Improvement of the Desorption of the Herbicide Norflurazon from Soils via Complexation with *β*-Cyclodextrin

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The effect of *β*-cyclodextrin (*β*-CD) on the removal of the herbicide norflurazon (NFL) from soils has been investigated. The interaction of NFL with *β*-CD in solution yielded the formation of a water-soluble inclusion complex at 1:1 stoichiometric ratio, which gave an increase in NFL solubility. Desorption studies of NFL previously adsorbed on six soils of different characteristics have been performed in the presence of 0.01 M *β*-CD or 0.01 M $Ca(NO_3)_2$ as extractant solutions. Positive hysteresis was observed in all soils when 0.01 M $Ca(NO_3)_2$ solution was used, indicating that desorption of NFL from these soils was not completely reversible. On the contrary, the application of *β*-CD solutions to soils where NFL had been previously adsorbed increased very much its desorption, and a negative hysteresis was obtained for all soils studied; that is, more NFL was desorbed with respect to NFL adsorption isotherm. A clear relationship was observed between the physicochemical characteristics of the soils and the *β*-CD concentration necessary to remove the herbicide, the percentages of desorption observed for each soil being inversely related to the values obtained for the Freundlich sorption capacity parameter of the herbicide, K_f. In general, high desorption yields can be obtained with very low *β*-CD concentrations, which is an important advantage from an economic point of view, although in those soils that present an extremely high NFL adsorption, higher amounts of *β*-CD should be used. The results obtained indicate the high extracting power of *β*-CD toward the herbicide previously adsorbed on the soils and the potential use of *β*-CD for in situ remediation of pesticide-contaminated soils.

KEYWORDS: Norflurazon; *β*-cyclodextrin; desorption; soils; remediation

INTRODUCTION

The remediation of soils and groundwater is the most costly and time-consuming part of site cleanups, because the natural attenuation of contaminated soil is effective only in a few cases (*1*). After the source of contamination has been removed and treated, contaminated soils and groundwater may remain and require treatment (*2*). Nowadays in situ technologies have become very attractive for treating contaminated soils and groundwater because of lower cost, less disruption to the environment, and reduced worker exposure to hazardous materials. Addition of agents such as organic cosolvents and surfactants is known to increase the transport of low-polarity organics from soils (*3–6*). Surfactants are important components of most pesticide formulations because they can function as spreaders, stickers, antifoamers, compatibility agents, or activators. However, it has been found that both cosolvents and surfactants have some disadvantages for soil remediation application (*7, 8*). Cosolvents are not effective in solubilizing the organics unless their volume-fraction concentrations are >10%, and surfactants form high-viscosity emulsions that are difficult to remove from the soils. Furthermore, synthetic surfactants inhibit microbial

activity in soils, thereby reducing their natural bioremediation capability. One type of these additives is microbially produced compounds, known as biosurfactants, which can enhance low-polarity and nonpolar organic contaminant removal without accumulating in the soil (*9–12*). Clyclodextrins (CDs) are a class of microbially produced compounds that are able to form inclusion complexes with organic compounds in solution, increasing their water solubility (*13*).

The application of CDs as solubility-enhancing agents has been investigated (*14–17*). A large number of papers in which the complexation with cyclodextrin is studied using pesticides that present problems can be found, from both agricultural and environmental points of view. Most of the pesticide−CD complexes have been prepared to improve the pesticides' solubility in water. Due to the importance of solubility in the foliar translocation and penetration of systemic herbicides and fungicides, Manolikar and Sawant (*18*) prepared and characterized *β*-cyclodextrin complexes of the herbicide isoproturon. Saikosin et al. (*19*) prepared inclusion complexes with the insecticide carbaryl to obtain formulations with lower toxicological effects. They obtained a solubility increase of 18.4-fold when the insecticide was complexed to methyl-*β*-cyclodextrin, but showed a lower toxicity than commercial carbaryl. 2,4-D−CD complexes have been also prepared to obtain some changes

