

Sorption behaviour of bifenthrin on cork

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Abstract

Bifenthrin, a known pyrethroid, was studied, aiming its removal from aqueous solutions by granulated cork sorption. Batch experiments, either for equilibrium or for kinetics, with two granulated cork sizes were performed and results were compared with those obtained with activated carbon sorption. Langmuir and Freundlich adsorption isotherms were obtained both showing high linear correlations. Bifenthrin desorption was evaluated for cork and results varied with the granule size of sorbent. The results obtained in this work indicate that cork wastes may be used as a cheap natural sorbent for bifenthrin or similar compounds removal from wastewaters.

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1. Introduction

Pyrethroids are pesticides commonly found in wastewaters of textile industries. Several pyrethroids are applied in cotton fields [1–3] as also for protection of cotton stocks. The same family of pesticide is also used in sheep to avoid parasites and later also for wool protection [4,5]. The textile industry is characterised by its high water consumption and is one of the largest industrial producers of wastewaters [6]. The occurrence of pesticides in aquifers is well recorded throughout the world and has become one of the major diffuse pollution risks to the world's drinking water supplies [7], so their removal is an important task to improve the water quality. Bifenthrin is one of the most stable pyrethroid in the laboratory and also the most persistent in the field, showing also one of the biggest bioaccumulation in the whole fish [8].

As the regulations for wastes purification have become more stringent, alternative treating technologies have been developed, such as the ones based on sorption methods, due to their economic, ecological, and technologic advantages [9].

There is a considerable amount of information in the literature concerning adsorption of organics onto activated carbon (AC). Despite this, there is still much to learn about the mechanisms of adsorption of these compounds, which is reflected in the empirical nature of many models employed in the literature to describe these systems. Models, with a theoretical basis, are a better tool to design and study the system considering a wide range of conditions, and to reduce the time spent in expensive pilot-plant studies. Moreover, they allow linking the model parameters to the physical and chemical properties of the systems, leading to a better understanding of the process [10].

Unknown data are available about bifenthrin removal of water or wastewaters. Different methods have been used for the removal of some pollutant compounds. Among these, AC adsorption is supposed to be best because of its efficiency, capacity, and application on large scale [11,12], due to its high surface areas. Another advantage of AC is that it can be regenerated by thermal desorption [13].

For the last decades, sorption of contaminants by sorbents of natural origin has gained important credibility due to the good performance and low cost of these complex materials [9]. A great variety of alternative low-cost materials like fly ash [14], chitosan fibre [15], resins [16], soil, wood chippings,

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tyre cuttings, coconut shell powder, hair, coal, etc., are being tried in place of activated carbon for the sorption of different pollutants like pesticides, detergents, heavy metals, dyes, etc. [17].

Besides the environmental advantages of using natural sorbents for remediation purposes, there is an important drawback of adsorption techniques with activated carbon for the family of pyrethroids, where bifenthrin is included—the regeneration step with thermal desorption may lead to the formation of dioxins [18].

The chemical and physical characteristics of sorbent materials, as well as those of sorbates, vary widely and it is difficult to recommend specific low-cost materials to sorb specific pollutants. Because of the huge volumes involved, purification methods for the removal of pesticides from water have to be efficient, fast, and inexpensive. There is a necessity to do experimental work with different materials to sorb different pollutants to understand the variations in the sorption phenomena [17].

In the western Mediterranean region, cultivation of cork oak, *Quercus suber*, is an important economic activity, with Portugal being the world's major producer. Besides the production of stoppers, an economically important product, the industry creates enormous volumes of waste formed by particles with very small dimensions, generally designated cork powder [19]. This industrial waste was the raw material used in this work and the aim of it is to evaluate new applications in environmental control. In the present study, efforts were made to use cork waste as a sorbent to remove a pyrethroids—bifenthrin from waters.

