

Comparative Study on the Sorption Capacity of Cyhalofop Acid on Polymerin, Ferrihydrite, and on a Ferrihydrite–Polymerin Complex

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A comparative study was performed on the sorption capacity of the phenoxy acid herbicide cyhalofop on polymerin (from olive oil mill effluents), ferrihydrite, and a ferrihydrite–polymerin complex, by using a batch equilibrium method. The most efficient sorbent showed to be ferrihydrite followed by the ferrihydrite–polymerin complex and polymerin. Cyhalofop acid bound to ferrihydrite by a combination of ionic and ion–dipole bonding, whereas the same herbicide bound to the ferrihydrite–polymerin complex by ionic bonding and to polymerin by hydrogen bonding. Simulated wastewaters contaminated with cyhalofop acid were completely purified by two sorption cycles on ferrihydrite and five cycles on the ferrihydrite–polymerin complex, whereas the same wastewaters maintained a constant residue even after five sorption cycles on polymerin. For the first time, the possible use of a mineral (ferrihydrite) and an organo-mineral complex (ferrihydrite–polymerin) as a filter for the control of the herbicide contamination in point sources is proposed and briefly discussed.

KEYWORDS: Sorption; cyhalofop acid; polymerin; ferrihydrite; ferrihydrite–polymerin complex; pollution point sources

INTRODUCTION

Agriculture has become extremely intensive and productive by using a large variety of pesticides. But this benefit is associated with the risk of environmental pollution, and the soil and surface waters are mostly exposed.

The quality of soil and water bodies deserves particular attention because of its importance in the survival of the ecosystem as well as in the water supply for human consumption; therefore, their protection and the development of new remediation technologies are a necessity of primary importance. Surface and ground waters have been shown to be contaminated with a range of pesticides (*1*). Research over recent years has focused on the nonpoint sources of pesticide contamination resulting from application to agricultural land. However, point sources such as nonapproved use, poor practice, illegal operations, accidental release from farmyards, and inputs of washings are increasingly recognized as contributing to water contamination (*2–5*). In particular, a large number of workers have indicated that point sources can contribute between 18 and 84% of the pesticide load measured in individual catchments (*6, 7*). Better training of sprayer operators and good machinery maintenance can reduce the number of spills, and releases to the farmyard due to spray

tank washings should be minimized (*8*). The application of treatment systems at the farm level could allow an improved management of the aquatic ecosystem and a reduction of water treatment costs. Several studies propose the use of natural organic materials or wastes as biosorbent (*9, 10*) due to the high sorption capacity of organic matter (*11, 12*).

The use of vegetal biomass with high sorption capacity for remediation of waters contaminated by pesticides or metals has been widely described in the literature over the last 10 years (*13*).

Olive oil mill wastewater (OMW) is a vegetable biomass waste produced in large amounts especially in Mediterranean countries, which are the main producers of olive oil worldwide. Its disposal represents a significant problem for these countries because OMW has high polluting properties, which are documented by high chemical oxygen demand (COD) and biological oxygen demand (BOD) (*14*). Nevertheless, OMW may also be regarded as an inexpensive source of vegetable biomass to be recovered for use in environmental biotechnology processes (*15*) with the potential advantage to eliminate the environmental impact deriving from its discharge.

In this light, the utilization of the polymeric organic fraction of OMW named polymerin could represent a convenient method for bioremediation of contaminated waters by pesticides because this material possesses humic acid-like characteristics and derives from a cost-free agricultural waste (*16*). Previously, we reported

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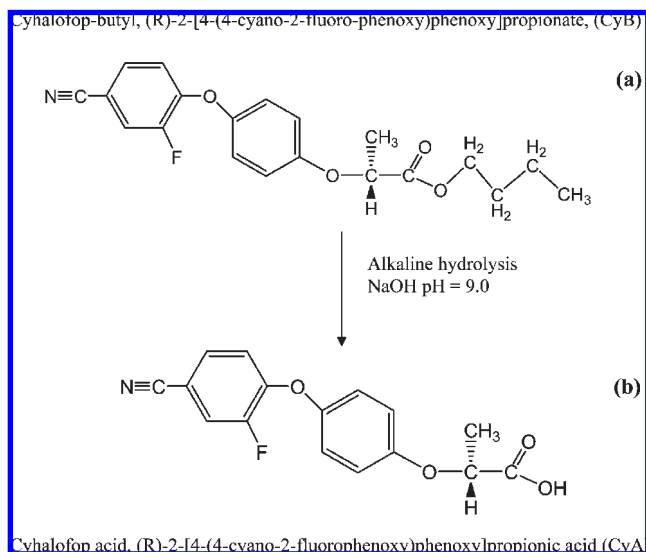


Figure 1. Structural formulas of Cyhalofop-butyl, (*R*)-2-[4-(4-cyano-2-fluoro-phenoxy)phenoxy]propionate (CyB) (a), and Cyhalofop acid, (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionic acid (CyA) (b).

polymerin to exhibit very interesting sorption capacities for cationic and anionic heavy metals (15, 17), ionic or ionizable pesticides (18), and hydrophobic organic compounds (19). However, the employment of polymerin as a possible biofilter for the removal of 2,4-D, chosen as the model compound of phenoxy acid herbicide, from wastewaters in pollution point sources (18), revealed some technological and economic limitations. In particular, (i) the high solubility of polymerin in water required a complex and expensive ultrafiltration system to separate the biosorbent after sorption with 2,4-D from the wastewaters, and (ii) a residual herbicide was still detected in the polluted waters even after many cycles of sorption on the renewed biosorbent. These data suggested that the improvement of the removal of a phenoxy acid herbicide from wastewaters could be performed by sorption of the pesticide on a system composed by polymerin immobilized on a mineral cationic sorbent or on the same raw mineral sorbent (18).