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Table 1. Different Properties of the Soils Studied

property	soil					
	1	2	3	4	5	6
pH	7.6	6.5	5.7	8.0	4.8	8.0
CaCO$_3$ (g kg^{-1})	0.0	0.0	0.0	241.0	0.0	69.0
CEC (cmol$_c$ kg^{-1})	17.2	3.5	5.8	39.0	20.1	4.8
organic matter (g kg^{-1})	19.0	5.10	13.8	17.6	53.4	7.92
sand (%)	16.4	92.8	56.7	2.7	61.1	87.6
silt (%)	61.2	4.4	23.8	31.5	29.0	4.0
clay (%)	22.6	2.5	19.5	65.9	9.8	8.4
amorphous Al$_2$O$_3$ (g kg^{-1})	9.4	0.3	0.3	3.5	12.3	0.2
amorphous Fe$_2$O$_3$ (g kg^{-1})	10.8	0.3	1.4	0.8	23.3	0.4

in the properties of 2,4-D, and the removal of this herbicide previously adsorbed on the soil has been improved using β-CD solutions (*20*, *21*). To achieve a good biological activity, fungicides must be used dissolved in water, which involves in most cases preparation of saltlike derivatives, and, if this is not feasible, the use of organic solvents. That is the reason why Lezcano et al. (*22*, *23*) selected eight quite low water-soluble fungicides to increase their solubility by complexation with CDs and to study the feasibility of the preparation of solid complexes of fungicide–cyclodextrins. Villaverde et al. (*24*, *25*) have obtained an increase in norflurazon solubility up to 5-fold with α- and β-cyclodextrins and up to 4-fold with γ-cyclodextrin. On the other hand, it has been also shown that molecular encapsulation by CDs increased the bioavailability of polycyclic aromatic hydrocarbons (PAHs) in soils, enhancing bioremediation (*26*–*31*). Cuypers et al. (*30*) demonstrated that HPCD extraction may provide a good method for the prediction of PAH bioavailability in contaminated sediments. Gruiz et al. (*26*) showed that biodegradation of hydrocarbons could be enhanced and their toxic effect on plants and soil microbes decreased by adding CDs. Fenyvesi et al. (*27*) used aqueous CD solutions to remove PAHs and pesticides from contaminated soils. However, studies about the application in situ of CDs for the remediation of pesticide-contaminated soils have not been yet carried out.

Norflurazon (NFL) was first registered as a pesticide in the United States in 1974. NFL is a selective preemergent herbicide widely used to control germinating annual grasses and broadleaf weeds in fruits, vegetables, nuts, cotton, peanuts, and soybeans (*32*). NFL presents problems with its retention in soils with high organic matter and iron oxides contents (*33*), and therefore it is a concern that NFL may persist in soils, implying a great risk as long-term contaminant, which could gradually be desorbed and available if the soil conditions change.

The aim of this work was to evaluate the effect of β-CD on NFL desorption focused to soil decontamination. Six soils with different characteristics were used to study the influence on NFL desorption by using β-CD as extractant solution, in comparison to the removal obtained with 0.01 M Ca(NO$_3$)$_2$ solution.

MATERIALS AND METHODS

Materials. Technical NFL (purity of 97.8%) was kindly supplied by Novartis and β-CD (99%) by Roquette (Lestrem, France). Six different soils were employed to carry out the adsorption–desorption experiments. They were taken from the superficial horizon (0–20 cm), and their main physicochemical properties are shown in **Table 1**. All other materials were of analytical reagent grade and used as received. All soils are from southwestern Spain except soil 5, which is from Scotland. They were analyzed for pH in saturated paste, total carbonate content, particle size distribution, cationic exchange capacity, and organic matter content (OM). Organic carbon content (OC) was

determined as follows: OC (%) = 0.58 × OM (%). The amorphous and organically bound iron and aluminum oxides were determined using ammonium oxalate–oxalic acid (*34*).

Methods. *Solubility Studies in Aqueous Phase.* The phase solubility studies were performed according to the method reported by Higuchi and Connors (*35*). NFL (5 mg) was added to aqueous solutions (10 mL) containing various concentrations of β-CD (between 0 and 0.012 M). The flasks were shaken at 25 °C for 1 week. This time of reaction was chosen from preliminary kinetic studies (not shown). After that, the suspensions were filtered through a 0.22 μm Millipore glass fiber membrane filter and properly diluted, and the concentration of NFL in the filtrate was determined by HPLC equipped with a fluorescence detector. β-CD was not detected using this analytical method, and therefore, it did not interfere with the assay. The conditions were as follows: mobile phase, acetonitrile/water (60:40); flow, 0.6 mL/min; temperature, 30 °C; chromatographic column, Kromasil C18 reverse phase; fluorescence detector (Shimadzu RF-535), with excitation and emission wavelengths of 310 and 405 nm, respectively.

