



## Sorption of arsenate and dichromate on polymerin, $\text{Fe}(\text{OH})_x$ -polymerin complex and ferrihydrite

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### ABSTRACT

Dihydrogenarsenate [ $\text{H}_2\text{AsO}_4^-$ , As(V)] or dichromate [ $\text{Cr}_2\text{O}_7^{2-}$ , Cr(VI)] at pH = 4.0 showed to be sorbed on a  $\text{Fe}(\text{OH})_x$ -polymerin complex and ferrihydrite to a greater extent than on polymerin, the organic polymeric fraction of olive oil mill wastewater (OMW). In particular, the maximum amount ( $x_m$ ) of arsenate sorbed on  $\text{Fe}(\text{OH})_x$ -polymerin complex was similar to that on ferrihydrite (880.26 and 743.02  $\text{mmol kg}^{-1}$ , respectively), and was much greater than that sorbed on polymerin (384.25  $\text{mmol kg}^{-1}$ ). The sorption of dichromate was to a comparable extent on  $\text{Fe}(\text{OH})_x$ -polymerin complex and ferrihydrite (205.90 and 254.88  $\text{mmol kg}^{-1}$ , respectively). Cr(III), a less toxic chromium form, mainly, and Cr(V) were indeed the effective forms sorbed on polymerin (200  $\text{mmol kg}^{-1}$ ), as a consequence of the redox reaction of the strongly toxic Cr(VI) with the  $\text{CH}_2\text{OH}$  groups of the polysaccharide moiety of this bio-sorbent, according to the data deriving from XPS and DRIFT analyses. The potential exploitation of the selected sorbents for the removal of As(V) or Cr(VI) from aqueous effluents is briefly discussed.

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### 1. Introduction

The anthropogenic release of heavy metals creates public health problems due to their toxicity and persistence in the environment. There are many sources of metal pollution including manufacturing processes, smelting and refining, electricity generation, and agricultural fertilization [1]. The traditional techniques for the removal of metal ions from aqueous effluents that include ion-exchange, activated carbon sorption, electrodepositing and chemical precipitation are either not able of reducing concentrations to the levels required by law or prohibitively expensive. Biosorption of heavy metals by microbial biomass has been suggested as a potential alternative to the existing physico-chemical technologies for detoxification and recovery of toxic and valuable metals from wastewater [2–4]. The major drawback of these microbial systems is the cost of growing a sufficient quantity of bacterial or algal biomass.

The removal of ion metals by plant tissues has been examined using a variety of biomasses which represent byproducts from other

commercial processes. For example, decaying leaves of *Plantanus orientalis* (Plane tree) can remove Cr and Ni from solution [5]. In a similar fashion, the residues from an apple juice processing factory have been shown to bind a number of heavy metals from aqueous solution [6]. The most promising alternative method for removal of the metal ions uses the sorption by waste materials which requires no cost and are abundant [2,7–9]. More specifically, biomaterials such as condensed tannin gel [10], grape stalk [11] and sphagnum peat moss have shown interesting capacity for the removal of hexavalent chromium. The cost of these biomaterials is negligible if compared to the cost of activated carbon or ion-exchange resins [12,13].

Olive oil mill wastewater (OMW) is a vegetable waste produced in high amounts in numerous Mediterranean countries. The high polluting properties of OMW, as documented by the high chemical oxygen demand (COD) and biological oxygen demand (BOD) [14] render this material inadequate to be discharged into soil and waters. However, the humic-like fraction named polymerin, recovered from OMW [15], could be regarded as a very promising biorganic sorbent for remediation of waters contaminated with heavy metals and/or metalloids, as previously documented for heavy metal cations [8].

Arsenic and chromium are potential contaminants that enter the environment in elevated levels primarily due to anthropogenic

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activities. Arsenate acts as an analogue of phosphate and can uncouple substrate-level phosphorylation in the glycolytic pathway [16]. It may be present at elevated concentrations in surface and subsurface waters as a consequence of the natural weathering of arsenic-bearing minerals [17]. Arsenic concentrations can also increase as a consequence of the anthropogenic discharge of arsenic waste from petroleum refining, glass melting, and smelting of metal sulphide ores or from the use of arsenic-containing pesticides and fertilizers [18]. Consequently, there is increasing public concern about arsenic contamination in water and its effects on human health [19–21].