To this end, a ferrihydrite was selected as a cationic mineral in the present study, and cyhalofop [(*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionic acid] (CyA) (Figure 1b) was selected as a further phenoxy acid herbicide because of its very intensive use. Indeed, the commercial form of CyA is its butyl ester, cyhalofop-butyl [butyl (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionate] (CyB) (Figure 1a), recently introduced by Dow AgroSciences. CyB is an aryloxyphenoxypropionate herbicide for the postemergence control of grasses in rice, mainly against barnyard grass (*Echinochloa* spp.) and silver top (*Lepthochloa fusca*) in rice (20, 21). The ester of the acid acts as a pro-herbicide. The formulation as ester facilitates uptake through the plant cuticle, and once it has entered into the plant, it is transformed within a few hours into CyA, which is the effective active form (22, 23). Moreover, CyA is the effective form occurring in water after its application on the crop because it originates by the rapid hydrolysis of its corresponding butyl ester form.

Therefore, the main objective of this article was to find, by a comparative study on the sorption of CyA on polymerin, ferrihydrite, and a ferrihydrite–polymerin complex, the most efficient and convenient sorbent among the three selected matrices, to be used as a potential filter for the decontamination of wastewaters in point sources.

Comparative studies were carried out on (i) the sorption capacity of CyA on polymerin, ferrihydrite, and the

ferrihydrite–polymerin complex and (ii) the removal of CyA from simulated wastewaters by cyclic sorption of the herbicide on the selected sorbents renewed at each cycle.

With the aim to elucidate the different sorbing capacities of CyA on the selected matrices, the interaction mechanism was also studied, mainly by DRIFT analysis.

MATERIALS AND METHODS

Materials. Cyhalofop-butyl, (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionate (CyB), (Figure 1a) was supplied by Dow Agrosciences B. V. Rotterdam (The Netherlands) (99.0% purity). Its corresponding acid, (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionic acid (CyA) (Figure 1b), was prepared by alkaline hydrolysis of CyB. In particular, an aqueous solution of NaOH (0.5 N) was added to 100 mL of CyB suspension (1 g) in CH₃CN/H₂O 50/50 v/v, up to pH 9.0 under stirring at room temperature. The pH of the mixture was checked throughout and brought to a value of 9.0 by NaOH addition until the suspension turned into solution. CH₃CN was evaporated, and diluted HCl was added to the solution. A white precipitate was obtained, which was filtered and repeatedly washed with H₂O to give the pure compound CyA (24).

All solvents were of HPLC grade (Carlo Erba, Milan, Italy) and were used without further purification. All other chemicals were obtained from Sigma-Aldrich unless otherwise specified.

Preparation and Characterization of Polymerin, Ferrihydrite, and Ferrihydrite–Polymerin. Polymerin was prepared and characterized according to the procedure previously reported (15, 16). Ferrihydrite was prepared according to the following procedure. A stock solution (1 L) of 0.1 M FeCl₃ was potentiometrically titrated (TIM 856 Titration Manager automatic titrator, Analytical De Mori, Milano, Italy) to pH 6.0 by adding 1 M NaOH at a feed rate of 0.5 mL min⁻¹. The precipitate was kept in a propylene container and aged at 20 °C for 24 h. After aging, the sample was centrifuged, washed, and dialyzed in deionized water and freeze-dried, obtaining an iron oxy-hydroxide mineral [(Fe(OH)_x] known as a ferrihydrite (25). The ferrihydrite–polymerin complex was obtained by adding 1.0 g of polymerin to a 0.1 M FeCl₃ solution (500 mL) and by titrating the solution with 1 M NaOH to reach pH 6.0 using an automatic titrator (TIM 856 Titration Manager). The precipitate obtained was washed, dialyzed against deionized water to reach a conductivity of 1.0 μS, and then lyophilized.

Physical and Chemical Analysis. Specific surface area (SSA) was determined from the nitrogen adsorption isotherm using the BET method with a Gemini 2370 instrument (Micromeritics, U.S.A.). Carbon elemental analysis was performed using a Fisons EA 1108 elemental analyzer (Fisons Instruments S.p.a., Milano, Italy) for hydrogen, carbon, nitrogen, and sulfur (HCNS). The metals were determined by a Perkin-Elmer Instruments (AAnalyst 700 U.S.A.) atomic absorption spectrometer equipped with deuterium arc background correction (15). Air–acetylene flame was used as the atomization source. Stock standard solutions of each metal cation (1.0 g L⁻¹) were obtained from BDH Reagents (Poole, U.K.). The average and standard deviation of three absorption measurements were recorded for each sample.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) Analysis. Sample preparation for DRIFTS determinations was performed as follows: a quantity of herbicide corresponding to the maximum sorption value obtained on the isotherm of CyA was added to each matrix at the optimal sorption pH (pH 4.5 for polymerin and pH 3.5 for ferrihydrite and ferrihydrite–polymerin). After incubation, the samples were centrifuged, and the precipitates were washed twice with 0.03 M KCl to remove the excess herbicide; then the samples so obtained were lyophilized. Finally, 0.20 mg of each sample was mixed with 200 mg of KBr (FTIR grade, Aldrich, Chemical, Co., Milwaukee, WI, USA). The mixture was finely ground in an agate mortar and transferred to a sample holder. Its surface was smoothed with a microscope glass slide, and DRIFT spectra were recorded. The DRIFT spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer (U.S.A.). The instrument had a special resolution of 1 cm⁻¹, which was used in all spectral determinations.