The apparent stability constant, K_c, was calculated from the straight line obtained in the phase solubility diagram, following the equation proposed by Higuchi and Connors (*35*)

$$K_c = \text{slope}/S_0(1 - \text{slope}) \qquad (1)$$

where S_0 is the NFL equilibrium concentration in aqueous solution in the absence of β-CD and slope is the slope of the phase solubility diagram.

Adsorption–Desorption Experiments in Soil. NFL adsorption experiments in soils were carried out in quadruplicate in 50 mL centrifuge tubes, by mixing 10 g of each soil with 20 mL of 0.01 M Ca(NO$_3$)$_2$ solution (used to maintain the ionic strength in the aqueous solution), containing various concentrations (4, 8, 12, 16, and 20 mg L^{-1}) of NFL. The samples were shaken for 24 h at 20 ± 1 °C. This time of reaction was chosen from preliminary kinetic studies (not shown), which showed that adsorption had reached equilibrium. After that, the samples were filtered and analyzed. NFL adsorbed was calculated from the difference between its concentrations in the supernatant before and after equilibrium. Adsorption isotherms were obtained by plotting the amount of NFL adsorbed by the soil (μmol/kg) versus the respective concentrations in equilibrium (μmol L^{-1}). Sorption isotherms were fitted to the logarithmic form of the Freundlich equation to calculate the adsorption capacity of each soil used:

$$\log C_s = \log K_f + n \log C_e \qquad (2)$$

C_s (μmol kg^{-1}) is the amount of herbicide sorbed at the equilibrium concentration C_e (μmol L^{-1}), and K_f and n are constants that characterize the relative sorption capacity and the sorption intensity, respectively, for the herbicide. The fitted equation was used to calculate sorption distribution coefficients (K_d) at a selected C_e (10 μmol L^{-1}) in order to calculate the organic carbon normalized distribution coefficient (K_{oc}). K_{oc} is often used in the discussion of sorption of nonpolar hydrophobic compounds, the concept being compatible with the idea of organic carbon (OC) having the same affinity for a nonpolar compound independent of the OC source.

Desorption experiments were performed after adsorption equilibrium was reached, for the points corresponding to NFL initial concentrations of 4, 12, and 20 mg L^{-1}, by removing the supernatant after centrifugation, replacing it by 20 mL of 0.01 M Ca(NO$_3$)$_2$ solution or 0.01 M β-CD solution, allowing equilibration for an additional 24 h, and finally operating as in the adsorption experiments. Three consecutive desorptions were carried out.

In some cases, NFL desorption experiments were carried out using different concentrations of β-CD in solution to determine the lower β-CD concentrations needed for obtaining NFL desorption from soil. The concentrations used were 0.01, 0.5, 2.0, 5.0, 7.0, and 10.0 mM and also the concentration of β-CD corresponding to the millimoles of NFL adsorbed on each soil (1:1 molar ratio of β-CD and NFL adsorbed). The desorption procedure was the same as previously described with three consecutive desorption steps.
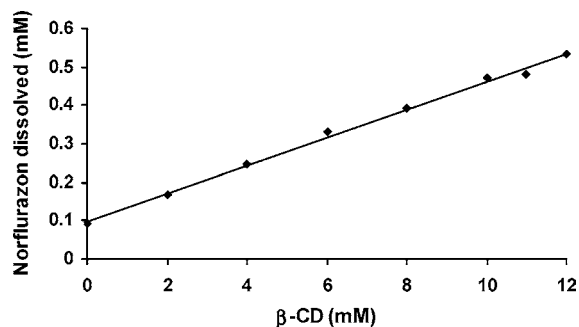
Figure 1. Phase solubility diagram of norflurazon in the presence of β-cyclodextrin.

