

Polymerin and Lignimerin, as Humic Acid-like Sorbents from Vegetable Waste, for the Potential Remediation of Waters Contaminated with Heavy Metals, Herbicides, or Polycyclic Aromatic Hydrocarbons

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Polymerin is a humic acid-like polymer, which we previously recovered for the first time from olive oil mill waste waters (OMWW) only, and chemically and physicochemically characterized. We also previously investigated its versatile sorption capacity for toxic inorganic and organic compounds. Therefore, a review is presented on the removal, from simulated polluted waters, of cationic heavy metals [Cu(II), Zn, Cr(III)] and anionic ones [Cr(VI) and As(V)] by sorption on this natural organic sorbent in comparison with its synthetic derivatives, K-polymerin, a ferrihydrite–polymerin complex and with ferrihydrite. An overview is also performed of the removal of ionic herbicides (2,4-D, paraquat, MCPA, simazine, and cyhalofop) by sorption on polymerin, ferrihydrite, and their complex and of the removal of phenanthrene, as a representative of polycyclic aromatic hydrocarbons, by sorption on this sorbent and its complexes with micro- or nanoparticles of aluminum oxide, pointing out the employment of all these sorbents in biobed systems, which might allow the remediation of water and protection of surface and groundwater. In addition, a short review is also given on the removal of Cu(II) and Zn from simulated contaminated waters, by sorption on the humic acid-like organic fraction, named lignimerin, which we previously isolated for the first time, in collaboration with a Chilean group, from cellulose mill Kraft waste waters (KCMWW) only. More specifically, the production methods and the characterization of the two natural sorbents (polymerin and lignimerin) and their derivatives (K-polymerin ferrihydrite–polymerin, polymerin–microAl₂O₃ and –nanoAl₂O₃, and H-lignimerin, respectively) as well as their sorption data and mechanism are reviewed. Published and original results obtained by the cyclic sorption on all of the considered sorbents for the removal of the above-mentioned toxic compounds from simulated waste waters are also reported. Moreover, sorption capacity and mechanism of the considered compounds on polymerins and lignimerins are evaluated in comparison with other known natural sorbents, especially of humic acid nature and other organic matter. Some of their technical aspects and relative costs are also considered. Finally, the possible large-scale application of the considered sorption systems for water remediation is briefly discussed.

KEYWORDS: Olive oil mill waste waters; cellulose mill Kraft waste waters; polymerin; lignimerin; ferrihydrite; aluminum oxides; nanominerals; humic acid; organic matter sorbent; DRIFT spectroscopy; heavy metals; ionic herbicides; polycyclic aromatic hydrocarbons; sorption; water remediation

1. INTRODUCTION

The protection of surface and groundwater from pollution by heavy metals, herbicides, and polycyclic aromatic hydrocarbons (PAHs), derived from agricultural and industrial activities, is a very important actual environmental and political question, considering also the viable importance of the water, especially in the poor countries in the world. For this reason, many studies have been carried out in the past 20 years by the international scientific community on water protection and remediation by

using sorption processes. In particular, several studies have dealt with sorbents of a vegetable nature derived from industrial and agricultural waste, with the double objective of recycling natural free-cost material and ecologically disposing of or reusing the exhausted sorbents (1–16).

Among many kinds of natural organic sorbents investigated in recent years, polymerin, a humic acid-like polymer, which we recovered for the first time from olive oil mill waste waters (OMWW) (5–8) only, has shown very high and versatile sorption capacities, which we ascertained either for toxic inorganic (9–11) or organic (12–15) compounds. For this reason, polymerin and its derivatives could potentially be suitable for the remediation of

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waste waters. More recently, the humic acid-like organic fraction, named lignimerin, which we recovered in collaboration with a Chilean group from cellulose mill Kraft waste waters (CMKWW) (16) only, was demonstrated to be very similar to polymerin and revealed good sorption capacity toward heavy metals (17).

Therefore, a review is presented on the removal, from simulated polluted waters, of cationic heavy metals [Cu(II), Zn, Cr(III)] (9, 10) and anionic ones [Cr(VI) and As(V)] (11) by sorption on polymerin, in comparison with its synthetic derivative, K-polymerin, a ferrihydrite–polymerin complex, and a ferrihydrite. An overview is also given of the removal from water of ionic herbicides (2,4-D, paraquat, MCPA, simazine, and cyhalofop) (12–14) by sorption on polymerin, a ferrihydrite–polymerin complex, and a ferrihydrite. Furthermore, a review of the removal of phenanthrene (phen), as a representative of PAHs, from water by sorption on polymerin in comparison with its complexes with micro- or nanoparticles of aluminum oxide (Al₂O₃) and with the respective particles alone (15), is included. The sorption of the considered herbicides and phen on the previously cited sorbents was analyzed, pointing out their employment in biobed systems, for protection of surface and groundwaters in point sources (4). Moreover, a short review is also reported on the removal of Cu(II) and Zn from simulated contaminated waters, by sorption on lignimerin and its derivative H-lignimerin, in comparison with polymerin and K-polymerin, and lignins (16, 17, 31, 32).

More specifically, a review is presented on (i) the production methods and characterization of the two natural organic sorbents (i.e., polymerin and lignimerin) and their synthetic derivatives; (ii) the sorption data, elaborated according to the Langmuir and/or Freundlich equation, as well as the sorption mechanism of the considered toxic compounds; and (iii) published and original results obtained by cyclic sorption on all of the considered sorbents, renewed at each cycle, for the removal of the previously mentioned toxic compounds from simulated waste waters. The sorption capacity and sorption mechanism of all considered compounds on polymerins and lignimerins are evaluated in comparison with other known natural sorbents, especially of humic acid nature and other organic matter. Some of their technical aspects and relative costs are also considered. Finally, the possible large-scale application of the considered sorption systems in water remediation is briefly discussed.

2. POLYMERIN AND ITS DERIVATIVES: PRODUCTION AND CHARACTERIZATION

Polymerin was recovered according to a scheme consisting of essentially three steps (7–9). In particular, from 1 L of OMWW up to 10 g of the brown complex polymer could be recovered (7–9).

Polymerin was shown to be a humic acid-like polyelectrolyte consisting of carbohydrates, melanin, and proteins. It also contained metals such as Ca, Mg, K, Na, and Fe(III), which were naturally bound and/or chelated through carboxylate anions and other characteristic nucleophilic functional groups (7–9). The distribution of polymerin relative molecular size was assessed to be approximately between 50.0 and 2.0 kDa by calibrated molecular weight gel filtration chromatography, indicating also that a fraction consisted of protein, melanin, and polysaccharide, strongly aggregated to each other in a supramolecular status by a combination of covalent and hydrogen bonds and CH/π interactions, and another fraction of only free polysaccharide (7–9). All of the chemical and physicochemical properties previously cited are reported in more detail in **Table 1**.

Moreover, the characteristic diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data of the native polymerin, which have been previously described (7–9), are reported in **Table 2**.

Table 1. Chemical and Physicochemical Data of Polymerin and K-Polymerin Compared with Those of Lignimerin, H-Lignimerin, and Humic Acids^a

	polymerin	K-polymerin	lignimerin	H-lignimerin	humic acid	ferrihydrite	ferrihydrite–polymerin	microAl ₂ O ₃	nanoAl ₂ O ₃
polysaccharide (%)	43.07	44							
protein (%)	22.4	23.8							
total aromatic compounds (%)	29.76	26.2	55.3	73.9					
metals (%)	4.77 (Na, K, Ca, Mg, Fe)	6.0 (Na, K, Ca, Mg, Fe)	6.93 (Ca, Mg, Na, Fe, Mn, Zn, Cu)	1.64 (Ca, Mg, Na, Mn, K, Zn, Cu)					
rel mol wt (mw, kDa)	first peak, 3.5 < rmw < 10 second peak, 45000	only one peak, 3.5 < rmw < 10	only one peak, 50 < rmw < 75	only one peak, 50 < rmw < 75	1 < rmw < 100				
UV (λ _{max} , nm, MeOH)	270 (shoulder) 410 (peak)	270 (shoulder) 410 (peak)	270 (shoulder) 410 (peak) 196 779	270 (shoulder) 410 (peak)					
COOH (mmol kg ⁻¹)	5826								
phenolic –OH (mmol kg ⁻¹)	3893								
carbon (%)	41.49								
point of zero charge	2.2								
surface area (m ² g ⁻¹)	312		6.72	6.72	3.60	9.4	484.2	7.3	8.5
E ₄ /E ₆	3.82						380.7	92	228

^a Chemical and physicochemical data of ferrihydrite, ferrihydrite–polymerin, microAl₂O₃, and nanoAl₂O₃. Adapted from refs 8, 10, and 15.

Table 2. DRIFTS Data (KBr, cm^{-1}) of Polymerin and K-Polymerin Compared with Those of Lignimerin, H-Lignimerin, and Humic Acids^a

lignimerin	K-polymerin	H-lignimerin	polymerin	humic acids
3300 (phenol and alcohol OH)	3266 (phenol and alcohol (OH))	3400 (phenol, alcohol, and carboxylic acid OH)	3313 (phenol, alcohol, and carboxylic acid OH)	3400–2900
2920 (C–H of ether OCH_3)		2920 (C–H of ether OCH_3)	2924 (C–H of ester OCH_3)	1725–1720
1587 (aromatic nucleus + symmetric COO^-)	1594 (aromatic nucleus + symmetric COO^-)	1710 (O=COH)	1723 (OC– OCH_3 carbonyl ester + COOH)	1590–1517
1420 (asymmetric COO^-)	1390 (asymmetric COO^-)	1600 (aromatic nucleus)	1639 and 1514 (aromatic nucleus + C=O peptide + symmetric COO^-)	1400–1390
1075 (alcoholic OH)	1074 (alcoholic C–OH)	1260 (C–O of COOH)	1439 and 1354 (asymmetric COO^- and symmetric and asymmetric OCH_3 ester)	1280–1200
1042 (alcoholic OH and C– OCH_3 ether)		1075 (alcoholic C–OH)	1261 (OCO– CH_3 ester)	1170–950
		1042 (alcoholic OH and C– OCH_3 ether)	1072 (alcoholic C–OH)	
			1042 (alcoholic OH and OC– OCH_3 ester)	

^a Adapted from refs 10 and 16.

Here we have also reported in detail chemical, physicochemical, and DRIFTS data for polymerin compared with those of humic acids (**Tables 1** and **2**). This humic acid-like polymer represents the characteristic dark polymeric pigment of OMWW.

More recently, polymerin has been also identified by LC-MS in olive oil mill wastes from a two-phase system of production of olive oil (18).

A potential exploitation of polymerin in agriculture as bio-amendment and/or metal biointegrator has not only been proposed on account of the humic acid-like nature, but also of the native richness in macro- and micronutrients such as K, Ca, Mg, Fe, and Zn and the scarce phytotoxicity compared with that of the raw OMWW (8).

Polymerin was transformed into its derivative, salified and saturated with potassium, called K-polymerin (9). Its chemical, physicochemical, and spectroscopic data are shown in **Tables 1** and **2**. All of its organic components (carbohydrates, melanin, and proteins) were also strongly linked in a supramolecular aggregated status like polymerin, and the relative average molecular size proved to be 6.3 kDa. This conversion was performed with the aim of producing a sorbent with increased metal cation sorption capacity with respect to polymerin (7, 9). In fact, the percentage composition of metal in K-polymerin was higher than that in polymerin, particularly with regard to K, as a consequence of the hydrolysis of the ester linkages present in polymerin, which produced further carboxylate anions with the consequent increase of negative sorption sites. These characteristics have been confirmed by the analysis of its DRIFT spectrum compared with that of polymerin, according to previous results (7, 9). The respective data are reported in **Table 2**.