2. Experimental

2.1. Reagents and solutions

A Norit GAC 1240 PLUS activated carbon from Norit N.V. (Amersfoort, The Netherlands) was used. This carbon was selected because it is an acid washed granular activated carbon, which offers good adsorption properties for water applications and a high purity level. According to the supplier specifications, it has a neutral pH and a size between 0.5 and 1.5 mm.

Bifenthrin was obtained from Riedel-de Haën (Hanover, Germany). Methanol was pro-analysis grade and *n*-hexane and hydrochloric acid were high-performance liquid chromatography (HPLC) grade, from Merck (Darmstadt, Germany). Water conductivity was lower than 1 μ S/cm.

Stock solutions of the pesticide were prepared in *n*-hexane (500 mg/l) and were kept in darkness at 4 °C up until 6 months.

2.2. Apparatus

A Chrompack 9001 model chromatograph equipped with an on-column injector and a ⁶³Ni Electron Capture Detec-

tor were employed and connected to a Chrompack “Maestro” data acquisition system. Chromatographic separation of pesticide was performed at a CP-SIL 8CB WCOT column (25 m \times 0.25 mm i.d. \times 0.25 μ m film). Both carrier and make-up gas were nitrogen (purity \geq 99.999%) and flow rates through column and make-up were 0.5 ml/min and 41 ml/min, respectively. Nitrogen was obtained from Linde Sogás (Porto, Portugal).

To extract pesticide for chromatographic analysis, a MILLIPORE vacuum system connected to a vacuum pump from DINKO D-95 was used. The disks for solid phase extraction (SPE), with 47 mm of diameter containing octadecylsilica (C18), were obtained from Supelco (Bellefonte, USA).

For cork adsorption assays, a SBS 30 Shaker Bath with orbital stirrer from Stuart connected to a Julabo F70 refrigerator were required.

2.3. Procedure

2.3.1. Granulated cork preparation

The cork, with a diameter (*d*) of 1 mm $< d < 2$ mm and 3 mm $< d < 4$ mm, was supplied by Amorim & Irmãos, S.A., Santa Maria de Lamas, Portugal. To remove exceeding powder the granulated material was washed with distilled water and dried at 105 \pm 5 °C for 4 days.

2.3.2. Characterisation of the cork

The iodine number for both diameter corks was determined according to the standard methods as described in ASTM for determination of iodine number of activated carbon D4607-94 (1999).

2.3.3. Kinetic studies

Batch experiments were performed, using a series of Erlenmeyer flasks of 500 ml capacity with glass stoppers, containing 200 ml of bifenthrin solutions (30 μ g/l), kept in a thermostatic shaking water bath at 25 \pm 1 °C. A known amount of sorbent (cork or carbon) was added to each flask. At given time intervals, an Erlenmeyer solution was analysed.

2.3.4. Adsorption studies

The sorption experiment was conducted also by batch equilibrium technique. A known amount of each adsorbent (0.6 g for cork and 0.05 g for carbon) was weighted into each erlenmeyer and placed with 200 ml of aqueous solution of bifenthrin of varied concentration (20–100 μ g/l), in a shaker bath at 25 °C during 24 h for cork and 48 h for carbon. Each tested concentration was studied in different pieces of cork and carbon samples. The difference between initial bifenthrin concentration and the equilibrium concentration was assumed to be the amount of bifenthrin adsorbed. Control samples were prepared in the same manner, but without cork or carbon, being considered the initial concentration in the above control samples.

2.3.5. Desorption studies

Desorption experiments were performed only with cork granules, using a single-cycle, withdraw-and-refill batch technique. After a predetermined desorption period (24 h), separation of the sorbent with a sieve from the aqueous phase and analysis of the solution was conducted, in the same manner as used for the original sorption isotherm.

2.3.6. Bifenthrin analysis

The bifenthrin was extracted from aqueous solutions (obtained from isotherms and kinetics studies) using a SPE (solid phase extraction) technique. A 1 ml volume of methanol was added to 200 ml solution sample with a pH \sim 4. This mixture containing 0.5% of methanol and pH \sim 4 was transferred to a C18 disk, which was conditioned with 7 ml of methanol and 7 ml of water. After sample loading, the disk was rinsed with 10 ml of water. The SPE disk was dried for 1 h by a vacuum. Elution of bifenthrin was performed with *n*-hexane until adequate volume. The coefficient of variation of extractions with bifenthrin was 7%.