RESULTS AND DISCUSSION

Studies in Aqueous Phase. The phase solubility diagram of NFL in the presence of different β-CD concentrations is shown in **Figure 1**. A linear increase up to 5-fold in NFL solubility is observed when β-CD concentration is increased, and a solubility limit is not obtained in the range of β-CD concentrations used. This is in agreement with an A_L classification according to Higuchi and Connors (*35*). The diagram is a straight line with a slope of <1, and it may be ascribed to the formation of a 1:1

complex stoichiometry in solution. The apparent formation constant (K_c) was calculated according to eq 1. In our case, a $K_c = 360$ M^{-1} was obtained.

Adsorption Experiments in Soils. NFL adsorption isotherms on the six soils under study in the presence of 0.01 M Ca(NO$_3$)$_2$ as background electrolyte are presented in **Figure 2**. These soils were selected to carry out NFL adsorption−desorption experiments due to their different physicochemical characteristics. All of the adsorption isotherms were "L" type (concave initial curvature) according to the classification of Giles et al. (*36*), and in all cases NFL adsorption isotherms were well described by the linearized Freundlich equation. The sorption isotherms were compared using the K_f parameter of the Freundlich equation (**Table 2**). The constant K_f is the amount of pesticide sorbed for an equilibrium concentration of 1 μmol L^{-1} and hence represents adsorption at low adsorbate concentration. K_f values are related to the adsorption capacity of the different soil samples toward NFL.

For the soils under study K_f was between 15.54 and 0.35 μmol kg^{-1}, indicating the strong influence of soil characteristics on NFL adsorption. NFL adsorption has been related to the organic matter (OM) of the soils by several researchers, and in some cases it has been also related to soil pH and cation exchange capacity (*37*), the clay content (*38*), or the type of
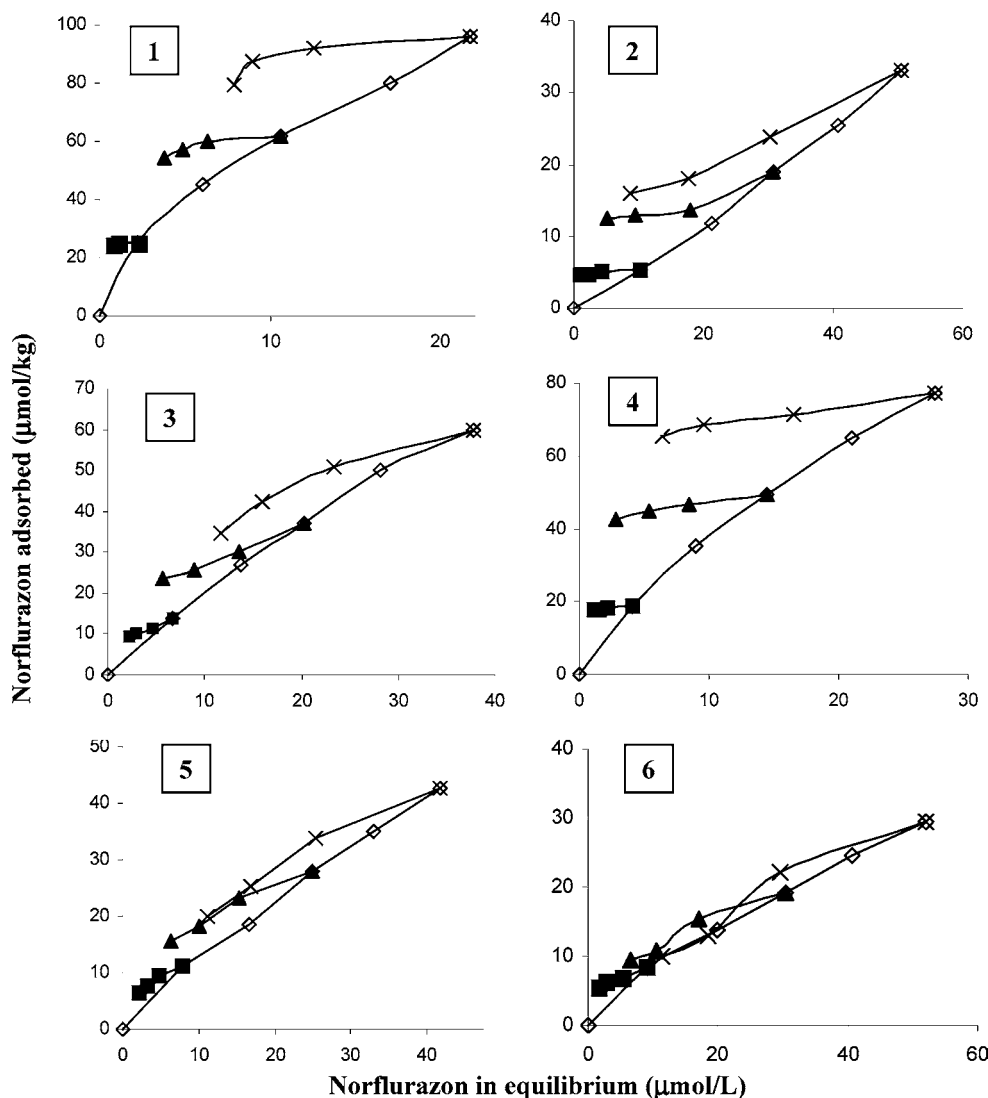