In conclusion, K-polymerin is a potassium salt derivative of polymerin. It is noteworthy that the DRIFT spectrum of K-polymerin (**Table 2**) was very close to the DRIFT spectra of Na- and Cu-humate, published by Piccolo and Conte (19).

Polymerin was also transformed into an organomineral ferrihydrite–polymerin complex to study the influence of ferrihydrite [$\text{Fe}(\text{OH})_x$], a poorly crystalline iron oxide, on the sorbing capacity of both heavy metals and herbicides on the biosorbent immobilized onto a solid matrix (11, 14). The chemical and physicochemical data of the organomineral complex have been previously described in comparison with the chemical properties of ferrihydrite and polymerin (11, 14) and are reported in **Table 1**.

Finally, polymerin was either immobilized on micro- (micro- Al_2O_3) or nanoparticles of aluminum oxides (nano- Al_2O_3) to obtain a new solid sorbent as a filter system (pol–micro- Al_2O_3 and pol–nano- Al_2O_3 , respectively) of waters contaminated with phen, as a representative of toxic PAHs (15). As polymerin itself was soluble in water, it could not be readily used in a filter system. The physicochemical properties of micro- Al_2O_3 and nano- Al_2O_3 are reported in **Table 1**.

In addition, by combining the DRIFTS data of polymerin, pol–micro- Al_2O_3 , and pol–nano- Al_2O_3 with the E_4/E_6 value of 3.8, determined for the natural organic sorbent and those (6.2 and 3.8, respectively) of the residual polymeric part remaining in the solution after the formation of the two complexes, it was inferred that the whole polymerin was fixed in the latter complex, whereas only the melanin part of polymerin was fixed on the former one (15).

Several studies have suggested the application of Al_2O_3 coated with anionic surfactants in wastewater treatment techniques (20, 21). Polymerin could represent an advantageous alternative to the use of surfactants. Its use instead of synthetic surfactants might be convenient because it is derived from a cost-free material.

Therefore, polymerin and its organic and organomineral derivatives have been mainly proposed as sorbents for the potential

Table 3. Langmuir and Freundlich Parameters of Zn, Cu(II), Cr(III), Cr(VI), and As(V) Individually Sorbed on Polymerin, K-Polymerin, Ferrihydrite, and Ferrihydrite–Polymerin^a

	Langmuir parameters			Freundlich parameters		
	S_m (mmol kg ⁻¹)	K	R^2	K_F (mmol kg ⁻¹)	N	R^2
polymerin + Zn ^b						
polymerin + Cu(II)	1501	0.87	0.99			
polymerin + Cr(III)	2419	1.76	0.99			
polymerin + Cr(VI)	195	54.3	0.99	218	3.42	0.96
polymerin + As(V)	384	1.29	0.99	194	1.68	0.97
K-polymerin + Zn ^c						
K-polymerin + Cu(II)	1888	1.32	0.99			
K-polymerin + Cr(III)	2797	4.38	0.99			
ferrihydrite–polymerin + Cr(VI)	206	136	0.99	238	6.37	0.96
ferrihydrite + Cr(VI)	255	228	0.99	279	13.4	0.96
ferrihydrite–polymerin + As(V)	880	1103	0.99	1001.8	15.41	0.97
ferrihydrite + As(V)	743	392	0.99	781	16.3	0.95
lignimerin + Zn	370.4	0.54	0.98			
H-lignimerin + Zn	312.5	0.86	0.99			
lignimerin + Cu(II)	666.7	0.65	0.98			
H-lignimerin + Cu(II)	232.5	0.91	0.97			

^a Adapted from refs 10 and 11. Langmuir parameters of Zn and Cu(II) individually sorbed on lignimerin and H-lignimerin. Adapted from ref 17. ^b 550 mmol kg⁻¹ extrapolated from the respective isotherms (10). ^c 750 mmol kg⁻¹ extrapolated from the respective isotherms (10).

remediation of waters contaminated with heavy metals (9–11), ionic herbicides (12–14), or PAHs (15).

3. REMOVAL OF CU(II), ZN, CR(III) AND CR(VI), OR AS(V) FROM CONTAMINATED WATERS BY SORPTION ON POLYMERIN, K-POLYMERIN, A FERRIHYDRITE–POLYMERIN COMPLEX, AND A FERRIHYDRITE

The anthropogenic release of heavy metals creates public health problems due to their toxicity and persistence in the environment. The removal of heavy metals by their biosorption on no-cost and abundant vegetable biomass has been suggested recently as a potential alternative to the existing physicochemical technologies for detoxification and recovery of toxic and valuable metals from polluted waters (10, 22–46). More specifically, heavy metals such as Zn, Cu(II), and Cr(III) can originate from sources of pollution including agricultural fertilization, manufacturing processes, smelting and refining, refuse and wastewater treatment, and fuel combustion (10, 22–24, 31, 32).

Among the contaminant metalloids, chromium as Cr(VI) (Cr₂O₇²⁻ and/or CrO₄²⁻, depending on the pH of the solution) enters the environment in elevated levels, primarily due to anthropogenic activities. Cr(VI) is also very toxic to living organisms, as a strong oxidant, a potential carcinogen, and a corrosive agent (33). On the contrary, Cr(III), at low concentration, is not toxic to plants and is necessary in animal nutrition (29). In addition, it is used in many industrial processes such as plating, alloying, and tanning of animal hides and as a water corrosion inhibitor. The hazards invoked by Cr(VI) underscore the importance of processes that remove this species from the aqueous phase, reducing or eliminating its bioavailability.

In this regard, several studies have been published, which dealt with the sorption and concomitant reduction of Cr(VI) into Cr(III) by sorption on biosorbents (25–35). In this light we also carried out studies on the sorption of this metal in the form of dichromate (Cr₂O₇²⁻), at pH 4.0, on polymerin, in comparison with ferrihydrite and a ferrihydrite–polymerin complex (11). This last system was chosen because of its versatility to remove Cr(VI) from aqueous solution by iron(III) hydroxide loaded on organic matter, such as on sugar beet pulp (30).

As(V) is also a contaminant metalloid that enters the environment in elevated levels, primarily due to anthropogenic waste from petroleum refining, glass melting, and smelting of metal sulfide ores or from the use of arsenic-containing pesticides and fertilizers (36). Consequently, there is increasing public concern about arsenate contamination in water and its effects on human health (37–39).

The hazards invoked by arsenate also underscored the importance of processes that remove this species from the aqueous phase. In this regard, some studies have been published on the sorption of As(V) on low-cost sorbents (40, 45, 46). We also carried out studies on the sorption of As(V) by comparing low-cost materials of vegetable and mineral origin such as polymerin, a ferrihydrite–polymerin complex, and a ferrihydrite, respectively (11).

Therefore, in the following sections (3.1 and 3.2) we review the removal of cationic heavy metals, such as Zn, Cu(II), and Cr(III), and anionic ones, such as Cr(VI) or As(V), from simulated wastewater, by sorption on polymerin in comparison with its organic synthetic derivatives, K-polymerin and ferrihydrite–polymerin, and with other natural sorbents.

3.1. Sorption Data and Mechanism for the Heavy Metals and Metalloids. The individual sorbing capacities of Zn, Cu(II), and Cr(III) on polymerin were considerable and followed the order Cr(III) > Cu(II) > Zn, as shown by the respective isotherms (10) and the corresponding values of the Langmuir parameters (Table 3).

The individual sorption of the three metals on K-polymerin proved to be higher than those on polymerin, following the same order, Cr(III) > Cu(II) > Zn (Table 3). The high sorption of the selected heavy metals on both polymerins was consistent with the presence of negative sites on their surface. In particular, their greater sorption capacity on K-polymerin was consistent with the increase of negative sites on this sorbent with respect to polymerin, as explained previously in section 2.

The sorption of Zn, Cu(II), and Cr(III) on this biorganic material was very high and not lower than that on other biomass byproducts used as metal biosorbents, which were widely described in the literature (10, 22–24, 31, 32).

The individual sorption of the selected metals on ferrihydrite–polymerin proved to be significant but much lower than that on polymerin (10).

A study on the mechanism for sorption of the selected heavy metals on polymerin, which was performed using a combination of DRIFTS and AAS analyses of polymerin samples saturated with the heavy metals, indicated that Cr(III) was substantially sorbed on polymerin by ion exchange of the heavy metal with Ca, K, and Mg (87%) naturally occurring in polymerin (10).

A concomitant complexation with the OH groups of the polysaccharide component of this biosorbent occurred, as previously indicated by the DRIFTS analysis (10). The other two native metals of polymerin, Na and Fe(III), were not involved in the exchange mechanism, consistent with their strong fixation on the sorbent, as already demonstrated in our previous work (8). The same sorption mechanism was also revealed for Cu(II) and Zn [occurring by 86 and 96% for exchange with the alkaline metals (10)].

The individual sorption of the selected metals on a ferrihydrite–polymerin complex proved to be significant, but much lower than those on polymerins. As an example, the individual sorption capacity of Zn on the above organomineral compared with K–polymerin was 250/500 mmol kg⁻¹, respectively, at the same equilibrium concentration of 1.5 mmol L⁻¹ (10).

Studies were also carried out on the sorption of the selected metals in binary and ternary combination by polymerin and ferrihydrite–polymerin, because of greater convenience in the preparation of the two sorbents, in view of their potential application in wastewater remediation processes (10).

With specific regard to polymerin, the presence of both Zn and Cu(II) did not affect the capacity of Cr(III) to be sorbed on polymerin. Vice versa, the presence of Zn and/or Cr(III) reduced Cu(II) sorption. At an equilibrium concentration of 2 mmol L⁻¹, the presence of Zn reduced Cu(II) sorption by 15%, and the concomitant presence of Zn and Cr(III) decreased Cu(II) sorption by about 50%, showing that Cr(III) was much more effective than Zn in preventing Cu(II) sorption. Finally, at an equilibrium concentration of 2 mmol L⁻¹ Zn, the presence of Cu(II) or Cu(II) and Cr(III) decreased the sorption of Zn by about 70 and 79%, respectively, indicating that both Cu(II) and Cr(III) strongly inhibited Zn fixation on polymerin.

Sorption studies were also conducted on the Cr(VI) form of chromium. In particular, the individual sorption of Cr(VI) on the three considered sorbent systems was characterized by the corresponding isotherms, which fitted the Langmuir and Freundlich equations and parameters (Table 3).

X-ray photoelectron spectroscopy (XPS) and DRIFTS investigations showed that on polymerin Cr(III), mainly (75%), and Cr(V) (25%) were the effective sorbed chromium forms, which formed by the redox reaction at pH 4.0 of Cr(VI) with the CH₂OH groups of the polysaccharide moiety of this sorbent (11).

The specific colorimetric analysis of Cr(VI) indicated the presence of this chromium form only in the supernatants, its amounts being coincident with the total amount 1.20 mmol L⁻¹ detected by AAS (11). These findings suggested Cr(VI) to be present in the supernatant as the remaining part of an unreacted oxyanion (11).