Chromate is also very toxic to living organisms, as a strong oxidant, a potential carcinogen and corrosive agent [22]. On the contrary, Cr(III), at low concentration, is not toxic to plants and is necessary in animal nutrition [9]; in addition it is used in many industrial processes such as plating, alloying, tanning of animal hides, and as a water corrosion inhibitor. Elevated soil and water concentrations of this potentially harmful element result principally from industrial wastes and spills [23].

The hazards invoked by both arsenate and chromate underline the importance of processes that remove these species from the aqueous phase, reducing or eliminating their bioavailability.

In this paper we report a study in acidic conditions (pH = 4.0) on the individual sorption of dihydrogenarsenate [ $\text{H}_2\text{AsO}_4^-$ , As(V)] and dichromate [ $\text{Cr}_2\text{O}_7^{2-}$ , Cr(VI)] on polymerin, ferrihydrite and  $\text{Fe}(\text{OH})_x$ -polymerin complex, this latter prepared in order to immobilize the polymerin on ferrihydrite and for the significant capacity of  $\text{Fe}(\text{OH})_x$ -organic matter to adsorb heavy metals [24]. In addition, a study of the sorption mechanism of Cr(VI) on polymerin was performed. This investigation was carried out at pH 4.0 because this pH represents a more convenient condition for two reasons: (i) at pH 4.0 Cr(VI) is present completely as dichromate and As(V) as dihydrogenarsenate (i.e. with a single negative charge), and (ii) at this pH polymerin presents a more reduced negative surface ( $\text{p}K_a = 4.5$ ), allowing less repulsion between the surface of this matrix and the two oxyanions. Consequently, for a homogeneous comparative study the same pH conditions have been utilized for ferrihydrite and  $\text{Fe}(\text{OH})_x$ -polymerin complex.

Finally, the environmental, safety and industrial advantages deriving from the possible utilization of these sorbents for the potential removal of the selected oxyanions from wastewater is discussed.

## 2. Materials and methods

### 2.1. Preparation and characterization of the sorbents (polymerin, ferrihydrite and $\text{Fe}(\text{OH})_x$ -polymerin)

Polymerin was prepared and characterized according to the procedure previously reported [15,8].

Ferrihydrite [ $\text{Fe}(\text{OH})_x$ ] was prepared according to the following procedure. A stock solution of 0.01 M  $\text{Fe}(\text{NO}_3)_3$  was potentiometrically titrated to pH 5.5 by adding 1 M NaOH at a feed rate of 0.5 mL  $\text{min}^{-1}$ . A Potentiograph E 536 Metrom Herisau automatic titrator in conjunction with an automatic syringe burette 655 Dosimat was used. The suspension was kept in a propylene container and aged at 20 °C for 1 week. After ageing, the sample was collected and dialyzed in deionized water, freeze-dried and lightly ground to pass through a 100  $\mu\text{m}$  mesh sieve [25].

The  $\text{Fe}(\text{OH})_x$ -polymerin complex was obtained by adding 2.0 g of polymerin to a 0.1 M  $\text{FeCl}_3$  solution (500 mL), and by titrating the solution with 1 M NaOH to reach pH 6.0 using an automatic titrator (Vit 90, Abu 93 Triburet). The precipitate obtained was washed, dialyzed against distilled water to reach a conductivity of 2.0  $\mu\text{s}$ , and then lyophilized.

Specific surface area (SSA) was determined by  $\text{H}_2\text{O}$  adsorption at 20% relative humidity [26]. For X-ray diffraction (XRD) analyses the sample was mounted onto a holder to obtain random particle orientation and analyzed using a Rigaku Geigerflex D/max III C X-ray diffractometer equipped with Fe-filtered  $\text{Co K}\alpha$  radiation generated at 40 kV and 30 mA and a scan speed of  $1^\circ 2\theta \text{ min}^{-1}$ .

The elemental carbon and the metal composition of polymerin and  $\text{Fe}(\text{OH})_x$ -polymerin were determined by HCNS and AAS analysis, respectively, according to the methods described below.

### 2.2. Chemical analysis

The carbon elemental analysis was performed using a Fisons EA 1108 elemental analyzer for hydrogen, carbon, nitrogen and sulphur (HCNS). The metals were determined by a Perkin-Elmer model 3030 B atomic absorption spectrometer equipped with deuterium arc background correction [8]. All glassware, plasticware and storage bottles used were previously immersed for several hours in a solution containing 10% (w/v) concentrated HCl and 20% (w/v) concentrated  $\text{HNO}_3$  (Carlo Erba, Milan, Italy) to avoid any kind of contamination and air dried before use. Stock standard solutions of each metal cation ( $1.0 \text{ g L}^{-1}$ ) were obtained from BDH Reagents (Poole, U.K.). The average and standard deviation of three absorption measurements were recorded for each sample.