Figure 2. Adsorption−desorption isotherms of norflurazon employing 0.01 M Ca(NO$_3$)$_2$ as desorbent: ($\diamond$) adsorption curves; ($\blacksquare$, $\blacktriangle$, $\times$) desorption curves.

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Table 2. Freundlich Adsorption Isotherm Parameters (K_f and n Values), Coefficients of Determination (R^2) and Distribution (K_d), and Organic Carbon Normalized Distribution Coefficients (K_{oc}) of Norflurazon Sorption on the Soils Used

soil	OM (g kg^{-1})	$K_f \pm SD^a$ (μmol kg^{-1})	$n \pm SD^a$	R^2	$K_d{}^b$	K_{oc}
1	19.0	15.54 ± 0.54	0.61 ± 0.01	0.998	6.33	575
2	5.10	0.35 ± 0.02	1.15 ± 0.02	0.999	0.49	166
3	13.8	2.80 ± 0.26	0.85 ± 0.03	0.999	1.98	247
4	17.6	6.56 ± 0.25	0.75 ± 0.01	0.998	3.69	361
5	53.4	2.00 ± 0.21	0.81 ± 0.03	0.995	1.29	42
6	7.92	1.70 ± 0.15	0.72 ± 0.03	0.995	0.89	193

^{a} Mean values ± standard deviation of three replicates. ^{b} Determined at $C_e =$ 10 μmol L^{-1}.

soil cation (*39*). Moreover, in a previous paper (*33*) the influence of amorphous oxides and OM on NFL adsorption in soils was also found.

K_f values of our isotherms (**Table 2**) indicated that the affinity of the soils for NFL was related to their OM content (**Table 1**). The only exception was soil 5, with the highest OM content but lower adsorption capacity, indicating that OM content may not be the only factor determining NFL adsorption in this soil. Even soil 5 also presented high contents of amorphous and organically bound iron and aluminum oxides (23.3 and 12.3 g kg^{-1}, respectively), besides its high OM content (53.4 g kg^{-1}), but, despite this, NFL adsorption was not very high, and, for this reason, its K_{oc}, was very low (*42*). Some authors have reported that the interassociation processes among different soil components may block sorptive functional groups on mineral and organic surfaces (*40*). Morillo et al. (*33*) demonstrated previously that amorphous iron and aluminum oxides were covering the organic surfaces on this soil, decreasing sorption by blocking the organic surface of the soil. They concluded that, although both soil constituents favor NFL adsorption on soils, the contribution of the organic matter was higher than that of the amorphous oxides, and the masking of the soil organic surface with such oxides may decrease the herbicide adsorption. This special feature observed in soil 5 will influence its behavior in relation to NFL removal from this soil, as will be shown later.

The role of hydrophobic bonds on the adsorption of nonpolar hydrophobic herbicides on OM of soils can be compared by normalizing the distribution coefficient, K_d, to the percentage of organic carbon (OC) of the different samples (K_{oc}). The more hydrophobic a molecule is, the higher the probability for partition from the aqueous phase to the organic phase. K_{oc} can be used as a measure of this property in soils, and it is independent of other soil properties. When hydrophobic bonds with the OM are responsible for the adsorption of a herbicide, K_{oc} values should be relatively constant among different soils. In the present paper, the K_{oc} values obtained were not constant (**Table 2**), varying between 575 and 42 μmol kg^{-1}, indicating the different natures of the organic matter of these soils and/or the influence of the interassociation among the different soil components.