Estimation of the Point of Zero Charge (PZC). The point of zero charge (PZC) of raw polymerin was determined according to the method reported by using the potentiometric titration curve as a function of pH at different ionic strengths (26).

As regards ferrihydrite and the ferrihydrite–polymerin complex, the determination of PZC was performed according to the method described by Mustafa et al. (27). Dry samples (100 mg) were dissolved in 40 mL of 0.001 M KCl solution as a background electrolyte and equilibrated for 30 min by means of a magnetic stirrer. Successively, the initial pH of the solution was adjusted to pH 4.0 by the addition of either 0.1 M HCl or 0.1 M KOH. The suspension was equilibrated for another 10 min, and the pH was then measured. The suspension pH was recorded every 2 min as a function of volume of titrant added until pH 10 was reached. The PZC of two sorbents was determined from the variation of surface charge density as a function of pH.

Sorption Methodology. Stock solution of pesticide was prepared by dissolving 125 mg of CyA in 500 mL of KCl 0.03 M and alkalizing the solution at pH 10.0 with KOH (final concentration 0.830 mmol L⁻¹). This solution was then kept refrigerated. The sorption experiments were conducted at a solid/liquid ratio of 0.5 obtained by adding 10 mg of sorbent dried at 100 °C for 1 h, to a final volume of 20 mL at 25 °C. The pH was controlled by the addition of 0.01 mmol L⁻¹ HCl or KOH to the suspension. After incubation, the samples containing polymerin were centrifuged at 4500 rpm for 30 min using Centrifugal Filter Devices equipped with Amicon Ultra membrane with a cutoff of 3000 Da, while those containing ferrihydrite or ferrihydrite–polymerin were only centrifuged at 7000 rpm for 30 min.

The amount of herbicide sorbed on each matrix was calculated as the difference between the initial quantity of pesticide added and that present in the equilibrium solution.

Analytical Determination of CyA. CyA was analyzed with an Agilent 1200 Series HPLC apparatus (Wilmington U.S.A.), equipped with a DAD array and a ChemStation Agilent Software. A Macherey-Nägel Nucleosil 100-5 C18 column (stainless steel 250 × 4 mm) was utilized. An isocratic elution was performed at a flow rate of 1 mL min⁻¹ with acetonitrile (50%) and phosphate buffer (50%) (0.04 M, pH 2.95). The detector was set at 250 nm. A sample volume of 20 μL was used for injection. The quantitative determination of CyA was performed elaborating the corresponding calibration curve, 0.016–0.75 mmol L⁻¹.

Effect of pH. Experiments were carried out by adding a fixed pesticide concentration, 0.17 mmol L⁻¹, and varying the pH (from 3.0 to 11.0). The suspensions were shaken for 24 h. The herbicide solution was separated from the sorbent and analyzed as described above.

Effect of Time. Experiments were performed using 0.17 mmol L⁻¹ of CyA at pH 4.5 for polymerin and pH 3.5 for ferrihydrite and ferrihydrite–polymerin, respectively. The suspensions were stirred for 0.25, 0.5, 1, 2, 4, 6, 8, 24, 30, 48, and 72 h.

Sorption Isotherms. Different volumes of a stock solution of herbicide (0.83 mmol L⁻¹) were added to each sorbent to give an initial concentration ranging from 0.030 to 0.60 mmol L⁻¹ of CyA. The pH of each suspension was kept constant at pH 4.5 for polymerin and pH 3.5 for ferrihydrite and ferrihydrite–polymerin, respectively, by the addition of 0.10 or 0.01 mol L⁻¹ HCl or KOH. The samples containing ferrihydrite were shaken for 4 h and those with polymerin or ferrihydrite–polymerin for 24 h; then after centrifugation, the supernatants were analyzed as described above.

Cyclic Sorption on Polymerin, Ferrihydrite, and Ferrihydrite–Polymerin. Cyclic experiments for the sorption of CyA were carried out at pH 4.5 for polymerin and pH 3.5 for ferrihydrite and ferrihydrite–polymerin. In the first cycle, a predetermined quantity of herbicide stock solution was pipetted into the flasks to give 0.575 mmol L⁻¹.

The samples were treated according to the procedure previously described. After the contact time, the sorbent was separated from the suspension, and the filtrate was analyzed to determine the amount of sorbed pesticide. For the second cycle, 20 mL of filtrate was added to the fresh sorbent (10 mg). The experiments were repeated until the equilibrium concentrations remained constant.

Data Analysis. All of the experiments were performed in triplicate, and the relative standard deviation was lower than 4%. The kinetic data were analyzed using the Lagergren equation (28): $\log(qe - q) = \log qe - K_a t/2.303$, where qe and q are the amount of herbicide sorbed (mmol kg⁻¹) at equilibrium and at time t , respectively, K_a is the rate constant of sorption (min⁻¹), and t is the time (min).