The maximum sorption capacity of chromium [Cr(III) and Cr(V)] was 195 mmol kg⁻¹ on polymerin, corresponding to 100 mmol kg⁻¹ of Cr(VI) (i.e., 21.60 g kg⁻¹) (11). This latter amount was almost comparable to that (35.00 g kg⁻¹) reported by Dupont and Guillon (29) for the sorption of the same oxyanion on a lignocellulose substrate, where it proved to be analogously transformed into Cr(III) in acidic medium.

A much higher sorption capacity of Cr(VI) (287 g kg⁻¹) on dry tannin gel was observed at pH 2.0 (27). The sorption mechanism on condensed-tannin gel consisted of four reaction steps: the esterification of chromate with tannin molecules, the reduction of Cr(VI) to trivalent chromium Cr(III), the formation of carboxyl group by the oxidation of tannin molecules, and the ion exchange of the reduced Cr(III) with the carboxyl and hydroxyl groups (27).

Umesh et al. (34) reported that the removal of Cr(VI) on sugar cane bagasse, maize corn cob, and Jatropha oil cake ranged between 28 and 82 g kg⁻¹ at pH 2.0, but no reduction of Cr(VI) to Cr(III) was indicated.

Hasan et al. (35) reported that the capacity of maize bran to sorb Cr(VI) at pH 2.0 and 40 °C was 312.52 g kg⁻¹. Moreover, the effect of pH showed that maize bran was not only removing Cr(VI) from aqueous solution but also reducing toxic Cr(VI) into the less toxic Cr(III).

With regard to the sorption of Cr(VI) on ferrihydrite and the ferrihydrite–polymerin complex, the isotherms also fitted the Langmuir and Freundlich equations (11). The sorption of chromium on both sorbents increased slowly with increasing metal equilibrium concentration, according to an L-form. Furthermore, the maximum amount of Cr(VI) sorbed on ferrihydrite–polymerin was lower than on ferrihydrite (Table 3), despite the larger surface area of the former. This behavior could be explained by considering the occurrence of positively charged groups (–OH₂⁺) on ferrihydrite capable of binding the dichromate ions [Cr₂O₇²⁻] by electrostatic interactions. The decrease of the sorbed chromium on ferrihydrite–polymerin is attributable to the presence of the organic component (polymerin), which partially covers the positive available sites of the Fe(OH)_x species of ferrihydrite. The only chromium species present in this system was Cr(VI) (10.72 g kg⁻¹), very likely because of the presence of a very low amount of polymerin (Table 1) and, therefore, a scarce involvement of this organic component in the redox reaction with the same Cr(VI) (11).

On the other hand, the maximum total chromium-removal efficiency on a composite adsorbent prepared from sugar beet pulp by loading with iron(III) hydroxide at the final pH of 4.4 and 25 °C was 5.12 g kg⁻¹ (30). In this latter case the authors found that the reduction of Cr(VI) occurred during the sorption process.

With respect to As(V), the sorption isotherms of this metalloid on the three sorbents, that is, polymerin, ferrihydrite–polymerin complex, and ferrihydrite, fitted the Langmuir equation (11). In particular, arsenate, in the form of dihydrogenarsenate [H₂AsO₄⁻] at pH 4.0, showed sorption on the ferrihydrite–polymerin complex and ferrihydrite to a greater extent than on polymerin, as confirmed by the corresponding S_m values reported in Table 3.

The sorption of As(V) on polymerin increased slowly when the oxyanion equilibrium concentration increased. Very probably, dihydrogenarsenate bound to polymerin through hydrogen bonds with alcoholic, phenol, and carboxymethyl groups occurring in the sorbent.

On the contrary, the shape of the curves obtained with ferrihydrite–polymerin and ferrihydrite indicated a high-affinity behavior, the sorption being characterized by a rapid rise at low As(V) equilibrium concentration (11).

In particular, As(V) sorbed on the three sorbents following the order ferrihydrite–polymerin > ferrihydrite > polymerin. This trend was confirmed by analyzing the values of the Langmuir constants, S_m and K (Table 3).

The data also fitted the Freundlich equation (Table 3). The high sorption of As(V) on ferrihydrite was attributable to the formation of inner-sphere complexes (41–44).

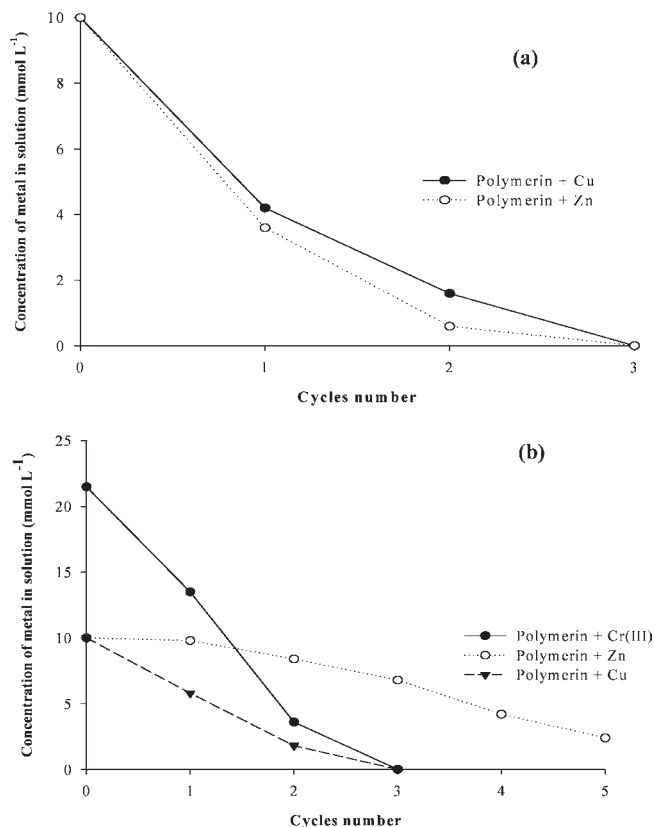


Figure 1. Removal of Zn + Cu(II) (a) or Zn + Cu(II) + Cr(III) (b) from equimolar solutions by cyclic sorption on polymerin (sorbent was renewed in each cycle). Adapted from ref 10.

The Freundlich isotherm used for the removal of arsenic by rice husks showed a value of K_F corresponding to $4430 \text{ mmol kg}^{-1}$ (45), against 194 mmol kg^{-1} sorbed on polymerin (Table 3).

Guo and Chen (46) utilized iron oxyhydroxide-loaded cellulose beads for arsenate removal from water. The sorption capacity for arsenate was 240 mmol kg^{-1} at pH 7.0 for the $\text{Fe}(\text{OH})_x$ -cellulose beads, against $1001.8 \text{ mmol kg}^{-1}$ sorbed on ferrihydrite-polymerin and 781 mmol kg^{-1} on ferrihydrite alone, at pH 4.0 (Table 3).

3.2. Cyclic Sorption Process for the Removal of Heavy Metals from Simulated Waste Waters and Its Potential Application in Water Remediation. Among the sorbents above investigated for their sorption capacity and low-cost production, polymerin was selected as the most convenient to perform the experiment with cyclic sorption to remove the cationic heavy metals from simulated waste waters (10).

Figure 1a shows that the total removal of Cu(II) and Zn from a solution containing equimolar amounts of these cations was performed after three cycles, as shown by the two respective curves. Furthermore, the removal of Cu(II) and Cr(III) from a solution containing Cr(III) and equimolar amounts of Cu(II) and Zn was complete in three cycles, whereas about 20% of Zn initially added remained after five adsorption cycles (Figure 1b). In view of an environmental technology application, the latter findings suggested that greater amounts of polymerin should be employed to render the remediation process more efficient.

In addition, the employment of polymerin in wastewater remediation processes should not only decontaminate the waters from heavy metals but also enrich them in nutrients such as Ca, Mg, and K, which were released from polymerin during the cleanup process, as also inferred from the sorption mechanism. In addition, the material obtained after the wastewater cleanup

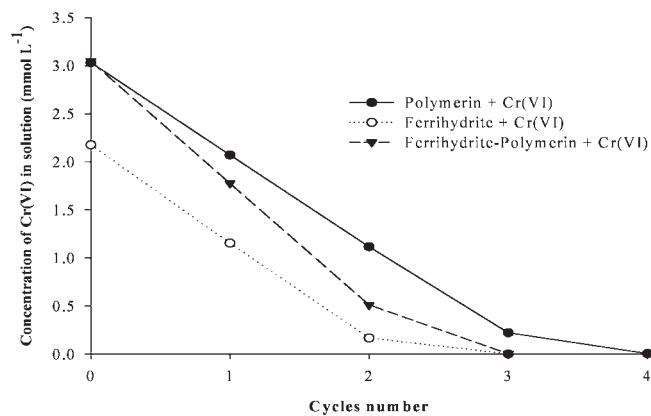


Figure 2. Removal of chromium(VI) from solution by cyclic sorption on polymerin, ferrihydrite-polymerin, and ferrihydrite (sorbents were renewed in each cycle).

process could potentially be reused as a potential source of metals after desorption or incineration processes.

The removal from water of the considered metals by cyclic sorption on other waste biomass should be less efficient than on polymerin, requiring more sorption cycles, as a consequence of a minor sorption capacity (22–24, 31, 32).

With regard to the removal of Cr(VI) from water, the previous data suggested that polymerin could be the most convenient one, even if in this latter form it was sorbed to a lesser amount (100 mmol kg^{-1}) compared to ferrihydrite ($S_m = 255 \text{ mmol kg}^{-1}$) and ferrihydrite-polymerin ($S_m = 206 \text{ mmol kg}^{-1}$). In fact, Cr(III) was the main effective form fixed on polymerin, which was produced by the redox reaction of Cr(VI) with this sorbent, as explained above. The remaining nonreacted Cr(VI) could be totally removed by cyclic sorption on polymerin renewed at each cycle, applying the same procedure previously described for the purification of waters contaminated with Cr(III) (10).

In particular, the cyclic sorption process to remove Cr(VI) from simulated wastewater, which is here described for the first time (procedure not reported), indicated that the metalloid was removed by four sorption cycles on polymerin and three sorption cycles on both ferrihydrite-polymerin and ferrihydrite (Figure 2). The further advantage with regard to the use of polymerin should be the purification of waters contaminated with the strongly toxic Cr(VI) and the recovery of less toxic Cr(III), which is also of considerable biological and industrial interest (11).

As an example of a possible application in environmental technology processes, polymerin could be potentially utilized to regenerate Cr(III) from Cr(VI) formed in the oxidation process of some tannery plants, Cr(III) being the effective chromium form discarded.

The removal of Cr(VI) from water with the concomitant reduction to Cr(III) was also performed by sorption either on dry tannin (287 g kg^{-1}) (27) or on maize bran (312.52 g kg^{-1}) (35).

The removal of Cr(VI) from water was also carried out by sorption on other above indicated vegetable waste ($28\text{--}82 \text{ g kg}^{-1}$) (34), but no reduction of Cr(VI) to Cr(III) was observed.

However, in all of these cases more drastic experimental conditions were used (pH 2 and higher temperature) with respect to those used for polymerin and lignocellulose, even if, very probably, fewer sorption cycles should be required for the total removal of chromium from water. In any case, an ultrafiltration plant, which is normally laborious and expensive, should be required to perform the cyclic process.

