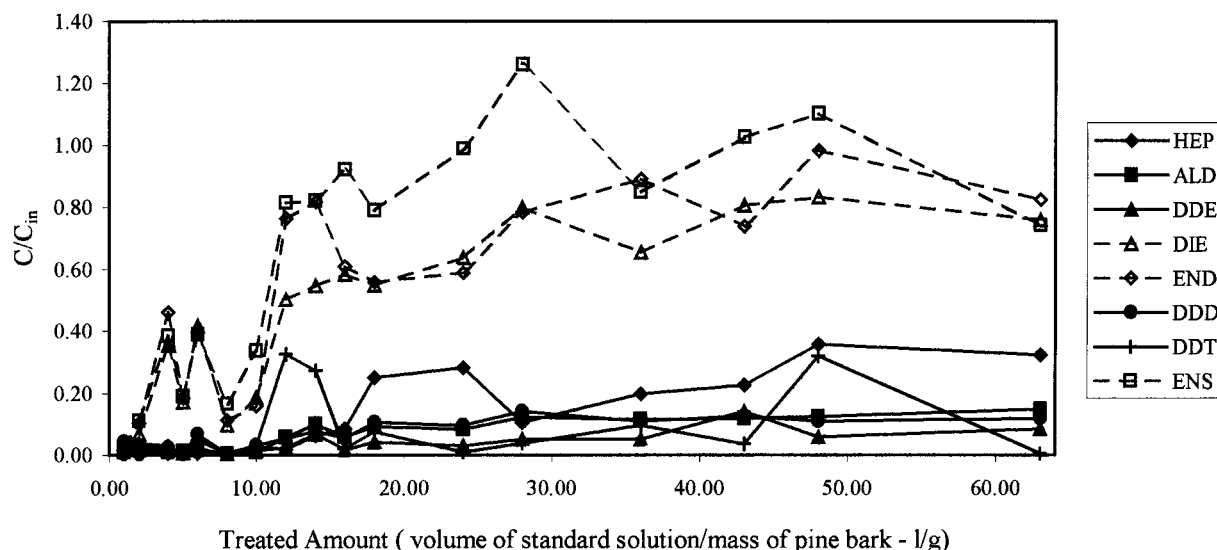

FIGURE 1. Breakthrough curves for individual pesticides. Feed concentrations (C_{in}) are as follows: HEP, 2.70 μg/L; ALD, 4.76 μg/L; DDE, 2.80 μg/L; DIE, 2.96 μg/L; END, 4.40 μg/L; DDD, 3.20 μg/L; DDT, 4,16 μg/L; ENS, 5.06 μg/L.

TABLE 6. Some Properties of the Pesticides Extracted from Refs *19* and *20*

	MW	S_w (mg/L)	log K_{ow}	K_{oc}
LIN	290.85	7.0	4.80	1 300
HEP	373.35	0.056	4.4–5.5	24 000
ALD	364.93	0.027	5.663	20 000
ENS	406.95	0.321	3.13	12 400
DDE	318.03	0.065	5.69–6.96	381 000
DIE	380.93	0.14	3.692–6.20	12 000
END	380.93	0.24	3.209–5.339	10 000
DDD	350.46	0.05	5.061–6.217	231 000
DDT	350.50	0.03	5.982	24 000

TABLE 7. Physical Properties of Activated Carbon and Pine Bark (125–300 μm Particle Size)

	pine bark	activated carbon
bulk density (g/cm³)	0.3132	0.7854
apparent density (g/cm³)	1.3629	1.4236
specific surface, BET (m²/g)	0.687	8.60
pore volume (cm³/g)	0.003227	0.004012
pore size (Å)	188.0461[a]	16.6626[b]

[a] Determined for pores lower than 5591.7627 Å. [b] Determined for pores lower than 4168.3159 Å.
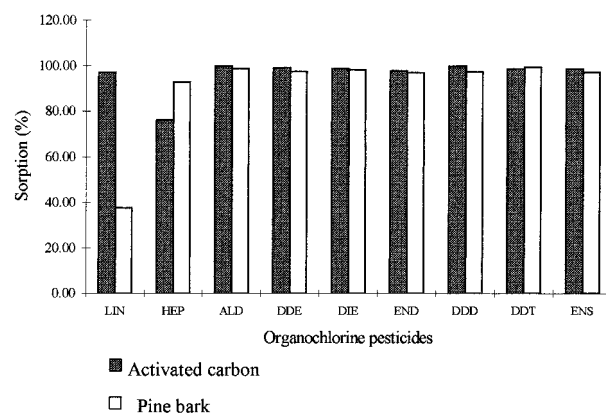

FIGURE 2. Comparative study between activated carbon and pine bark adsorption (for both experiments the pesticide solutions have the same concentration).

in the experiments were probably far from the saturation of the adsorbent. Nevertheless, the results obtained agree with the adsorption properties described in the literature (Table 6), where the lower K_{oc} corresponded to the three pesticides referred to above. K_{oc} is defined as the ratio K_p/oc, where K_p is the partition coefficient of a compound between water and sediment and oc is the fractional mass of organic carbon of the same sediment. In fact the three pesticides mentioned— endosulfan, dieldrin, and endrin—have the higher molecular weight (MW), water solubility (S_w), and lower log K_{ow} and K_{oc} values.