The sorption data were analyzed according to the Langmuir equation, which can be written as follows: $x = x_m kc/(1 + kc)$, where x is the amount

of pesticide sorbed (mmol kg⁻¹), k (L mmol⁻¹) is a constant related to the binding energy, x_m is the maximum amount of pesticide sorbed (mmol kg⁻¹), and c is the equilibrium concentration of pesticide (mmol L⁻¹), according to Giles et al. (29). The sorption data were also analyzed according to the Freundlich equation: $x = Kc^{1/N}$, where x and c are defined in the equation reported above, K [(mmol kg⁻¹)/(mmol L⁻¹)^{1/N}] and N (dimensionless) are constants that give estimates of the sorptive capacity and intensity, respectively.

The distribution coefficient, K_d [defined as the ratio of the concentration of pesticide sorbed per unit weight of sorbent to its equilibrium concentration (L kg⁻¹)] at saturation was also determined.

RESULTS AND DISCUSSION

Characterization of Polymerin, Ferrihydrite, and Ferrihydrite–Polymerin. Polymerin was recovered from OMW and characterized chemically and spectroscopically according to the procedure described by Capasso et al. (16). This polymeric mixture was confirmed to be a humic-like polyelectrolyte consisting of carbohydrates, melanin, and proteins. It also contains metals such as Ca, Mg, K, Na, and Fe that are naturally bound or chelated through carboxylate anions and other characteristic nucleophilic functional groups present in polymerin.

Polymerin was coprecipitated with Fe to obtain an insoluble organo-mineral complex called ferrihydrite–polymerin, in order to study the influence of ferrihydrite, an iron oxy-hydroxide, on the sorption capacity of organic component. The organo-mineral complex showed a surface area (380.7 m² g⁻¹) lower than that of ferrihydrite (484.2 m² g⁻¹) because of the presence of polymerin (312 m² g⁻¹), which partially covers the ferrihydrite surface. The chemical and physicochemical properties of the selected sorbents are reported in **Table 1**.

Sorption Studies. The results obtained by studies of sorption of CyA on the selected sorbents as a function of pH showed the greatest sorption capacity of CyA on polymerin at pH 4.5 and on both ferrihydrite–polymerin and ferrihydrite at pH 3.5, whereas a significant decrease of the herbicide on all of the matrices was shown up to pH 6.0 (**Figure 2**).

Polymerin could be considered as a weak acid polyelectrolyte because of its carboxylic and phenol groups, and characterized by a pK_a of 4.5 (16) and a PZC of 2.2 (18). Sorption process could be very probably attributed to the prevalent formation of hydrogen bonding between the OH alcoholic groups of the polysaccharide

Table 1. Chemical Properties of Polymerin, Ferrihydrite, and the Ferrihydrite–Polymerin Complex

Polymerin	
chemical composition (% w/w)	
polysaccharide	43.07
protein	22.40
melanin	29.76
metals	4.77
carbon	41.49
range of molecular weight (Da)	first peak: 3500 < rmw < 10000 second peak: 45000
point of zero charge (PZC)	2.2
surface area (m ² /g)	312
Ferrihydrite	
point of zero charge (PZC)	9.4
surface area (m ² /g)	484.2
Ferrihydrite–Polymerin Complex	
point of zero charge (PZC)	7.7
surface area (m ² /g)	380.7

component and the nitrile group, the ethereal groups, and the undissociated carboxylic group of CyA ($pK_a = 3.8$) (30). Therefore, at pH 4.5 the effect of hydrogen bonding is higher than the repulsion between the ionized carboxylic groups of polymerin and the herbicide. On the contrary, a significant reduction of sorbed CyA was detected at pH > 4.5 because the herbicide and polymerin carboxylic groups were mainly in dissociated form, with a consequent dominant effect of the repulsion. This behavior was confirmed in previous studies conducted on the sorption of the phenoxy acid 2,4-D on polymerin as a function of pH (18).

The results reported in Figure 2 showed a greatest sorption at pH 3.5 on ferrihydrite and the ferrihydrite–polymerin complex. At this pH, both the sorbents had the completely positive surface by OH_2^+ groups because of the PZC value, 9.4 for ferrihydrite and 7.7 for ferrihydrite–polymerin (Table 1), whereas the proportions of un-ionized and ionized herbicide carboxylic groups were roughly estimated as 50/50%. This means that the ionized carboxylic groups ($-\text{COO}^-$) of CyA formed ionic bonds with the positive surface of both sorbents. The hydrogen bond to the protonated hydroxylic group presents a very high mobility due to the positive charge on the O atom. In these conditions and

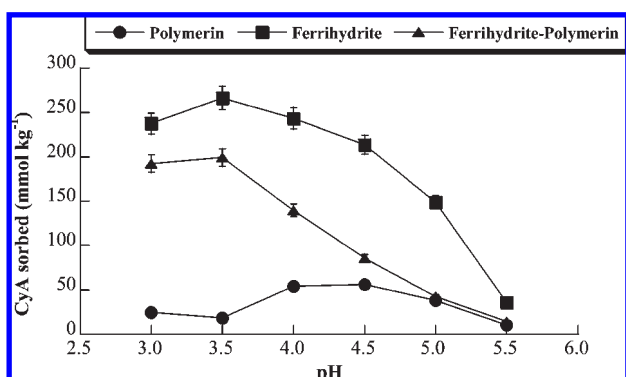


Figure 2. Effect of pH on the sorption of CyA by polymerin, ferrihydrite, and ferrihydrite–polymerin.