To avoid this problem, it should be more advantageous to remove the chromium by sorbing the metalloid on systems such as

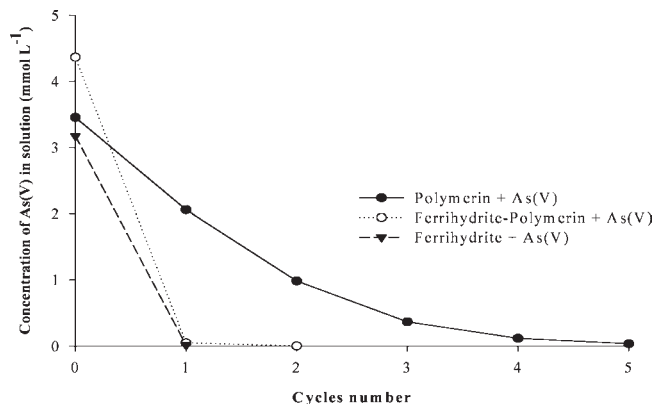


Figure 3. Removal of As(V) solution by cyclic sorption on polymerin, ferrihydrite–polymerin, and ferrihydrite (sorbents were renewed in each cycle).

ferrihydrite–polymerin or sugar beet loaded with iron(III) hydroxide, as indicated above.

Among the three systems investigated for the sorption of As(V), the most convenient for the potential removal of this oxyanion from wastewater proved to be ferrihydrite–polymerin ($S_m = 880.26 \text{ mmol kg}^{-1}$), followed by ferrihydrite ($S_m = 743.02 \text{ mmol kg}^{-1}$), and, to a much lesser extent, polymerin ($S_m = 384.25 \text{ mmol kg}^{-1}$). On the basis of these results, a cyclic sorption process of As(V) on the three sorbents was set up to clean up simulated wastewater contaminated with this metalloid.

The data (Figure 3), here reported for the first time (procedure not reported), indicated that five sorption cycles were necessary for the total removal of As(V) from simulated wastewater by sorption on polymerin. Instead, two cycles were sufficient to totally remove the metalloid by sorption on ferrihydrite–polymerin and only one cycle on ferrihydrite. The cyclic process indicated ferrihydrite potentially to be the most convenient sorbent for the clean up of waters contaminated with As(V), also because a simple filtration or centrifugation process should be necessary to separate the purified waters from the saturated sorbing system, and the latter could be easily recycled.

Other sorbents of interest for the removal of As(V) from water are reported in the literature, such as the above cited rice husks (45) and iron oxyhydroxide-loaded cellulose beads (46); however, ferrihydrite or ferrihydrite–polymerin should be the most suitable for the clean up of wastewater contaminated with this metalloid.

In conclusion, polymerin has been shown to be the most suitable material for the removal of the considered heavy metal cations from water by cyclic sorption, with the additional advantage of releasing in water useful metals such as K, Mg, and Ca, natively occurring in the sorbent.

Among the sorbents investigated for the removal of Cr(VI), many options should be evaluated for the selection of the most convenient system to be applied in a cyclic sorption process. In particular, the sorption capacity on the sorbent of Cr(VI) correlated with the concomitant reduction to Cr(III) and the separation method (ultrafiltration, centrifugation, or filtration) as well as the sorption experimental conditions have to be considered. Therefore, in this case the cost-benefit should be evaluated in view of scaling up of the cyclic sorption process.

Ferrihydrite or ferrihydrite–polymerin should be the most convenient for the clean up of wastewater contaminated with As(V).

4. REMOVAL OF THE IONIC HERBICIDES 2,4-D, MCPA, PARAQUAT, SIMAZINE, AND CYHALOFOP ACID FROM CONTAMINATED WATERS BY SORPTION ON POLYMERIN, A FERRIHYDRITE–POLYMERIN COMPLEX, AND A FERRIHYDRITE

Contamination arising from sources such as nonapproved use, poor practice, illegal operations, accidental releases from the farmyard, and inputs of washings is increasingly recognized as contributing to water contamination and is defined as *point source* (47–50). The application of treatment systems at the farm level could allow an improved protection of the aquatic ecosystem and a reduction of water treatment costs.

In this light, the possibility of using vegetable biomass wastes as a biofilter for the remediation of wastewater generated at *point sources* has been widely described (51–54).

In the past 10 years, biological systems, known originally as biobeds (4), were developed to remediate surface water *point-source* pollution from pesticides. A biobed is a simple and cheap construction that collects and degrades spills of pesticide on farms (4).

The final objectives of the utilization of this system are the recovery of cleanup water to be recycled on the farm and the prevention and protection of surface and groundwater.

The use of free-cost organic biomass from agricultural and industrial wastes could represent a cheap and effective method for protection of waters. In this light, we have previously investigated the sorption of acid and basic herbicides on polymerin (12, 13), as well as of cyhalofop acid herbicide on a ferrihydrite–polymerin and ferrihydrite (14), with the aim to employ these sorbents as possible components of a biobed system. To this end, paraquat and 2,4-D were selected as model herbicides (12).

Polymerin was able to sorb 907 mmol kg^{-1} of paraquat in native conditions (pH 5.7) and $183.1 \text{ mmol kg}^{-1}$ of 2,4-D at pH 3.0 after 4 and 24 h of interaction, respectively. However, the decontamination of simulated wastewater by cyclic sorption on this matrix, renewed at each cycle, indicated a total removal of paraquat (in native conditions) and a partial one of 2,4-D, respectively (12).

These models were utilized for the study of cleaning up of waters contaminated with the currently used herbicides 4-chloro-2-methylphenoxyacetic acid (MCPA) and simazine by sorption on polymerin, for a potential application of this matrix in the preparation of biobed systems (13).

However, the employment of polymerin as a possible biofilter for the removal of the ionic herbicides 2,4-D, MCPA, paraquat, and simazine from simulated wastewater in pollution *point sources* 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 this sorbent fixed with the herbicide from the wastewater and (ii) residual herbicide, except paraquat, was still detected in the polluted waters even after many cycles of sorption on renewed polymerin at each cycle (12, 13).

These data prompted us to study the improvement of the removal of an ionic herbicide from wastewater by using a system composed of polymerin immobilized on ferrihydrite and ferrihydrite alone, both sorbents being investigated in comparison with polymerin (14).

To this end, cyhalofop [(R)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionic acid (CyA)] was selected as a further ionic herbicide because of its very intensive use (14). Indeed, the commercial form of CyA is its butyl ester, cyhalofopbutyl [butyl (R)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionate (CyB)], but CyA was the effective form occurring in water after

Table 4. Langmuir and Freundlich Parameters for the Ionic Herbicides 2,4-D, Paraquat, MCPA, Simazine, and Cyhalofop Acid (CyA) Individually Sorbed on Polymerin, Ferrihydrite, and Ferrihydrite–Polymerin at Solid/Liquid (S/L) Ratios of 0.5, 1.25, and 2.50^a

S/L ratio ^b	sorbent + sorbate	Langmuir parameters			Freundlich parameters		
		S_m (mmol kg ⁻¹)	K	R^2	K_F (mmol kg ⁻¹)	N	R^2
0.5	polymerin + paraquat	907	3.9	0.98	631.1	3.1	0.99
1.25	polymerin + paraquat	581	2.3	0.98	355.5	2.3	0.98
2.5	polymerin + paraquat	532	1.8	0.99	305.4	1.8	0.98
0.5	polymerin + 2,4-D	183.1	8.5	0.98	214.8	2.4	0.98
1.25	polymerin + 2,4-D	92.6	5.7	0.98	102.9	2.1	0.98
2.5	polymerin + 2,4-D	66.6	4.5	0.98	79.1	1.6	0.99
0.5	polymerin + simazine				83.1	1.28	0.99
0.5	polymerin + MCPA				380.2	0.92	0.99
0.5	polymerin + CyA	195	3.45	0.98	229.4	1.13	0.98
0.5	ferrhydrite + CyA	797	27.1	0.99	951.5	4.52	0.98
0.5	ferrhydrite-polymerin + CyA	492	10.1	0.98	551.1	2.89	0.99

^a Adapted from refs 12–14. ^b Solid/liquid ratio of the sorbents adopted in the sorption experiments (12–14).

its application on the crop because it originated from the rapid hydrolysis of its corresponding butyl ester form (14).

Therefore, an overview of the removal from simulated wastewater of the above cited ionic herbicides by sorption on polymerin, a ferrihydrite–polymerin complex, and ferrihydrite is reported in comparison with other natural sorbents.

4.1. Sorption Data and Mechanism for the Herbicides. Sorption studies were carried out on the individual sorption of paraquat and 2,4-D on polymerin at three different solid/liquid ratios (0.5, 1.25, and 2.5) (12). In particular, kinetic runs carried out at native pH (5.7) by adding 0.27 mmol L⁻¹ of paraquat or 0.22 mmol L⁻¹ of 2,4-D, respectively, showed paraquat to be significantly sorbed after 4 h of incubation, whereas 2,4-D was scarcely sorbed after an incubation time of 24 h.

Sorption experiments for the two herbicides carried out as a function of pH indicated that greatest sorption of both pesticides occurred at a solid/liquid ratio of 0.5 (12). The optimum pH for sorption was 5.7 for paraquat (coincident with the native pH of polymerin) and 3.0 for 2,4-D. The effect of time on sorption of paraquat at pH 5.7 showed that the process was very rapid, reaching the sorption equilibrium within 1–2 h. Instead, for 2,4-D, the data showed an increase in sorption up to 24 h, but this trend was not constant after this time (12).

The sorption isotherms of paraquat and 2,4-D on polymerin fit the Langmuir equation (12). The sorption of both herbicides on polymerin increased slowly with increasing pesticide equilibrium concentration, according to an L form. Furthermore, the amount of sorbed pesticide was always higher at a solid/liquid ratio of 0.5 than at ratios of 1.25 and 2.5. This behavior was confirmed by analyzing the values of the Langmuir constants, S_m and K , and the Freundlich constants, K_F and N (Table 4), which indicated that polymerin sorbed paraquat and 2,4-D with both the greatest binding energy and sorptive intensity at a solid/liquid ratio of 0.5. Thus, the sorption of the herbicides significantly increased with decreasing amount of polymerin. This was attributed to the greater accessibility of the sorption sites, probably associated with a conformational change in polymerin as the solid/liquid ratio changed from 2.5 to 0.5 (12).

The sorbing capacity on polymerin of the selected herbicides was very significant in comparison with other sorbents such as humic acid and other natural organic materials.

In particular, the maximum sorbing capacity of paraquat in our work (12) was 907 mmol kg⁻¹, at native pH (5.7), whereas a significant decrease (500 mmol kg⁻¹) was detected for a similar herbicide (diquat) on a humic acid (55).

The sorption of paraquat on ayous (*Triplochiton schleroxylon*) sawdust was 36.83 mmol kg⁻¹. Moreover, for pH values of < 3,

the removal percentage was about 20%, whereas 92.6% was removed at pH 11 (56).

Spent diatomaceous earth from wine processing and its activated product had a larger sorption capacity at a higher pH value over the range of 3–11, and at lower temperature, corresponding to 19 and 95 mmol kg⁻¹ (57).

The amount of 2,4-D sorbed on different humic substances (58,59) was always lower (37.0 mmol kg⁻¹) if compared with that (188 mmol kg⁻¹) sorbed on polymerin.

Instead, the sorption of 2,4-D on activated carbon derived from date stones (DSAC) (60) revealed a capacity (1076 mmol kg⁻¹) much higher than that (188 mmol kg⁻¹) on polymerin.