Activated Carbon vs Pine Bark Adsorption. Activated carbon is the best known adsorbent for many organic micropollutants in waters, especially pesticides. To compare the two adsorbents, duplicate experiments were performed under the same conditions: 500 mL of a spiked pesticide solution (feed concentration referred to in Table 3) was percolated through a mini-column packed with 500 mg of the adsorbent, either pine bark or activated carbon (Biofil, Anvite) with adsorbent size of 125–300 μm at 8 cm/min.

Comparative physical properties of the adsorbents (Table 7) revealed a higher surface area for the activated carbon. The determination of cumulative pore volume indicates that

there are essentially macropores in both, with an internal diameter higher than 1000 Å. Results obtained were very similar (Figure 2), except for lindane, where the degree of removal was significantly higher with activated carbon.

With the small particle sizes associated to the small feed concentrations used, film diffusion is probably the predominant mechanism. This fact, along with the strong affinity to hydrophobic molecules, leads us to the idea that mechanisms other than physical are responsible for the pine bark sorption of these compounds. This encouraging preliminary result will help in future work to determine adsorption isotherms, to elucidate the adsorption mechanisms involved, and to address engineering issues for implementing the process into practice. A very important aspect to be considered will be the interference of natural organic matter in water that can affect the adsorption capacity and the adsorbent life negatively.

Literature Cited

(1) Miliadis, G. E. *Bull. Environ. Contam. Toxicol.* **1993**, *50*, 247–252.
(2) Benoliel, M. J.; Caleiro, M. C. Water Pollution Research Report 11. Comission of the European Communties.
(3) Chevreuil, M.; Garmouma, M.; Teil, M. J.; Chesterikoff. *Sci. Total Environ.* **1996**, *182*, 25–37.
(4) Losada, A.; Fernandéz, N.; Diez, M. J.; Terán, M. T.; Garcia, J. J.; Sierra, M. *Sci. Total Environ.* **1996**, *181*, 133–135.
(5) Younos, T. M.; Wiegmann, D. L. *J. Water Pollut. Control Fed.* **1988**, *60*, 1199–1205.
(6) Waliszewski, S. M.; Pardío, V. T. S.; Chantiri, J. N. P.; Infanzón, R. M. R.; Rivera, J. *Sci. Total Environ.* **1996**, *181*, 125–131.
(7) Wu, S.; Gschwend, P. M. *Environ. Sci. Technol.* **1986**, *20*, 717–725.
(8) Nyholm, N.; Jacobsen, B. N.; Pedersen, B. M.; Poulson, O.; Damborg, A.; Schultz, B. *Water Res.* **1992**, *26*, 339–353.
(9) Stenzel, M. H. Merz, W. J. *Environ. Prog.* **1989**, *8*, 257–264.
(10) Poots, V. J. P.; McKay, G.; Healy, J. J. *Water Res.* **1976**, *10*, 1067–1070.
(11) Smith, E. F.; Mark, H. B., Jr. *Toxicol. Environ. Chem. Rev.* **1978**, *2*, 237–256.
(12) Allen, S. J.; Murray, M.; Brown, P.; Flynn, O. *Conserv. Rec.* **1994**, *11*, 25–39.
(13) Mitra, J.; Raghu, K. *Toxicol. Environ. Chem. Rev.* **1986**, *11*, 171–181.
(14) Marik, A.; Tarrejeva, U. *Am. Dyestuff Rep.* **1994**, *Oct*, 20–27.
(15) Vásquez, G.; Antorrena, G.; Parajó, J. C. *Wood Sci. Technol.* **1987**, *21*, 155–166.
(16) Vasconcelos, L. A. T. Utilização de Casca de Pinheiro na Remoção de Metais Pesados em Águas Contaminadas. Ph.D. Dissertation, Centro de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, 1989.
(17) Alves, M. M.; Beça, C. G.; Carvalho, R. G.; Castanheira, J. M.; Pereira, C. S.; Vasconcelos, L. A. T. *Water Res.* **1993**, *27*, 1333–1338.
(18) Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 2nd ed.; Ellis Horwood Limited Publishers: New York, 1988; pp 101–116.
(19) Kenaga, E. E. *Environ. Sci. Technol.* **1980**, *14*, 553–556.
(20) Herner, A. E.; Acock, B. *ARS Pesticide Properties Databse*; USDA-ARS, Remote Sensing & Modeling Laboratory: Beltsville, MD, 1995.
(21) Doucette, W. J.; Andren, A. W. *Environ. Sci. Technol.* **1987**, *21*, 821–824.
(22) Metcalf & Eddy, Inc. In *Waste Water Engineering–Treatment Disposal and Reuse*, 3rd ed.; Civil Engineering Series; McGraw-Hill International: New York, 1991; p 321.
(23) Hopman, R.; Meerkerk, M. A.; Siegers, W. G.; Kruithof, J. C. *Water Supply* **1994**, *12*, 197–207.