Desorption Experiments Using 0.01 M Ca(NO)$_2$ as Extractant Solution. Figure 2 also shows the desorption isotherms of NFL from the six soils under study employing 0.01 M Ca-(NO$_3$)$_2$ as the extractant solution. In all cases positive hysteresis was observed, indicating that desorption of NFL from these soils was not completely reversible, especially for soil AL, which has a high OM content and iron amorphous oxides. Total percentages of NFL desorbed (%D) for each concentration under

Table 3. Percentage of Norflurazon Desorbed from the Soils Studied

soil	NFL initial concn (mg L^{-1})	extractant solution 0.01 M Ca(NO$_3$)$_2$	0.01 M β-CD
1	4	2.0 ± 0.9	25.5 ± 2.4
	12	11.7 ± 0.3	49.1 ± 0.8
	20	13.7 ± 0.2	61.6 ± 0.4
2	4	31.5 ± 4.4	100.0 ± 3.2
	12	97.6 ± 5.6	100.0±4.3
	20	83.6 ± 5.5	100.0 ± 2.7
3	4	34.1 ± 2.0	83.9 ± 3.8
	12	36.6 ± 2.0	95.0 ± 7.5
	20	58.1 ± 1.6	100.0 ± 1.7
4	4	8.2 ± 1.7	92.8 ± 19.0
	12	13.8 ± 0.3	98.2 ± 2.6
	20	15.3 ± 1.4	97.6 ± 3.3
5	4	41.8 ± 0.5	100.0 ± 3.8
	12	44.4 ± 0.4	100.0 ± 3.3
	20	53.0 ± 1.0	100.0 ± 2.7
6	4	31.9 ± 5.7	89.0 ± 18.5
	12	54.3 ± 3.5	100.0 ± 3.6
	20	72.3 ± 8.0	100.0 ± 2.1

study are shown in **Table 3**. In general, NFL adsorption on soils was more irreversible (lower %D) at low concentrations adsorbed (desorption from an initial concentration of 4 mg L^{-1}); that is, NFL molecules are more strongly sorbed at low surface coverage, and consequently, it is more difficult to desorb them.

The percentages of desorption observed for each soil are in agreement with the values obtained for the sorption capacity parameter; that is, the higher the K_f value, the lower the percentage of NFL removed from the soil. Soil 5 presented a considerable %D, despite its high OM content, indicating that OM is not the only factor that controls NFL desorption from this soil, and the interaction between NFL molecules and soil surfaces is not very strong.

Desorption Experiments Using 0.01 M β-CD as Extractant Solution. Desorption isotherms employing 0.01 M β-CD can be observed in **Figure 3**, and %D values obtained for the six soils under study are shown in **Table 3**. In all cases a negative hysteresis can be observed; that is, more NFL was desorbed with respect to the adsorption isotherm. The same behavior described previously about the relative irreversibility of the NFL adsorbed is also observed, because NFL adsorption was more irreversible at the lowest NFL concentration adsorbed. This behavior can be specially observed in soils 1, 3, and 4, which presented the highest adsorption capacity. One hundred percent desorption was obtained in all cases except in soil 1, for which NFL desorption was not higher than 61.63% (with 20 mg L^{-1} NFL initial concentration). In soils 6 and 2 a dramatic desorption effect was observed, as was expected, because these soils showed a very low herbicide adsorption. Also, soil 5, which showed a slightly higher herbicide adsorption than soils 6 and 2, suffered a dramatic desorptive effect when β-CD solution was applied. The behavior observed in these three soils indicated that the herbicide presents a higher tendency to form complexes in solution with β-CD than to remain adsorbed on the soil component surfaces where it was previously adsorbed.