0.5 μ l of the extracted samples were analysed and quantified by capillary column gas chromatography with an ECD. The oven programme was: initial temperature 60 °C, held for 1 min, 26 °C/min ramp to 180 °C, held for 0.19 min, 5 °C/min ramp to 230 °C held for 0.3 min and finally a 7 °C/min ramp to 270 °C held for 7 min. The detector temperature was 310 °C.

The pesticide concentration was calculated from external standard method, where calibration curve was obtained with the standards extracted in the same conditions as in the samples. Three independent analyses were performed for each sample and each extract was injected in triplicate.

3. Results and discussion

3.1. Characterisation of the cork

Cork is a natural cellular material. The cells are closed, hollow and, on average, can be described as hexagonal prismatic [20]. Chemically, cork is composed of a complex mixture of fatty acids and heavy organic alcohol (\approx 45%), tannins (\approx 6%), polysaccharides (\approx 12%), lignin (\approx 27%), and alkanes. The mineral content is low (\approx 5%), the most abundant element being calcium [9].

The comparison of the adsorption capacity was estimated by the iodine number, where the iodine number on cork decreases as particle diameter increases, as expected [21].

Table 1
Adsorption capacities for iodine of the studied sorbents

Sorbents	Iodine number (mg/g)
Cork 1–2	83.9 \pm 0.7
Cork 3–4	33.6 \pm 0.5
Carbon	607 \pm 0.1

The iodine numbers obtained with cork (Table 1) are considerably lower than those for the studied activated carbon or even those presented in literature. Carbon has a surface structure with micropores and probably cork surface consists of macropores (diameters higher than 50 nm, accordingly to IUPAC). The fact that iodine number decreases with cork particles diameter reveals that the only available surface area for sorption is the external one. Although cork is a tissue of thin-walled cells, with no communication between contiguous cells, which are, therefore, closed units [22], it seems that the volume inside the cells is useless for adsorption.

3.2. Validation parameters of bifenthrin analysis

Solid phase extraction is one of the most used technologies, capable of isolating and enriching the trace materials from aqueous samples [23]. Disks extraction was chosen because samples can be loaded at high flow rates with a lower chance of clogging [24]. The performance of the disks was previously studied [25].

The parameters of validation of bifenthrin analysis were determined as shown in Table 2. The calibration curve obtained with five standard solutions, with concentrations in the range 10–100 μ g/l, showed a linear correlation, where the standards were extracted in the same manner of the samples. The intermediate precision of the chromatographic analysis was evaluated by the relative standard deviation of 12 injections of a standard solution of 10 μ g/l in different days. The limit of detection, calculated from the calibration curve [26], was 54 ng/l. The intermediate precision of the global methodology, estimated by four repeated assays of the standard of 10 μ g/l, with independent extractions, was 8% (expressed as relative standard deviation). The average recovery of six assays, evaluated by the standard addition method, was 79.3% \pm 6.4%. Therefore, this analytical technique proved adequate to satisfy the quantification needs of subsequent experiments.

Table 2
Validation parameters of bifenthrin analysis

Range of linearity	10–100 μ g/L	
Calibration curve	$Y = 0.0248C - 0.067$	$Y =$ bifenthrin area; $C =$ concentration (μ g/l)
Correlation coefficient of calibration curve, R^2	0.991	
Intermediate precision of chromatographic analysis	6.1%	Expressed as relative standard deviation, $n = 12$
Detection limit in samples	54 ng/L	Concentration factor included
Intermediate precision of the global methodology	8%	Four independent extractions
Recovery, $R\%$	79.3 \pm 6.4	