With regard to the mechanism for the individual sorption of paraquat on polymerin, our previous data indicated that the sorption was consistent with the ion exchange of the herbicide with Ca, Mg, and K naturally occurring in polymerin (12). These results were confirmed by the previous studies of Narine and Guy (55), Spark and Swift (61), and Nanseu-Njiki et al. (56), who demonstrated the same sorption mechanism on humic acids and other organic matter.

In contrast, the sorption mechanism of 2,4-D on polymerin was consistent with the formation of hydrogen bonding between the herbicide and the sorbent (12), according to the same behavior observed by Piccolo et al. (62) and Gianfreda et al. (58) in sorption studies of this herbicide on humic acids. In addition, a release of native Ca, Mg, and K from polymerin was also observed, but not through an ion exchange mechanism (12).

With respect to studies on the sorption of MCPA and simazine on polymerin, which were carried out only at the ratio of 0.5 (13), we found that the sorption efficiency for both the pesticides was pH dependent and improved at low pH. In particular, the optimum pH of sorption for simazine was 3.5, whereas for MCPA, the optimum pH was 4.5 (13). Kinetic studies carried out at pH 3.5 for simazine and at pH 4.5 for MCPA showed that MCPA was rapidly sorbed, reaching the sorption equilibrium within 4–8 h (13). With regard to simazine, the kinetic data showed increasing sorption until 24 h and no variation after this time (13).

The sorption isotherms of simazine and MCPA on polymerin gave a good fit to the linearized form of the Freundlich equation and were of S-type and L-type, respectively (13). Their values of the corresponding parameters are listed in Table 4. Polymerin sorbed MCPA more efficiently than simazine, as indicated by the K_F values of 380.2 and 83.1 $\mu\text{mol kg}^{-1}$, respectively.

With regard to the sorption mechanism of the two herbicides on polymerin, we hypothesized the formation of combined ionic and hydrogen bonding between simazine and polymerin and

hydrogen bonding between MCPA and polymerin by examining in combination either the physicochemical data of both the sorbent and herbicides or of their chemical structural analogies with the previous model herbicides (12, 13). Simazine, having a pK_a of 1.70, at pH 3.5 was weakly positively charged, whereas the acidic groups ($pK_a = 4.5$) of polymerin were 50% in neutral form, as R-COOH, and 50% in anionic forms, as R-COO⁻. Then, at pH 3.5 the sorption occurred probably either by hydrogen bonding between nitrogen of the triazinic ring and the secondary amino groups of the lateral chain of simazine and carboxylic, phenolic, and alcoholic functional groups of polymerin or through ionic bonding occurring between the little amount of its protonated secondary amino groups of the herbicide and the carboxylate anions of polymerin.

Some authors have reported that interactions of simazine with humic substances occurred through hydrogen bonding, involving carbonyl groups of humic acids and secondary amine groups of simazine and proton transfer processes (63). These findings suggested that the sorption of simazine occurred prevalently at pH 3.5 for the restoration of an equilibrium between protonated and deprotonated amino groups of simazine with functional groups of polymerin, which allowed the formation of ionic and hydrogen bonding.

MCPA, at pH 4.5, exists almost completely in the ionized form. Its sorption on polymerin involved the formation of hydrogen bonds between the remaining undissociated form of the pesticide and the carboxyl and -OH groups of polymerin.

With regard to the sorption studies of CyA, this herbicide showed the greatest sorption capacity on polymerin at pH 4.5 and on both ferrihydrite-polymerin and ferrihydrite at pH 3.5 (14).

The sorption isotherms of CyA on the three sorbents fit the Langmuir equation (14). 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. Therefore, the amount of CyA sorbed on all of the selected sorbents followed the order ferrihydrite > ferrihydrite-polymerin > polymerin. This trend was confirmed by analyzing both the Langmuir (S_m and K) and Freundlich constants (K_F and N), showing that ferrihydrite sorbed CyA with the greatest binding energy and sorptive intensity (Table 4).

The sorption capacity of CyA on polymerin was similar to that of the phenoxy acid herbicide 2,4-D (12). In particular, the maximum individual sorbed amounts (S_m) of 2,4-D and CyA on the previous biorganic sorbent were 183.1 and 195 mmol kg⁻¹, respectively. On the contrary, the corresponding constants related to the binding energy (K) showed opposite values (8.47 and 3.45 for 2,4-D and CyA, respectively) suggesting a weaker bonding affinity between the functional groups of CyA and the polymerin surface, compared with 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.

No significant sorption was observed for CyA on clays and DOM (64) in comparison with polymerin.

Furthermore, the sorption mechanism of CyA on polymerin, ferrihydrite-polymerin, and ferrihydrite was also investigated, with the aim of elucidating their different sorption capacities (14).

With regard to the sorption mechanism on polymerin, this was very probably consistent with the prevalent formation of hydrogen bonding between the OH alcoholic groups of the polysaccharide component and the nitrile group, the ethereal groups, and the undissociated carboxylic group of CyA ($pK_a = 3.8$).

Therefore, at pH 4.5 the effect of hydrogen bonding was higher than the repulsion between the ionized carboxylic groups of polymerin and the herbicide.

With regard to the sorption mechanisms of CyA on ferrihydrite and ferrihydrite-polymerin, the above results reported the greatest sorption at pH 3.5 on both sorbents. In particular, at this pH both sorbents had completely positive surfaces due to OH₂⁺ groups because of the PZC values, 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 (-COO⁻) of CyA formed ionic bonds with the positive surface of both sorbents. The hydrogen bond to the protonated hydroxylic group presented a very high mobility due to the positive charge on the O atom. In these conditions and considering the aqueous medium where the sorption occurred, it could be supposed that the formation of hydrogen bonds contributed 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 analysis of CyA-polymerin, CyA-ferrihydrite, and CyA-ferrihydrite-polymerin compared with that of CyA, polymerin, ferrihydrite, and ferrihydrite-polymerin (14).

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 for CyA, already observed in the corresponding Langmuir and Freundlich sorption parameters (Table 4): ferrihydrite > ferrihydrite-polymerin > polymerin.

4.2. Cyclic Sorption Process for the Removal of Herbicides from Simulated Wastewater and Its Potential Application in Water Remediation. Cyclic sorption experiments for the removal of paraquat or 2,4-D from simulated wastewater by sorption on polymerin, renewed at each cycle, were carried out at the three different ratios (0.5, 1.25, and 2.5) (12).

Figure 4a shows that total removal of paraquat from solution was achieved after three, five, and four cycles at 0.5, 1.25, and 2.5 solid/liquid ratio, respectively. In contrast, Figure 4b shows a significant but incomplete removal of 2,4-D at all of the ratios. In particular, the quantity of 2,4-D removed remained constant after two cycles at a ratio of 0.5 and no further removal was observed for ratios of 1.25 and 2.5 after four and seven cycles, respectively. These data indicated that a threshold concentration value (0.04 mmol L⁻¹) existed for 2,4-D at which no sorption occurred, and this value was independent of the amount of sorbent and number of cycles. This suggested that at the concentration of 0.04 mmol L⁻¹ the acid-base equilibrium of 2,4-D was strongly in competition with the sorption equilibrium between the undissociated form of 2,4-D and polymerin.

Experiments of cyclic sorption of MCPA or simazine were also performed on polymerin (13) using the same procedure followed for the above herbicides.

The results showed that no individual total removal was possible for both pesticides. Starting from an initial concentration

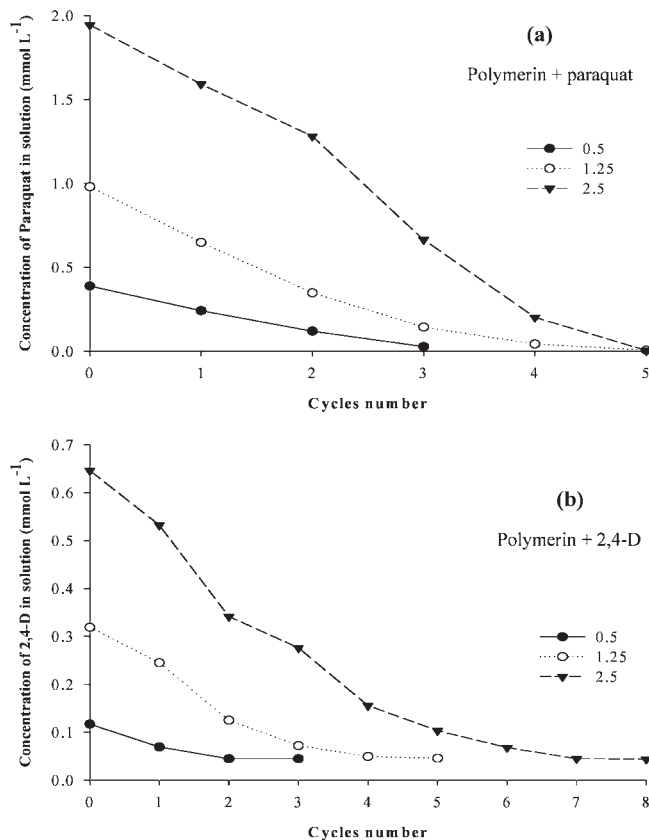


Figure 4. Removal of paraquat (a) or 2,4-D (b) from solutions at solid/liquid ratios of 0.5, 1.25, and 2.5 by cyclic sorption on polymerin (sorbent was renewed in each cycle). Adapted from ref 12.

of pesticides corresponding to 450 and 10.50 $\mu\text{mol L}^{-1}$ for MCPA and simazine, respectively, removals of 83 and 81% were achieved after four and six cycles of sorption, respectively.

The removal of MCPA and simazine from solutions by cyclic sorption on polymerin is shown in Figure 5.

The curves indicated that threshold concentration values of 79.50 and 2.1 $\mu\text{mol L}^{-1}$ for MCPA and simazine existed, at which no sorption occurred, and this value was independent of the amount of sorbent and number of cycles.

The capacity of polymerin to totally remove paraquat from contaminated waters, at native pH and very low ratio (0.5), identified this sorbent as a very suitable biofilter for the potential decontamination of water in point sources. In addition, the sorption caused the release of K, Mg, and Ca from the sorbent, which are macroelements essential in plant and animal nutrition. Therefore, this kind of water could be potentially recycled for irrigation in the same rural zones where point sources occur.

The removal of paraquat from water was performed most efficiently by sorption on polymerin (12) with respect to other considered sorbents, namely, humic acids (55, 61) and other biorganic sorbents (56, 57), suggesting that the most efficient cyclic sorption process should be performed on polymerin.

The removal of 2,4-D, MCPA, or simazine from water by sorption on polymerin (12, 13) proved to be more efficient than that on humic acids (58, 59, 62), but the cyclic sorption process evidenced the limitation that a constant residue remained even after many cycles.

2,4-D showed a high sorbing capacity on activated carbon (60), suggesting this sorbent to be very probably the most suitable for complete removal of the herbicide by cyclic sorption.

In any case, all of the sorption processes considered should require an ultrafiltration plant.