The results obtained indicate the high extracting power of β-CD toward the herbicide previously adsorbed on the soils, due to the formation of water-soluble inclusion complexes between NFL and β-CD. Similar results have been obtained in previous papers using β-CD as extractant solution for the herbicide 2,4-D from soil (*41*, *42*). In general, low-polarity pesticides have a high tendency to be adsorbed on soil surfaces,
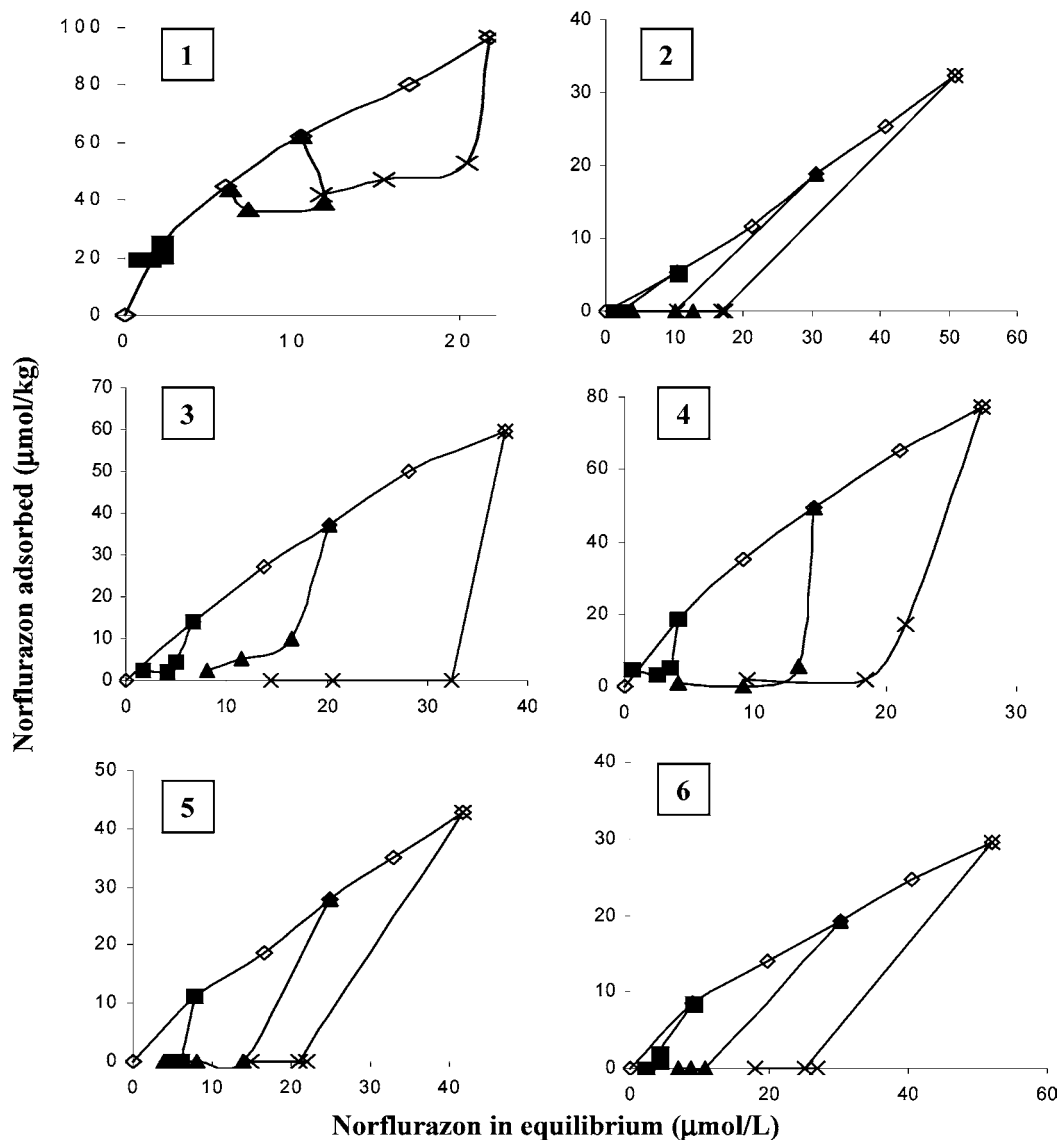
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Figure 3. Adsorption–desorption isotherms of norflurazon employing 0.01 M β-cyclodextrin as desorbent: ($\diamond$) adsorption curves; ($\blacksquare$, $\blacktriangle$, $\times$) desorption curves.

leading to their inactivation and low bioavailability and, sometimes, to soil contamination. If these pesticides are able to form inclusion complexes with CD and, as a consequence, to increase their solubility, the application of CD solutions to soils containing a high concentration of pesticide residues adsorbed can increase their removal and pass to the soil solution where they will have a higher bioavailability.