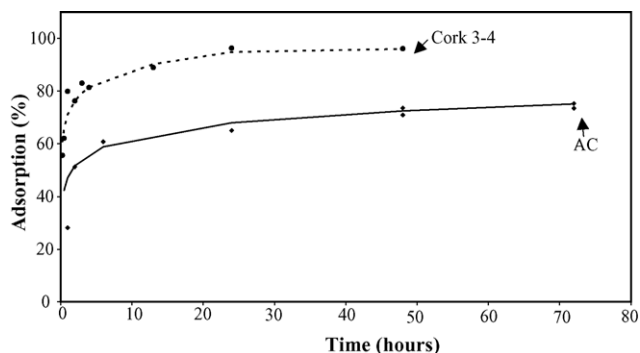


Fig. 1. Adsorption kinetic studies of bifenthrin in cork and AC.

3.3. Equilibrium time

The adsorption experiments were carried out for different contact times with a solution of 60 $\mu\text{g/l}$ of bifenthrin and a fixed sorbent weight: 0.05 g for carbon and 0.6 g for cork. The results are plotted in Fig. 1. The sorption kinetics correspond to a convex initial curvature or L type in the classification by Giles et al. [27], which means that as the adsorption sites are occupied, it becomes increasingly more difficult for adsorbate molecules to find vacant sites [28].

Equilibrium was considered to be achieved for cork granules with diameter 3–4 mm, after 24 h. Attending to preliminary results confirming the assumption, it was assumed that for particles with lower diameter (as 1–2 mm) it should be at least the same. Longer equilibrium time was necessary for activated carbon (48 h), as well as the percentage of adsorption was lower (about 75%) than that for cork (up to 90%).

3.4. Adsorption isotherms

Two models were tested to describe adsorption in the studied sorbents—Langmuir and Freundlich (Fig. 2).

The equilibrium adsorption data could be described by the Langmuir sorption isotherm:

$$q = \frac{K_L q_m C_{\text{eq}}}{1 + K_L C_{\text{eq}}} \quad (1)$$

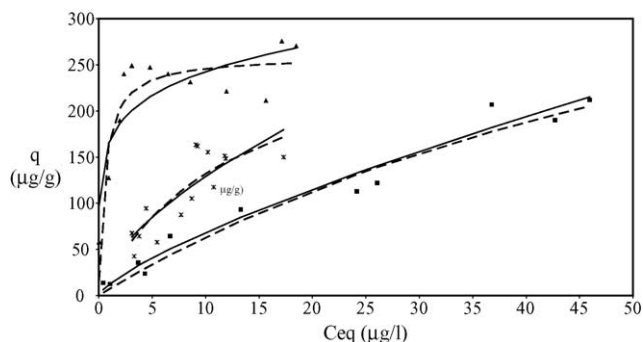


Fig. 2. Bifenthrin isotherms in cork with dimensions, between 1 and 2 mm (▲), between 3 and 4 mm (■) and GAC (Ж), fitted by Langmuir (---) and Freundlich (—) models.

or by the Freundlich sorption isotherm:

$$q = K_F C_{\text{eq}}^{1/n} \quad (2)$$

where q is the adsorbed amount ($\mu\text{g/g}$), C_{eq} the equilibrium concentration ($\mu\text{g/l}$), K_L the Langmuir constant, q_m the monolayer capacity, and K_F is the adsorption constant that represents the degree or strength of adsorption and the exponent $1/n$ takes in account non-linearity in the adsorption isotherm.

The Langmuir model considers that adsorption process takes place on a surface composed of a fixed number of adsorption sites of equal energy, one molecule being adsorbed per adsorption site until monolayer coverage is achieved. No other non-ideal effects are included in this model. This suggests that the Langmuir model is only a convenient and empirical mean of single component data correlation and constitutes a crude representation of the real behaviour of the system [29].

The Freundlich model is a generalization of the Langmuir model for a heterogeneous surface with a distribution function corresponding to an exponential decay [29].

Models parameters were determined using non-linear regression with the program SPSS (version 11.0 for windows) and results are presented in Table 3.