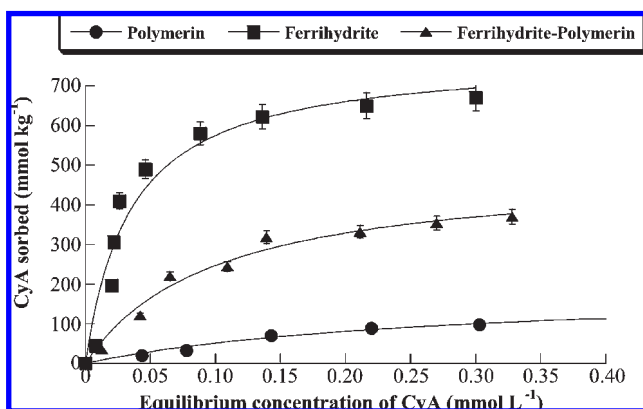


Figure 3. Sorption isotherm of CyA by polymerin at pH 4.5 and ferrihydrite and ferrihydrite–polymerin at pH 3.5.

considering the aqueous medium where the adsorption occurs, it can be supposed that the formation of hydrogen bonds contributes to the stabilization of the interaction between the anionic form of CyA and the positively charged surface of the matrices, very likely attenuating the ionic character of the bond. A moderate decrease of sorbed herbicide was evaluated on the ferrihydrite–polymerin complex due very probably to both the lower PZC and surface area with respect to ferrihydrite, which was attributable very likely to the presence on the mineral component of a small amount of the sorbed polymerin (content of carbon = 7.85%) (Table 1). An additional ion–dipole bond was hypothesized in the system CyA–ferrihydrite between the undissociated carboxylic group of the acid and the positive surface of ferrihydrite. All of the previous hypotheses were confirmed by the DRIFTS analyses reported later.

Previous studies confirmed that the iron oxides exhibited a strong sorption of ionic and ionizable pesticides at low pH and a decreasing sorption as pH increased (31).

Kinetic studies on the sorption of CyA on polymerin were carried out at pH 4.5 while on ferrihydrite–polymerin and ferrihydrite at pH 3.5. The results obtained by the Lagergren equation showed that the sorption of CyA on each sorbent fitted a first-order mechanism ($r^2 > 0.90$). However, this process was very fast on ferrihydrite, reaching the sorption equilibrium within 1–2 h, but was much slower on ferrihydrite–polymerin and polymerin, it being observed within 24 h. In correspondence, the rate constants determined from the slopes of the plots of $\log(qe-q)$ versus t were 0.43 for ferrihydrite and 0.23 and 0.11 min^{-1} for ferrihydrite–polymerin and polymerin, respectively. Therefore, an incubation period of 4 h for ferrihydrite and 24 h for polymerin and ferrihydrite–polymerin was utilized.

The sorption isotherms of CyA (Figure 3) on polymerin, ferrihydrite, and ferrihydrite–polymerin fitted the Langmuir equation (Table 2). The shape of the isotherms was different and was mainly distinguished by the initial slope. In fact, the sorbed amount of herbicide on polymerin increased slowly when the CyA equilibrium concentration increased, whereas an opposite behavior was detected with the other two sorbents, which showed a higher affinity. Actually, at a 0.20 mmol L^{-1} equilibrium concentration of CyA, the amount of sorbed herbicide significantly increased from 75 on polymerin to 300 and 600 mmol kg^{-1} on ferrihydrite–polymerin and ferrihydrite, respectively. Therefore, the amount of CyA sorbed on all of the selected sorbents followed the order ferrihydrite > ferrihydrite–polymerin > polymerin. This trend was confirmed analyzing both the Langmuir (x_m and k) and Freundlich constants (K and N), and also the K_d values (Table 2), showing that ferrihydrite sorbed CyA with both the greatest binding energy and sorptive intensity. The sorption capacity of CyA on polymerin was similar to that of the phenoxy acid herbicide 2,4-D (18). In particular, the maximum individual sorbed amount (x_m) of 2,4-D and CyA on the previous bio-organic sorbent was 183.15 and 195 mmol kg^{-1} , respectively. On the contrary, their corresponding constant related to the binding energy (k) showed opposite values (8.47 and 3.45 for 2,4-D and CyA, respectively) suggesting a weaker

Table 2. Langmuir and Freundlich Parameters for the Sorption of CyA on Polymerin, Ferrihydrite, and a Ferrihydrite–Polymerin Complex

	Langmuir parameters			Freundlich parameters			
	x_m (mmol kg^{-1})	k (L mmol^{-1})	r^2 ^a	K (mmol kg^{-1}) / (mmol L^{-1}) ^{1/N}	N	r^2 ^a	K_d ^b (L kg^{-1})
polymerin	194.97	3.45	0.99	229.40	1.33	0.98	194.77
ferrihydrite	796.98	27.12	0.98	951.48	4.52	0.98	3080.90
ferrihydrite–polymerin complex	492.01	10.05	0.99	551.188	2.89	0.99	1128.70

^a Determination coefficient. ^b Distribution coefficient.