Desorption Experiments Using Different β-CD Concentrations. To know the minimum β-CD concentration that is able to provoke good herbicide desorption results for each type of soil, different desorption experiments employing various β-CD concentrations were carried out. In **Table 4** are given the different NFL desorption percentages obtained (%D) corresponding to the six soils studied in this work. A clear relationship is observed between the physicochemical characteristics of the soils and the β-CD concentration necessary to desorb the herbicide from each soil. In the cases of soils 2 and 6, which showed the lowest capacity for herbicide adsorption (K_f values of 0.35 and 1.70, respectively), 100% of the herbicide initially adsorbed was desorbed after three consecutive desorption steps, even using 1:1 molar ratios of β-CD in relation to NFL adsorbed.

Soils 5 and 3, which presented a little higher K_f values (2.0 and 2.8, respectively), also showed a dramatic herbicide desorption (100%) using very low β-CD concentrations, except when the corresponding stoichiometric cyclodextrin concentration was used (95.59 and 71.72% desorbed, respectively).

However, in the case of soil 4, which showed a very high capacity for NFL adsorption (K_f value of 6.56), the total desorption of NFL was almost reached only when the maximum β-CD concentration was used, decreasing the percentage desorbed as the concentration of β-CD decreased. The same behavior is observed for soil 1, which showed the highest adsorption capacity for the herbicide ($K_f = 15.54$), reaching only a maximum desorption of 61.63% upon addition of the maximum β-CD concentration used (10 mM).

In general, a strong tendency to form an inclusion complex between β-CD and NFL is proved, because high desorption yields can be obtained with very low β-CD concentrations, $\sim 10^{-2}$ mM. These results indicate that β-CD can act as an effective extractant of herbicides from soils with different physicochemical properties, in most of the cases employing only an stoichiometric β-CD concentration. This is very important from environmental and economical points of view, because

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Table 4. Percentage of Norflurazon Desorbed (%D) from the Soils Studied, Employing Different β-Cyclodextrin Concentrations

soil	β-CD concn (mM)	%D	soil	β-CD concn (mM)	%D
1	5.43×10^{-2} [a]	25.4	4	4.12×10^{-2} [a]	32.9
	0.1	28.8		0.1	38.6
	0.5	32.4		0.5	44.5
	2.0	35.9		2.0	51.5
	5.0	45.8		5.0	77.1
	7.0	49.9		7.0	92.9
	10.0	61.6		10.0	97.6
2	1.48×10^{-2} [a]	100	5	1.92×10^{-2} [a]	95.6
	0.1	100		0.1	100
	0.5	100		0.5	100
	2.0	100		2.0	100
	5.0	100		5.0	100
	7.0	100		7.0	100
	10.0	100		10.0	100
3	2.68×10^{-2} [a]	71.7	6	1.32×10^{-2} [a]	100
	0.1	100		0.1	100
	0.5	100		0.5	100
	2.0	100		2.0	100
	5.0	100		5.0	100
	7.0	100		7.0	100
	10.0	100		10.0	100

[a] β-CD concentration (mM) = norflurazon adsorbed (mM).

by using a very low β-CD concentration, a high NFL concentration could be extracted for a subsequent effective biodegradation in soil. For such a low β-CD concentration a very little volume of water is needed, and NFL leaching toward groundwater will be minimized. On the other hand, on the basis of published data, it would appear that CDs are becoming comparable in cost with surfactant (*44*), although a detailed comparison on the costs of surfactants and CDs for polluted-site remediation is not found in the literature. However, because the cost of CDs has continuously decreased in recent years (*13*), investigations regarding their technical merits for subsurface remediation are justified.

In conclusion, β-CD can be considered as a very effective and economic in situ soil remediation tool. Because there is a great interest in developing systems that can enhance the transport of organic compounds through porous media, thus facilitating remediation, the high affinity of CDs for a great variety of pesticides makes them possible candidates for use as soil decontaminants, as has been already demonstrated in the case of remediation of soils contaminated with PAHs (*27, 29, 30, 43*) and containing other herbicides (*8, 27*).

ACKNOWLEDGMENT

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