Once again, the better results obtained with small cork particles may signify that cork has no micropores available for adsorption, i.e., only external area is available for bifenthrin. The capacity of adsorption of cork will increase with the decrease of size of the granule. This results confirm the already information provided by the iodine number.

Activated carbons are materials with amphoteric character; thus, depending on the pH of the solution, their surface might be positively or negatively charged [6]. So, activated carbons works very well for anionic, cationic, and polar compounds with increase of sorption behaviour at adjusted pH. In bifenthrin case, like almost all of pyrethroids, with a molecule very non-polar, the GAC seems not to be the best choice, or the pH must be careful evaluated.

3.5. Balances of adsorption and desorption

The calculations of balance of bifenthrin adsorbed and desorbed in 200 ml of water were based on the following equations:

$$[\text{Initial amount}] = [\text{Free amount}] + [\text{Adsorbed amount}] \quad (3)$$

The adsorbed amount could be analysed as follows:

$$[\text{Adsorbed amount}] = [\text{Desorbed amount}] + [\text{Final adsorbed amount}] \quad (4)$$

Desorption of hydrophobic organic chemicals (like bifenthrin) has frequently been observed to manifest apparent hysteresis. This hysteresis is often attributed to the occurrence of specific chemical reactions (e.g., formation of hydrogen or

Table 3
Langmuir and Freundlich parameters of bifenthrin adsorption in cork 1–2, 3–4 mm and carbon

	Langmuir			N^b	Freundlich		
	q_m ($\mu\text{g/g}$)	K_L ($l/\mu\text{g}$)	S.D. ^a		K_F (l/g)	n	S.D. ^a
Cork 1–2	$2.60 \times 10^2 \pm 15$	1.8 ± 0.8	27	12	$1.67 \times 10^2 \pm 15$	6.2 ± 1.6	33
Cork 3–4	$5.5 \times 10^2 \pm 2 \times 10^2$	0.013 ± 0.07	16	11	12 ± 3	1.33 ± 0.14	14
Carbon	$2.94 \times 10^2 \pm 96$	0.08 ± 0.04	24	14	$3.1 \times 10 \pm 10$	1.7 ± 0.4	23

$$^a \text{ S.D.} = \sqrt{\frac{\sum_{i=1}^N (q - q^{\text{calc}})^2}{N-1}}$$

^b Number of data points in isotherm.

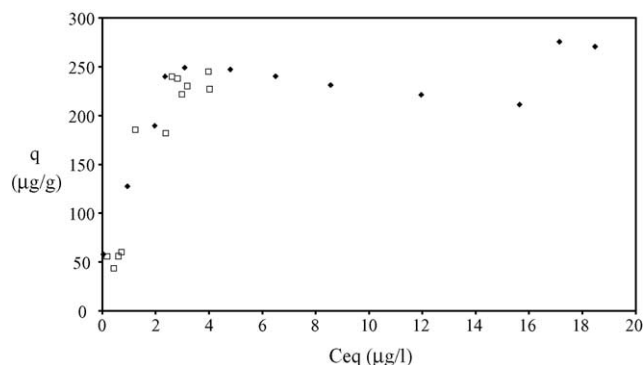


Fig. 3. Adsorption (■) and desorption (□) isotherms of bifenthrin in granule of cork between 1–2 mm.

covalent bonds) between polar organic chemicals and polar sites on adsorbent surfaces [30].

Hysteresis can be defined [31] as the difference between adsorption and desorption isotherms. Hysteresis is absent only if the adsorption and desorption isotherms are indistinguishable. In Figs. 3 and 4, the isotherm of adsorption and desorption of bifenthrin on cork 1–2 and 3–4 are represented, respectively.

The desorption hysteresis coefficient (H) can be calculated by taking ratio of n the values from the Freundlich equation for desorption ($1/n_{\text{des}}$) and adsorption ($1/n_{\text{ad}}$) [32] as,

$$H = \frac{1/n_{\text{des}}}{1/n_{\text{ad}}} \times 100 \quad (5)$$

The lower the hysteresis index, the higher the degree of hysteresis, i.e., more difficult to desorb [33].