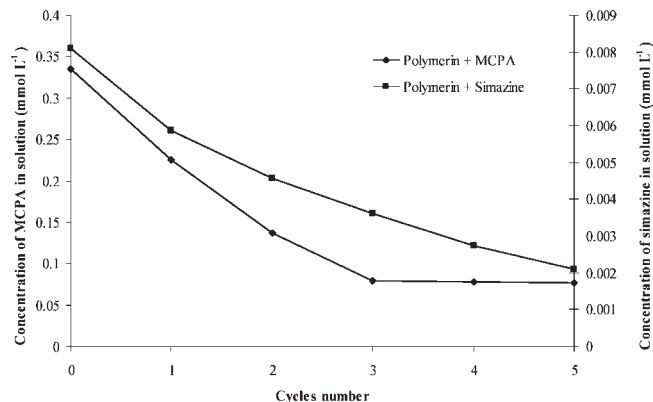


Figure 5. Removal of MCPA or simazine from solution at solid/liquid ratios of 0.5, by cyclic sorption on polymerin (sorbent was renewed in each cycle) (13).

To avoid all of the problems evidenced, experiments were conducted on the removal of CyA from simulated polluted waters by cyclic sorption on ferrihydrite and ferrihydrite-polymerin, in comparison with polymerin (14).

Figure 6 shows that a total removal of CyA on ferrihydrite and ferrihydrite-polymerin was obtained after four and six sorption cycles, respectively, whereas the decontamination was still incomplete on polymerin even after five cycles, leaving a constant residue of 0.11 mmol L^{-1} (14). Therefore, ferrihydrite was shown to be the most efficient sorbent for the removal of CyA from simulated contaminated waters.

In conclusion, among all of the herbicide sorption systems investigated, polymerin has proved to be extremely efficient only for the removal from water of a dicationic herbicide such as paraquat, with the additional advantage of being able to operate in native conditions and release in water useful metals such as K, Mg, and Ca.

Instead, 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 total removal of the herbicide from contaminated waters by four sorption cycles, using the usual procedure of centrifugation for the separation of purified waters. In addition, it could be prepared more easily and at lower cost than the other sorbents and could be recycled by incineration for potential further applications. Finally, ferrihydrite could represent the most efficient means for the individual removal of all the other considered acid herbicides from contaminated waters.

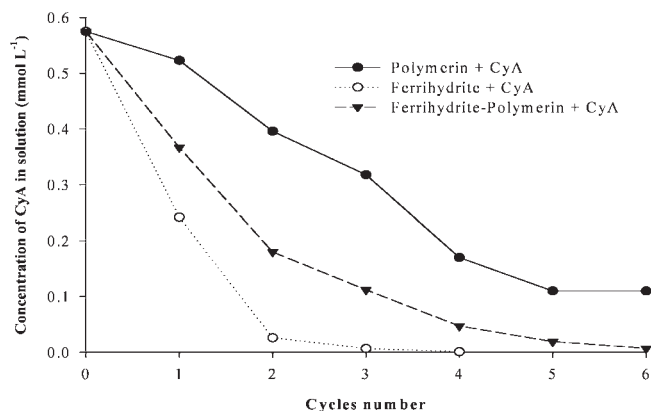
5. REMOVAL OF PHENANTHRENE FROM CONTAMINATED WATERS BY SORPTION ON POLYMERIN, MICRO- AND NANOPARTICLES OF ALUMINUM OXIDE, AND THEIR COMPLEXES

The studies reviewed until now regarded the binding of polar compounds with polymerin. In this section we deal with an overview of the interaction of a nonpolar compound, that is, phen, as a representative of PAHs, with polymerin itself and immobilized on micro- Al_2O_3 or nano- Al_2O_3 particles. Al_2O_3 possesses a positively charged surface, and due to the hydration layer, it is not an effective sorbent for PAHs. By coating the oxides with negatively charged organic matter, it is possible to change the hydrophilic surfaces into hydrophobic ones, which have greater affinity for PAHs.

Several studies have suggested the application of Al_2O_3 coated with anionic surfactants in wastewater treatment techniques (20, 21).

Table 5. Freundlich and Langmuir Parameters of Polymerin (Pol) Sorbed on MicroAl₂O₃ and NanoAl₂O₃ and of Phenanthrene (Phen) Sorbed on Polymerin, MicroAl₂O₃, NanoAl₂O₃, and Pol–MicroAl₂O₃ and Pol–NanoAl₂O₃ Complexes, and on the Corresponding Dpol–MicroAl₂O₃ and Dpol–NanoAl₂O₃ Dry Complexes^a

sorberent	sorberate	Freundlich parameters			Langmuir parameters		
		log K _F (μg kg ⁻¹)	N	R ²	S _m (mg of OC kg ⁻¹)	K	R ²
microAl ₂ O ₃	pol	2.043 ± 0.025	0.63 ± 0.02	0.969	2970 ± 80	0.02	0.990
nanoAl ₂ O ₃	pol	4.424 ± 0.029	0.43 ± 0.02	0.949	203800 ± 5300	0.08	0.994
microAl ₂ O ₃	phen	0.431 ± 0.039	1.06 ± 0.02	0.997	ND	ND	ND
nanoAl ₂ O ₃	phen	1.590 ± 0.024	1.04 ± 0.01	0.999	ND	ND	ND
pol	phen	3.642 ± 0.090	0.88 ± 0.05	0.967	ND	ND	ND
pol–microAl ₂ O ₃	phen	1.370 ± 0.021	0.97 ± 0.01	0.998	ND	ND	ND
dpol–microAl ₂ O ₃	phen	1.365 ± 0.018	0.97 ± 0.01	0.999	ND	ND	ND
pol–nanoAl ₂ O ₃	phen	3.051 ± 0.021	0.98 ± 0.01	0.997	ND	ND	ND
dpol–nanoAl ₂ O ₃	phen	3.270 ± 0.011	0.98 ± 0.01	0.999	ND	ND	ND

^a Adapted from ref 15.**Figure 6.** Removal of cyhalofop acid from solution at solid/liquid ratios of 0.5, by cyclic sorption on polymerin, ferrihydrate–polymerin, and ferrihydrate (sorbents were renewed in each cycle) Adapted from ref 14.

In particular, Valsaraj et al. (21) reported that the adsorption of phen on Al₂O₃ in the absence of surfactant aggregates, called hemimicelles, is generally negligible because nonionic organic compounds interact weakly and nonspecifically with mineral oxide surfaces.

Polymerin could represent an advantageous alternative to the use of surfactants. The use of polymerin instead of synthetic surfactants could be convenient because it derived from a cost-free material and its recovery was very simple and not expensive (the methanol used for precipitation can be totally recovered and recycled). Moreover, because polymerin by itself was soluble in water, it could not be readily used in biobeds, which need solid materials. Thus, by coating Al₂O₃ with polymerin, we might obtain a new solid sorberent for a biobed system.

Therefore, the arguments reviewed in this section are the analysis of the sorption behavior of polymerin on micro- or nanoAl₂O₃, as well as the sorption behavior of phen on polymerin, micro- and nanoAl₂O₃, and polymerin–microAl₂O₃ or polymerin–nanoAl₂O₃ systems (pol–microAl₂O₃ or pol–nanoAl₂O₃, respectively) (15).

Moreover, a possible application of these sorption systems as a filter for remediation of polluted waters contaminated with PAHs is discussed.

5.1. Sorption Data and Mechanism of Polymerin on Micro- and NanoAl₂O₃. The Langmuir isotherms of polymerin on micro- and nanoAl₂O₃ have been previously reported (15). The corresponding maximum sorption capacity (*S_m*) of nanoparticles was almost 2 orders of magnitude higher than that of microparticles (*S_m* = 203800 and 2970 mg of OC kg⁻¹, respectively), at native pH (6.0–6.4) (Table 5). The first reasonable explanation for such a large difference was initially related to the surface area, but, even

if the surface area significantly influenced the sorption, it was not enough to explain the 2 orders of magnitude enhancement: the nano-to-micro surface area ratio was only seven (228/32). Therefore, this high sorption difference of polymerin on micro- and nanoparticles was elucidated by combination of the different surface area and electrostatic attraction with another additional factor (15). In particular, polysaccharide, melanin, and proteins are the main components of polymerin, which is rich in hydroxyl and carboxyl groups and phenol rings. Polymerin also contains paraffinic carbon moieties [i.e., long aliphatic CH₂ chains (7)]. Reaching a microparticle, polymerin could find a wide surface with which to interact. Each macromolecule might bind a microparticle, using multiple functional groups from the same unit, spreading itself on the surface, assuming a *flat configuration* (Figure 7). With regard to nanoparticles, each polymerin macromolecule might find a limited area on the highly charged surface. Polymerin macromolecules might have only one or a few anchor points on the surface, but they should extend out their branches radially from the central focus of the particle toward the solution because they do not have enough space on the surface. Because the charge density is high, several macromolecules are attracted by the mineral surface, forming a *radiant configuration* (Figure 7). Moreover, after the first layer, other macromolecules could be sorbed via both polar and hydrophobic interactions. This *radiant configuration*, along with the contribution from the higher surface area and zeta potential, could explain such a large variation of sorption capacity (203800/2970) between the two different sizes of Al₂O₃ (15).

5.2. Sorption Data and Mechanism for Phen on Polymerin and Micro- and NanoAl₂O₃. The sorption isotherms of phen on the aluminum oxides or polymerin have been reported to fit the Freundlich equation (15). The values of their corresponding parameters are reported in Table 5. Nanoparticles of Al₂O₃ had a sorption capacity much higher than that of microparticles, but polymerin binding capacity was > 2 orders of magnitude higher than the nanoparticle sorption capacity.

The binding mechanism of phen by polymerin might be mainly due to π – π interaction between the catechol–melanine core of polymerin and the aromatic rings of the pollutant (65). Moreover, CH– π interactions with the aliphatic chains might occur, as well as induced dipole–dipole interactions (65). With regard to the mineral particles, phen sorption might be due to a partitioning process between the disorganized bulk aqueous solution and the vicinal water immediately adjacent to the solid surface, more organized and oriented (66).