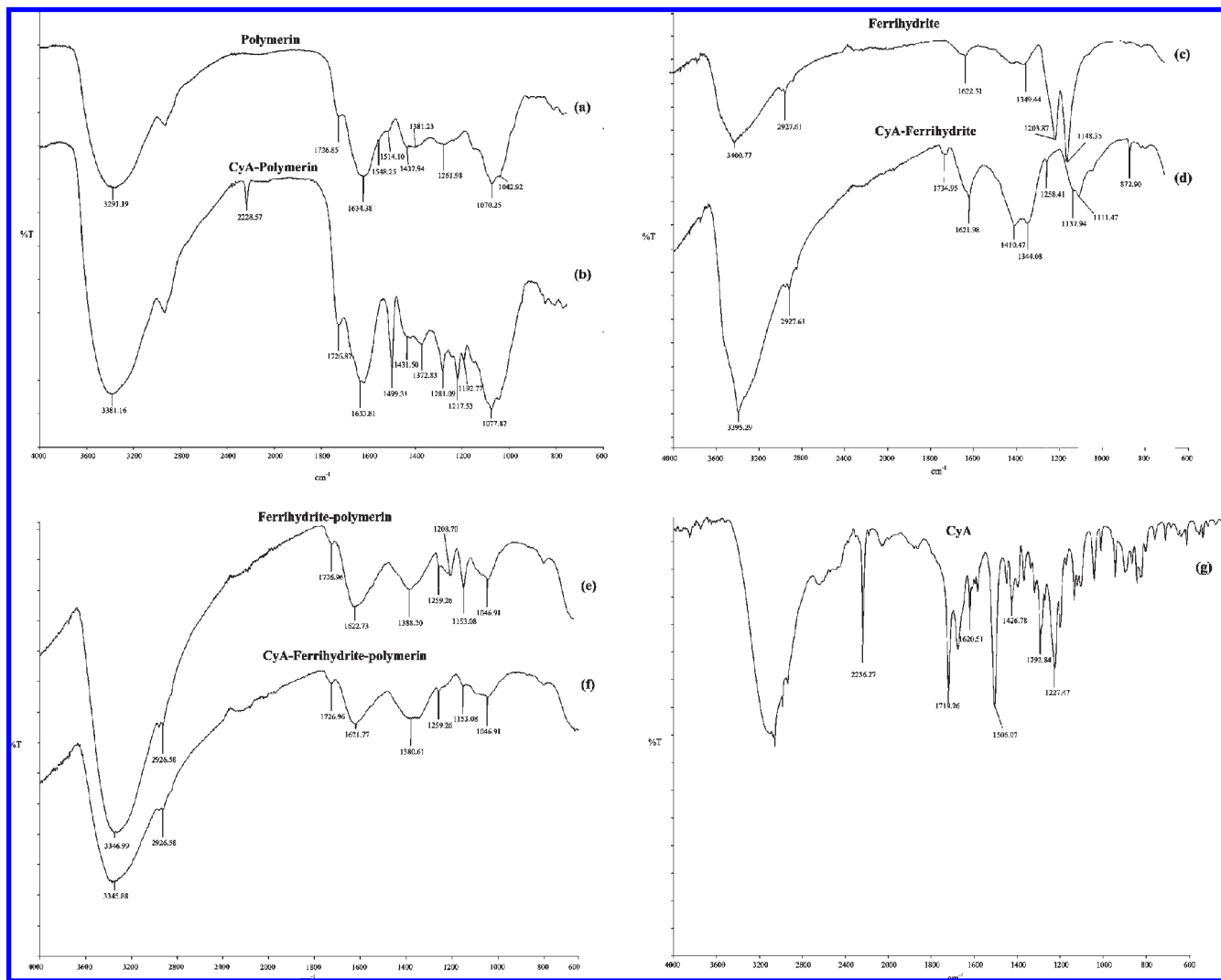


Figure 4. DRIFT spectra of polymerin (a), CyA–polymerin (b), ferrihydrite (c), CyA–ferrihydrite (d), ferrihydrite–polymerin (e), CyA–ferrihydrite–polymerin (f), and CyA (g).

bonding affinity between the functional groups of CyA and the polymerin surface, compared to that of 2,4-D. The weaker interaction of CyA than 2,4-D could be very probably due to a higher steric hindrance of the larger molecule of CyA, which was, however, balanced by the hydrogen bond between its several functional groups and polymerin.

Sorption Mechanism. The sorption mechanism of CyA on the selected sorbents was also investigated, by DRIFTS analysis, with the aim to elucidate their different sorption capacities. To this end, the preliminary DRIFTS characterization of the selected three matrices was performed.

In particular, the DRIFT spectrum of polymerin (**Figure 4a**), registered at pH 4.5, confirmed the characteristic bands previously observed in the literature (15, 16). In fact, it showed a very strong and broad band at 3291.19 cm^{-1} (OH groups), four weak, albeit correlated, bands at 1726.85 and 1261.98 cm^{-1} , and 1437.94 and 1381.23 cm^{-1} (stretching of methylester groups, and symmetric and asymmetric bending of the corresponding CH_3 groups, respectively), and absorption at 1634.38 cm^{-1} (aromatic ring and CO peptide groups stretching). The absorptions at 1548.25 and 1514.10 cm^{-1} were also assignable to aromatic ring stretching. Moreover, the absorption at 1634.38 cm^{-1} included the symmetric stretching of COO^- groups, to which the asymmetric stretching of the same group included in the band at 1437.94 cm^{-1} was correlated. A very strong absorption at

1070.25 and 1042.92 cm^{-1} (stretching of the C–OH bond of the polysaccharide component of polymerin) was finally observed.