Table 4
Freundlich parameters of bifenthrin desorption in cork 1–2 and 3–4 mm

	Freundlich			N^b	Hysteresis				
	K_F (l/g)	n	S.D. ^a		H	HI			
						1 $\mu\text{g/l}$	4 $\mu\text{g/l}$	6 $\mu\text{g/l}$	12 $\mu\text{g/l}$
1–2	115 ± 13	1.7 ± 0.3	29	12	3.59	–	0.09	–	–
3–4	29 ± 3	1.6 ± 0.1	8.4	10	0.89	1.40	–	46.58	78.44

$$^a \text{ S.D.} = \sqrt{\frac{\sum_{i=1}^N (q - q^{\text{calc}})^2}{N-1}}$$

^b Number of data points in isotherm.

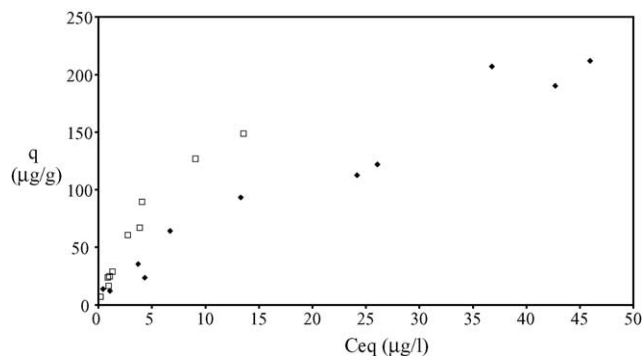


Fig. 4. Adsorption (■) and desorption (□) isotherms of bifenthrin in granule of cork between 3 and 4 mm, both fitted by Freundlich model.

Another hysteresis index may be obtained with this formula [34],

$$HI = \frac{q_{\text{eq}}^{\text{d}} - q_{\text{eq}}^{\text{s}}}{q_{\text{eq}}^{\text{s}}} \Big|_{T, C_{\text{eq}}} \quad (6)$$

where q_{eq}^{s} and q_{eq}^{d} are the solid phase solute concentrations for the single-cycle sorption and desorption experiments, respectively, and the subscripts T and C_{eq} specify conditions of constant temperature and residual solution phase concentration.

Both hysteresis parameters, H and HI , at constant temperature (25 °C) and at three different concentration levels were calculated for each sample using the Freundlich model sorption. Desorption parameters and calculated results of hysteresis are included in Table 4.

The values obtained from both hysteresis parameters prove the idea given by the Figs. 2 and 3, showing hysteresis only in corks 3–4. One possible explanation for this behaviour

is the existence of irreversible reactions. However, Huang et al. [35] as described a hysteresis artefact when equilibrium is attained in the sorption but not in the desorption step (due a longer time). It seems possible this last hypothesis because corks 1–2 show no hysteresis.

4. Conclusion

Granules of cork, an exceeding waste material from Portuguese industry, were found to be effective for the removal of bifenthrin from wastewaters. The batch experiments showed a high sorption capacity at equilibrium (above 80%), which is even higher than that obtained for activated carbon (up to 70%). The non-polarity of the studied molecule may explain this behaviour, but the chemical nature of the surface available for adsorption may also play an important role in the phenomena. Future work will comprise the elucidation of the chemical surface of cork granules. Cork granules of dimension 1–2 mm showed a maximum sorption capacity related to the total cover of the surface ($q_m = 260 \mu\text{g/g}$), similar as that obtained for activated carbon ($q_m = 294 \mu\text{g/g}$).

Results for hysteresis assumption were not elucidative, because it was shown for cork granules 3–4 mm (that exhibit a great heterogeneity) but not for 1–2 mm. Although the data show that apparent hysteresis increase with the concentration, it means for higher concentrations it's more difficult to desorb.

The results obtained in this work indicate that cork wastes may be used as a cheap natural sorbent for bifenthrin or for similar compound separation from wastewaters.

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