5.3. Sorption of Phen on Normal and Dried Complexes of Polymerin with MicroAl₂O₃ (Pol–MicroAl₂O₃) and with NanoAl₂O₃ (Pol–NanoAl₂O₃). The complexes composed of polymerin and micro- or nanoAl₂O₃ (15) are referred to as pol–microAl₂O₃

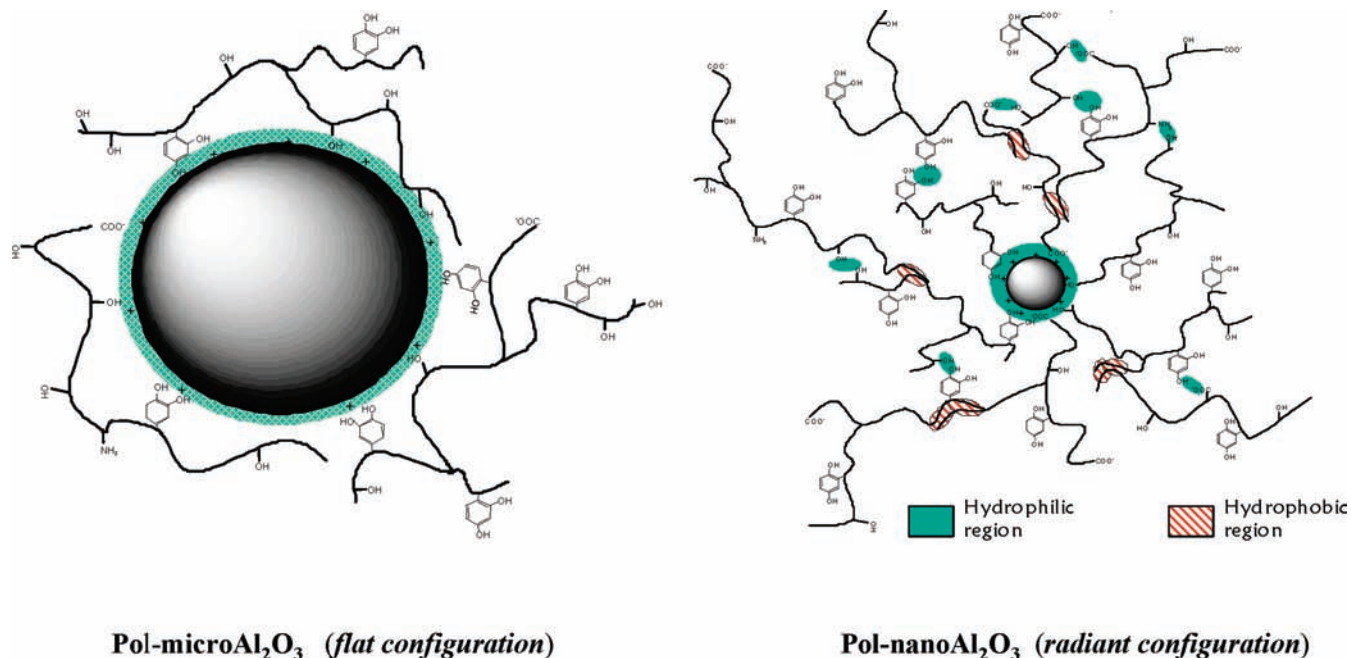


Figure 7. Schematic illustration of the hypothetical interaction between polymerin and aluminum oxides: (left) *flat configuration* of polymerin on microAl₂O₃ (pol-microAl₂O₃); (right) *radiant configuration* of polymerin on nanoAl₂O₃ (pol-nanoAl₂O₃). Adapted from ref 15.

and pol-nanoAl₂O₃, respectively, and their dried forms as dpol-microAl₂O₃ and dpol-nanoAl₂O₃.

The drying treatment of pol-microAl₂O₃ produced dpol-microAl₂O₃, which revealed substantially unchanged sorption capacity of phen with respect to the former complex, as shown by the corresponding log *K_F* values (Table 5). In contrast, the drying treatment of pol-nanoAl₂O₃ produced dpol-nanoAl₂O₃, which showed increased sorption of phen, with respect to the former complex (Table 5).

Because there was no difference between wet and dry complexes in terms of polymerin sorption on the particles, this result can be explained in terms of the conformational change of polymerin chains of the radiant configuration, as previously suggested (15). In particular, in pol-nanoAl₂O₃ the polymerin chains extended their branches in solution, exposing hydrophilic domains and leaving the lipophilic ones relatively inside. During the freeze-drying process, water molecules gradually left the complex, changing the chain configuration. Water molecules on the surface left more rapidly than the ones inside the complex. Therefore, hydrophilic groups of polymerin would rearrange to make contact with the water molecules inside. This rearrangement led polymerin branches to fold, exposing a relatively lipophilic surface and creating hydrophilic domains relatively inside the matrix, so obtaining dpol-nanoAl₂O₃.

In conclusion, among all of the considered sorption systems of phen, polymerin showed the highest sorption capacity, followed by the others in this order: pol > dpol-nanoAl₂O₃ > pol-nanoAl₂O₃ > nanoAl₂O₃ > pol-microAl₂O₃ ~ dpol-microAl₂O₃ > microAl₂O₃ (Table 5).

5.4. Cyclic Sorption Process on Polymerin, Dpol-NanoAl₂O₃, or NanoAl₂O₃ for the Removal of Phen from Simulated Wastewater and Its Potential Application in Water Remediation. PAH contamination is an actual problem. The main anthropogenic sources are the wide and intensive industrial areas. PAHs in the air are in gaseous form or adsorbed on particulates, which tend to fall onto soil, surface water, and plants with the rain. Plants and fruits can also receive PAHs through direct deposition from the air (67); then, once on the skin of the fruits, these pollutants can enter the food chain. The presence of PAHs in fruits, vegetables, and

their transformation products, cultivated in allotments close to industrial areas (67, 68), has been widely demonstrated. Therefore, other than accidental release, the water coming from the washing of the fruits before processing is another typical example of PAH *point-source* polluted water.

As reported in the preceding section, polymerin showed the best sorption capacity of phen, as a representative of PAHs; however, it is a low weight soluble polymer, which requires a more complex and expensive ultrafiltration plant. These findings suggested the use of polymerin associated with Al₂O₃ nanoparticles in a dry complex, that is, dpol-nanoAl₂O₃, for removing PAHs from simulated wastewater.

To this end, a comparative cyclic sorption process of phen on pol, nanoAl₂O₃, or dpol-nanoAl₂O₃, renewed at each cycle, was performed. Experiments of cyclic sorption on these sorbents were conducted for the total removal of phen from simulated polluted waters (procedure not reported).

The results obtained and here reported for the first time (Figure 8) indicate that only two cycles were necessary for the total remediation of water using either pol or dpol-nanoAl₂O₃, whereas too many cycles were required using nanoAl₂O₃ alone (not shown).

These findings supported the application of polymerin associated with Al₂O₃ nanoparticles for removing PAHs in *point sources*.

Polymerin represents a cheap sorbent, and its use could minimize OMWW disposal problem. Thus, the use of polymerin along with Al₂O₃ nanoparticles in water treatment could give both economic and ecologic advantages. In addition, the complex, which is an insoluble solid phase, should be easily filtered by a simple filter system and, so, utilizable in a classical biobed system. Therefore, two reactors in series, equipped with an agitator system, might contain the sorbent. A porous septum between adjacent reactors might avoid sorbent passage. A flow of wastewater could be merged into the system and react with the complex. After the sorption saturation, the dpol-nanoAl₂O₃ system might be recycled by incinerating the organic fraction. The mineral fraction could be recovered and reused for further applications. After the treatment, water passed through the biobed could be reused for irrigation (69).

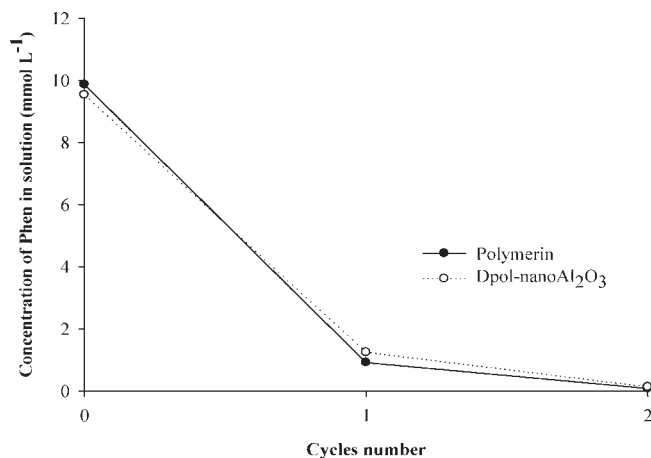


Figure 8. Removal of phenanthrene (phen) from solution by cyclic sorption on polymerin and dpol-nanoAl₂O₃ (sorbents were renewed in each cycle).

As previously reported by Vasaraj et al. (21), even though the specific adsorption capacity of modified alumina may be smaller than that of activated carbon, the former offers other advantages that are of significance: (1) the specificity of removal of target compounds using specific surfactants; (2) removal and recovery of surfactant and solute from a concentrated mixture by conventional unit operations (e.g., distillation); and (3) reuse/recycle of both surfactant and alumina for several treatment cycles.

6. LIGNIMERIN AND H-LIGNIMERIN: PRODUCTION AND CHARACTERIZATION

The cellulose industry is estimated to produce 300 million tons of pulp per year worldwide, generating between 30 and 110 m³ of liquid wastewater per ton of pulp (16, 17). The main environmental impact of the liquid effluent from the cellulose industry on bodies of water is a result of biochemical oxygen demand (BOD₅), toxicity, and the color of the effluent (16, 17). The nonbiodegradable fraction is mainly composed of lignin, tannin, wood extractive compounds, monomers, and halogenated organic compounds, of which lignin and tannin are the main components (16, 17).

Hence, a study was geared toward developing and optimizing a process for obtaining from KCMWW an organic material, named lignimerin (16, 17). Moreover, lignimerin was transformed into its acid derivative, named H-lignimerin, by a cationic exchange method, and both lignimerins were studied in comparison with the previously cited polymerins (polymerin and K-polymerin) (16, 17).

Therefore, an overview is here reported on the production and chemical and spectroscopic characterization of the lignimerins, by comparison with polymerins and pointing out the humic acid-like nature of all the considered complex polymers.

Lignimerin was recovered as a dark and complex salified organic polymeric mixture from KCMWW. The methodology used to recover lignimerin consisted of eight steps, starting from the raw KCMWW. The key steps were the initial filtration, the intermediate precipitation and dialysis, and the final lyophilization, according to the scheme previously reported (16, 17).

Lignimerin was transformed into its protonated derivative, H-lignimerin, by passing the aqueous former organic material through a H⁺-exchange resin and then lyophilizing the eluate of the resin (16, 17).

Tables 1 and 2 show the chemical, physicochemical, and spectroscopic data of the lignimerins in comparison with the polymerins. In particular, **Table 1** shows that the four complex polymers have a characteristic polyphenol content, lignimerin having the highest total aromatic content among

them. The strong UV absorption at 270 nm (**Table 1**) confirmed the presence of the chromophoric phenol rings occurring in the lignin system of lignimerin and melanin system of polymerins. Both systems conferred the brown color to lignimerin and polymerin and consequently to KCMWW and OMWW, respectively.

The DRIFTS data of lignimerin revealed a very strong, broad band at 3300 cm⁻¹, which was consistent with the overlapping of the absorption of the alcoholic OH groups of the lignin system (**Table 2**). A sharp and weak band appeared at 2920 cm⁻¹, arising from the stretching of CH groups of the OCH₃ groups, bound to the phenol rings of lignin, and, in addition, of C-H groups of the CH₂OH. Correspondingly, a band appeared at 1075 cm⁻¹, due to the stretching of the C-OH alcoholic bonding, and another at 1042 cm⁻¹, due to the C-O-C bonding stretching of OCH₃ group. Two other characteristic bands appeared at 1587 and 1420 cm⁻¹, corresponding to the symmetric and asymmetric stretchings of the carboxylate ions, respectively. On the other hand, the low acidity detected in the considered complex polymer, as well as its low amounts of COOH and phenol OH per kilogram (**Table 1**) confirmed the presence of carboxylate and phenolate ions, respectively. Lignimerin showed a metal cation content of 6.93% (**Table 1**), which consisted mainly of Ca (5.19%) and, in decreasing order, Mg and Na (0.41%), Al (0.30%), Fe (0.28%), Mn (0.17%), K (0.09%), Zn (0.05%), and Cu (0.03%) (16, 17).