The DRIFT spectrum of ferrihydrite (**Figure 4c**), registered at pH 3.5, showed a characteristic and very intense band at 3400 cm^{-1} (stretching of the OH groups present in high amount in the mineral) and two other strong and intense and correlated bands at 1203.87 and 1148.35 cm^{-1} (bending of the OH groups).

The DRIFT spectrum of the ferrihydrite–polymerin complex (**Figure 4e**), registered also at pH 3.5, showed a strong and broad band at 3346.99 cm^{-1} (OH stretching), deriving from the overlap and the shift of the broad bands observed at 3400 and 3291.19 cm^{-1} in the spectrum of ferrihydrite and polymerin, respectively, and very likely attributable to the ion–dipole bonding between the ionic OH_2^+ groups of the former matrix and the dipole OH groups of the latter matrix.

In fact, the PZC of ferrihydrite is 9.4, whereas that of polymerin is 2.2; therefore, the OH groups of the former matrix are totally positively charged, and the alcoholic OH groups of the latter are not charged at all but are in dipole form. In other terms, the formation of a H-bond is to be excluded in this conditions.

In addition, the spectrum of **Figure 4e** evidenced two weak and correlated bands at 1726.96 and 1259.26 cm^{-1} (stretching of methyl ester groups of polymerin), and two intense and broad bands at 1622.73 and 1388.20 cm^{-1} corresponding to the respective symmetric and asymmetric stretching of the polymerin

COO⁻ groups bound by ionic linkage to OH₂⁺ groups of ferrihydrite, which originate from the shift of the respective bands at 1634.38 and 1381.23 cm⁻¹ observed in the polymerin spectrum (Figure 4a). Finally, the DRIFT spectrum of the ferrihydrite–polymerin complex showed that a medium band appeared centered at 1046.91 cm⁻¹, which derived from an intense and split band at 1070.25 and 1042.92 cm⁻¹ (C–OH stretching of polymerin polysaccharide component), respectively, originally present in the polymerin spectrum and attributable to the ion–dipole bond as previously described. In summary, all of the previous data clearly indicated that polymerin was fixed on ferrihydrite by a combination of the dipole–ion bonding between the OH groups of the former organic matrix and the OH₂⁺ groups of the latter mineral matrix, and ionic bonding between the COO⁻ groups of the organic sorbent and OH₂⁺ groups of the mineral sorbent.

The sorption mechanism of CyA on the selected matrices was then assessed by the DRIFTS analysis of CyA–polymerin, CyA–ferrihydrite, and CyA–ferrihydrite–polymerin systems.

In particular, the DRIFT spectrum of the CyA–polymerin system, registered at pH 4.5 (Figure 4b), compared to that of polymerin (Figure 4a), showed the appearance of a new band at 1499.31 cm⁻¹ due to the stretching of CyA benzene rings, which was slightly shifted with respect to the band at 1506.07 cm⁻¹ observed in the spectrum of the herbicide (Figure 4g). Two new bands at 1281.09 and 1217.53 cm⁻¹, in addition (Figure 4b), evidenced a shift and reduction with respect to those observed at 1292.84 and 1227.47 cm⁻¹ in the spectrum of CyA (Figure 4g). The considered absorptions were assignable very probably to the stretching modifications deriving from hydrogen bonding between each ethereal oxygen of the herbicide (Figure 1b) and the OH alcoholic groups of polymerin. Still, the DRIFTS spectrum of CyA–polymerin (Figure 4b) showed a band at 2228.57 cm⁻¹ reduced and shifted as compared to the characteristic sharp and intense band that appeared at 2236.27 cm⁻¹ in the CyA spectrum (Figure 4g), attributable to the stretching of CyA nitrile group as well as the weak band, which appeared at 1077.87 cm⁻¹ (Figure 4b), originating from the modification and reduction of the signal at 1070.25 and 1042.92 cm⁻¹ present in the spectrum of polymerin (Figure 4a) and due to the stretching of the OH groups of the polysaccharide component of polymerin. All of the last modifications concerning the spectrum of Figure 4b were attributable to the formation of hydrogen bonds between the OH groups of the polymerin polysaccharide component and the nitrile group, and the ethereal groups and the undissociated carboxylic group of CyA.

The DRIFT spectrum of CyA–ferrihydrite (Figure 4d) showed a new band at 1734.95 cm⁻¹ by comparison with the spectrum of ferrihydrite (Figure 4c). It was the shifted band with respect to that observed at 1719.60 cm⁻¹ in the CyA spectrum (Figure 4g), due very likely to the stretching variation of the CyA undissociated carboxylic group, as a consequence of dipole–ion bonding between this latter group and the OH₂⁺ groups of ferrihydrite. In addition, the bands observed at about 1621.98 cm⁻¹ and 1410.47 cm⁻¹ very likely originated from the modification of those appearing in the spectrum of CyA at 1620.51 cm⁻¹ and 1426.78 cm⁻¹ (Figure 4g), respectively. These latter were very probably attributable to the asymmetric and symmetric stretching of CyA COO⁻ groups, which interacted by ionic bonding with the positive OH₂⁺ groups of ferrihydrite. In addition, the band at 1621.98 cm⁻¹ in the spectrum of Figure 4d included the band at 1618.25 cm⁻¹ observed in the spectrum of ferrihydrite (Figure 4c). Furthermore, the strong bands at 1203.87 and 1148.35 cm⁻¹ observed in the ferrihydrite spectrum, due to the OH bending, appeared strongly modified in the spectrum of CyA–ferrihydrite

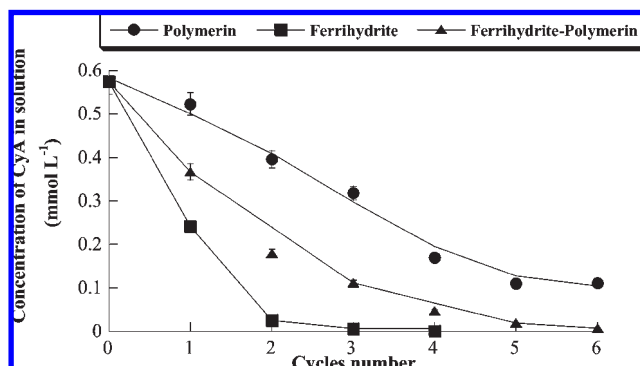


Figure 5. Cyclic removal of CyA by polymerin, ferrihydrite, and ferrihydrite–polymerin from simulated wastewaters (the sorbent was renewed in each cycle).

(Figure 4d), where the first disappeared, and the second was reduced and shifted to 1111.47. Such a modification could be also attributed to an ionic bonding between the OH₂⁺ groups of ferrihydrite and COO⁻ groups of CyA.

Finally, the DRIFT spectrum of CyA–ferrihydrite–polymerin, registered at pH 3.5 (Figure 4f), showed, as a main modification with respect to the spectrum of ferrihydrite–polymerin complex (Figure 4e), the disappearance of the band at 1208.70 cm⁻¹ and the strong reduction of the band at 1153.08 cm⁻¹ (both corresponding to the OH bending of ferrihydrite), due very probably to the ionic bonding between the COO⁻ groups of CyA and the OH₂⁺ groups of ferrihydrite. The broadband at 1621.77 cm⁻¹ and the broad and slightly split band at 1380.61 cm⁻¹ observed in the spectrum of Figure 4f appeared, even weakly, modified with respect to the corresponding bands observed in the spectrum of Figure 4e at 1622.73 and 1388.20 cm⁻¹ (symmetric and asymmetric stretching of polymerin COO⁻ groups bound by ionic linkage to OH₂⁺ groups of ferrihydrite) because of the contribution of the bands previously identified at 1621.98 cm⁻¹ and 1410.47 cm⁻¹ in the spectrum of CyA–ferrihydrite (see Figure 4d).

In conclusion, CyA bound to polymerin by hydrogen bonding, to the ferrihydrite–polymerin complex by ionic bonding and to ferrihydrite by a combination of dipole–ion and ionic bonding. These results could confirm the following sorption capacity order, ferrihydrite > ferrihydrite–polymerin > polymerin for CyA, already observed in the corresponding sorption isotherms (Figure 3 and Table 2).

Cyclic Removal of CyA by Polymerin, Ferrihydrite, and Ferrihydrite–Polymerin from Simulated Wastewaters. Experiments on cyclic sorption investigated the potential to remove CyA from simulated wastewaters. Figure 5 shows that almost a total removal of CyA on ferrihydrite and the ferrihydrite–polymerin complex was performed after two and five sorption cycles, respectively, whereas decontamination was still incomplete on polymerin even after five cycles, leaving a constant residue of 0.11 mmol L⁻¹. A similar behavior was observed in a previous study on the cyclic sorption of 2,4-D on polymerin (18), also confirming for the CyA–polymerin system that the acid–base equilibrium of CyA was strongly in competition with the sorption equilibrium between the undissociated form of herbicide and polymerin. Therefore, ferrihydrite showed to be the most efficient sorbent for the removal of CyA from contaminated waters.

In conclusion, among the selected investigated sorbents, ferrihydrite proved to be the most convenient for possible use as a filter for the control of wastewater contamination with CyA in point sources. In fact, this matrix allowed the almost total removal of the herbicide from contaminated waters by only two

sorption cycles, using the usual procedure of centrifugation for the separation of purified waters. In addition, it can be prepared more easily and at lower cost than the other two sorbents and could be recycled by incineration for potential further applications. Finally, the use of a mineral (ferrihydrite) and an organo-mineral complex (ferrihydrite-polymerin) as filter for the remediation of waters contaminated with CyA from point sources is proposed here for the first time, with ferrihydrite being much more advantageous than ferrihydrite-polymerin.

ACKNOWLEDGMENT

CyA was prepared according to the procedure described above and kindly supplied by Professor A. Pusino of the Department of Agricultural and Environmental Sciences Agro-Food Biotechnology, University of Sassari, Italy.

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Received February 18, 2009. Revised manuscript received May 11, 2009. Accepted May 12, 2009. This research has been supported by grants partly from PRIN 2004 and partly from PRIN 2006 of Ministry of University and Scientific Research, Italy; contribution DiSSPAPA 193.