The metal content decreased from 6.93% in lignimerin to 1.64% in H-lignimerin (**Table 1**). Correspondingly, the total acidity of H-lignimerin strongly increased as well as the values of milliequivalents of carboxylic and phenol OH functional groups (**Table 1**), indicating the transformation of the carboxylate and phenolate ions occurring in lignimerin into the corresponding carboxylic and phenol functional groups in H-lignimerin. The strong and middle bands occurring in the H-lignimerin DRIFT spectrum respectively at 1710 cm⁻¹, due to the CO stretching of carboxyl group, and 1260 cm⁻¹, due to the C-OH stretching of the same group, and the increase the intensity of the band at 3400 cm⁻¹, due the O-H stretching of carboxylic and phenolic groups, confirmed the presence of carboxylic groups in this polymer (**Table 2**).

A comparison of the binding between the samples run in polyacrylamide gel revealed that lignimerin and H-lignimerin presented a molecular mass distribution between 50 and 75 kDa (**Table 1**).

Lignimerin is similar to K-polymerin (10): both showed very similar chemical compositions (**Table 1**) as well as very similar DRIFTS data (**Table 2**). In particular, lignimerin and K-polymerin were shown to be salified to very close extents, 6 and 6.93 mg 100⁻¹ of metal content, respectively, with the only difference being in the metal nature, Ca being the main ion in lignimerin and K in K-polymerin (**Table 1**).

K-polymerin, obtained by hydrolysis and saturation with K of polymerin, might be considered a humate-type polymeric mixture, confirming previous evidence (7, 8). Therefore, lignimerin might also be considered a humate-type polymeric mixture. Direct comparison of the spectroscopic and physicochemical properties of H-lignimerin and humic acids further supported the humic acid characteristics of the former, this being the acid derivative of the humate-type lignimerin (**Table 1**).

In conclusion, lignimerin and H-lignimerin, as well as polymerin and K-polymerin, have been shown to be humic acid-like complex polymers. The only significant difference was that the humification level (E_4/E_6 ratio = 6.72) of the lignimerins was lower than that of polymerins (E_4/E_6 ratio = 3.82) (**Table 1**), this latter value being much closer to that of humic acids (16, 17).

7. REMOVAL OF CU(II) OR ZN FROM CONTAMINATED WATERS BY SORPTION ON LIGNIMERIN AND H-LIGNIMERIN, COMPARED WITH POLYMERINS

Several previous studies have dealt with the use of tannin or lignin as bio-organic sorbents of heavy metals, which are used in the processes of mining, metallurgy, galvanizing, and paint, pigment, and chemical industries, among others (10,11,26,30,31). In particular, recent studies have demonstrated that lignin presented a potential use as a sorbent material for removing metals from liquid media (30, 31). Analogously, lignocellulose material has been investigated for the sorption of Cu(II) and Pb (28).

Hence, both lignimerin and H-lignimerin, described above, were investigated to evaluate their capacity to sorb heavy metals using copper and zinc sorption assays (16, 17). Therefore, an overview is reported on the sorption by both the lignimerins of Zn and Cu(II), dissolved in simulated contaminated waters, by comparison with polymerins and lignins.

Moreover, the data of cyclic sorption of the two metals individually performed on both lignimerins, renewed at each cycle, are reported for the first time, and the potential application of this process in water remediation is briefly discussed.

7.1. Sorption Data and Mechanism for Heavy Metals. The kinetic data for the sorption of Cu(II) and Zn on lignimerin and H-lignimerin were similar in the two sorbents (16). In particular, the sorption equilibrium in the two materials was reached in a contact time of approximately 30 min. The sorption kinetics observed in lignimerin and H-lignimerin was favorable when one considers the projection of a continuous flow water treatment system. The results obtained were comparable to those found for the metal sorption in lignin by Celik and Demirbas (31), with a time for sorption equilibrium of approximately 20 min for most of the metals studied.

Sorption isotherms of Cu(II) and Zn were conducted to supply the maximum sorption capacities of these metals in the sorbents (16). The Langmuir model was used to represent the experimental data. The values of the maximum extraction capacity (S_m) of the material and the affinity constant (b), obtained through the linearization of the Langmuir equation, are previously reported in comparison with polymerin and K-polymerin and are shown in Table 3. The Cu(II) and Zn sorption capacities followed the order lignimerin > H-lignimerin, mainly with regard to the first metal. In particular, lignimerin proved to be the best sorbent for both Cu(II) and Zn, whereas H-lignimerin proved to be a better sorbent for Zn than for Cu(II) (Table 3). The sorption capacity of Cu(II) on polymerin was comparable with that on lignimerin, whereas the sorption capacity of Zn was higher than that on both lignimerins (Table 3). The sorption capacity of both heavy metals on K-polymerin proved to be much higher than on either polymerin or lignimerins (Table 3). However, in view of a potential application in wastewater treatment, the employment of K-polymerin might be less convenient because a further step of production was required, compared with the other sorbents investigated. Anyway, the maximum sorption capacity of both Cu(II) and Zn on lignin (360 and 172 mmol kg⁻¹, respectively) (31) was lower than that on polymerins and lignimerins (Table 3).

The analyses of the sorption mechanism of the lignimerins showed that the surfaces of the sorbents contained mainly acid sites, attributed to carboxylic and hydroxyl surface groups, the hydroxyl sites having a higher affinity for metal ions than the carboxylic sites (16). The metal ion sorption on deprotonated hydroxyl and carboxylic groups was the dominant mechanism, which might explain the sorption behavior observed in lignimerin and H-lignimerin (16).

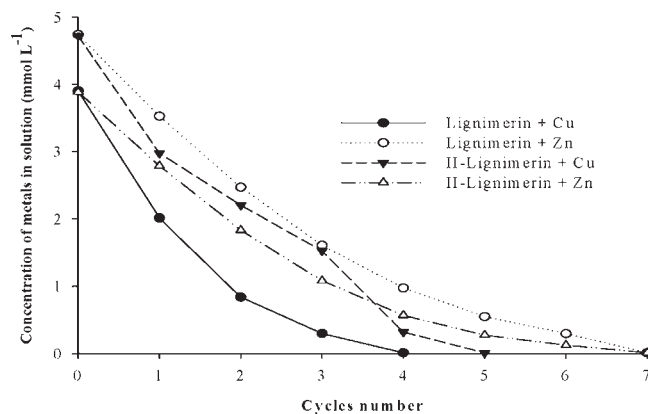


Figure 9. Removal of Zn or Cu(II) from solution by cyclic sorption on lignimerin and H-lignimerin (sorbents were renewed in each cycle).

7.2. Cyclic Sorption Process on Lignimerin and H-Lignimerin for the Removal of Zn or Cu(II) from Simulated Wastewater and Its Potential Application in Water Remediation. The sorption capacity indicated that lignimerins had a potential use as a sorbent for Cu(II) and Zn removal from liquid media. On this basis a cyclic sorption process was conducted, renewing the sorbents at each cycle (experimental procedure not reported).

The data, here reported for the first time (Figure 9), indicated that four sorption cycles on lignimerin and five on H-lignimerin were necessary to totally remove Cu(II) from water, whereas seven cycles were necessary to remove Zn, using either lignimerin or H-lignimerin. These findings indicated lignimerin as more convenient than H-lignimerin for a potential cleanup process of waters in situ, mainly those contaminated with Cu(II), in view also of the ecological exploitation of raw KCMWW. In addition, the material obtained after the wastewater cleanup process could potentially be reused as a potential source of metal after desorption or incineration processes. However, polymerin proved to be a more efficient sorbent than lignimerins and, possibly, than lignin, because three sorption cycles were enough for total individual removal of the two metals from polluted waters (Figure 1a).

8. CONCLUSIONS AND POSSIBLE APPLICATIVE DEVELOPMENT

Polymerin has been shown to be very suitable for the removal of heavy metal cations from simulated polluted waters by cyclic sorption, with the additional advantage to release in water useful metals such as K, Mg, and Ca, natively occurring in the sorbent. More specifically, it has been shown to remove very efficiently Cr(III) and Cu(II), individually or mixed, but, to lesser extent, Zn.

This sorbent has also been shown to be very efficient for the removal of Cr(VI), an anionic form of chromium, because its polysaccharide component was able to transform by redox reaction Cr(VI) into Cr(III), which is the main effective metal retained by the biosorbent and much less toxic than the more oxidized form.

Other sorbents have been reviewed for the removal of Cr(VI) by a cyclic sorption process. It was inferred that the selection of the sorbing system of Cr(VI) was correlated with the concomitant reduction to Cr(III) and the separation method (ultrafiltration, centrifugation, or filtration) as well as the sorption experimental conditions. Therefore, cost-benefit should be evaluated in view of scaling up of the cyclic sorption process.

Polymerin has proved also to be the most efficient sorbent for the removal from water in native conditions of paraquat or phen, representative of dicationic herbicides and PAHs, respectively.

However, the use of polymerin as a biosorbent presents some technological and economical limitations, namely, its very high solubility in water and relative low molecular weight, which require an ultrafiltration plant for a remediation process.

Anyhow, cost-benefit should be evaluated at the industrial-scale level, in view of its possible application, which entails the purification of waters contaminated with cationic heavy metals, cationic herbicides, or phen (and, consequently, PHAs).

On the contrary, polymerin did not appear to be suitable at all for the purification of waters individually contaminated with the herbicide 2,4-D, MCPA, or simazine, because many sorption cycles were required for the abatement of the concentration of the toxic compound and still left a residue at the end of the cyclic sorption process.

2,4-D showed a high sorbing capacity on activated carbon, suggesting this sorbent to be very probably the most suitable for a complete removal of the herbicide by cyclic sorption, but in this case also an ultrafiltration plant should be required.

On the other hand, ferrihydrite and ferrihydrite–polymerin proved to be the most suitable for complete purification of waters individually contaminated with the anionic As(V) and the acid herbicide cyhalofop. As well, dpol–nanoAl₂O₃ was very suitable to purify waters contaminated with phen. In addition, in a potential large-scale application, their solid form could be readily used, for example, in a biobed system, which needs solid materials, avoiding the use of an ultrafiltration plant.

Therefore, a possible exploitation of polymerin complexed with ferrihydrite or nanoaluminum oxide should provide environmental and industrial advantages. First, it was the main byproduct originating from OMWW, and it had a low phytotoxicity (4) and very low BOD and COD values (2). Its use could contribute to the resolution of the problem of disposing of OMWW, which is a highly polluting biomass.

Furthermore, on the basis of the above reviewed studies, both ferrihydrite–polymerin and ferrihydrite could represent the most efficient sorbents for the general removal from contaminated waters of either acid herbicides or metalloid oxianions. Analogously, dpol–nanoAl₂O₃ could represent the most efficient sorbent for the removal PAHs from contaminated waters.

Finally, these matrices could also be easily recycled, by desorption or incineration processes, recovering useful metals.

Lignimerin has been shown to be very suitable mainly for the removal of Cu(II) from simulated polluted waters, so the potential use in situ of lignimerin for cleanup process of waters contaminated with this heavy metal could allow the ecological exploitation of the raw KCMWW. However, in this case also the solubility and the small size of this sorbent deserve to be conveniently evaluated for a possible industrial application.

An outcome of this review also suggests that the use of all of the considered active sorbents, when conveniently mixed together, could be environmentally, technologically, and economically very advantageous for an efficient remediation process of wastewater usually contaminated with mixtures of all of the considered toxic inorganic and organic compounds, exploiting their integrated sorbing capacities toward these compounds.

Finally, with regard to lignimerin and H-lignimerin, even if only one study has been carried out until now of their use as a sorbing system, that is, for heavy metals, their high similarity to polymerin also suggests that further studies for the production of sorbing systems for potential wastewater remediation would be useful.

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