### 2.3. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis

Sample preparation for DRIFTS determinations was as follows: 0.20 mg of 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 PerkinElmer Spectrum One FT-IR. The instrument had a resolution of  $1 \text{ cm}^{-1}$ , which was used in all spectra determinations.

### 2.4. X-ray photoelectron spectroscopy (XPS) analysis

X-ray photoelectron spectroscopy (XPS) spectra of raw polymerin and polymerin sorbed with chromium (polymerin-Cr) were performed using a Thermo VG Theta Probe spectrometer equipped with a micro-spot monochromatized Al  $\text{K}\alpha$  source (spot size: 400  $\mu\text{m}$ ). The base pressure of the instrument was  $10^{-9}$  mbar. Neutralization of sample charging was achieved by means of a flood gun using low-energy electrons and  $\text{Ar}^+$  ions. Both survey and high-resolution spectra were acquired in fixed analyzer transmission mode with a pass energy of 150 eV and 100 eV, respectively. Calibration of the binding energy (BE) scale was obtained by fixing the C-C component at BE values of 284.8 eV. Data analysis and curve-fit procedures were carried out using the Thermo Advantage software (version 3.28). XPS characterizations were used to investigate the chemical status of chromium element in the bulk; curve fitting of signals was carried out according to procedure described in Banarjee and Nesbitt (1999) and references therein [27].

### 2.5. Sorption methodology

A 100 mg aliquot of sorbent (polymerin, ferrihydrite,  $\text{Fe}(\text{OH})_x$ -polymerin) previously dried at 100 °C for 1 h, was equilibrated at 20 °C with 20 mL of  $0.03 \text{ mol L}^{-1}$   $\text{KNO}_3$ . Solutions of  $0.10 \text{ mol L}^{-1}$  arsenate or dichromate [as  $\text{NaH}_2\text{AsO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , respectively], were added to each sorbent to give an initial concentration ranging from 0.25 to  $5.00 \text{ mmol L}^{-1}$  for As(V) and 0.25 to  $2.00 \text{ mmol L}^{-1}$  for Cr(VI). The pH of each suspension was kept

constant at pH 4.0 for 24 h by addition of 0.10 or 0.01 mol L<sup>-1</sup> HCl or KOH.

The final suspensions (ferrihydrite or Fe(OH)<sub>x</sub>-polymerin) were centrifuged at 10,000 × g for 30 min and filtered through a 0.22 μm Millipore filter; those containing polymerin as sorbent were centrifuged at 5500 × g for 30 min using Centrifugal Filter Devices equipped with Amicon Ultra membrane with cutoff of 5000 Da.

The final concentration of the two oxyanions was determined in equilibrium solution. As(V) was analyzed by ionic chromatography using a Dionex DX-300 Ionic Chromatograph (Dionex Co., Sunnyvale, CA), an Ion-Pac AS11 column (4.0 mm), an eluent of 0.05 mol L<sup>-1</sup> NaOH at a flow rate of 2.0 mL min<sup>-1</sup>, and a CD20 Conductivity Detector combined with autosuppression [28].

Total chromium in solution was determined by atomic absorption spectrometry (AAS). Cr(VI) in solution was detected by the diphenylcarbazide method [29]: 1,5-diphenylcarbazide forms a pink complex in the presence of Cr(VI) ions in acidic solutions. The concentration of Cr(VI) was calculated from the absorbance at 542 nm using a UV-vis PerkinElmer spectrophotometer. The amount of each oxyanion retained on the sorbents was determined by the difference between the initial quantity added and that present in the equilibrium solution. Sorption isotherms were obtained by plotting the sorbed oxyanion versus its equilibrium concentration in solution. The effective nature and the quantity of sorbed chromium on polymerin was determined by XPS and DRIFTS analyses.

The experimental data were calculated by a computed nonlinear regression analysis, according to the Langmuir equation by the least-squares method.

### 2.6. Automatic potentiometric titration of raw polymerin and polymerin sorbed with Cr(VI)

The potentiometric titration was carried out on dry samples (250 mg) of raw polymerin and polymerin added with Cr(VI) (polymerin-Cr) which were individually dissolved in 100 mL of ultrapure water, brought to pH 12.0 with 2.0 mol L<sup>-1</sup> NaOH and successively brought to pH 2.00 with 0.05 mol L<sup>-1</sup> HCl by an automatic titrator (VIT 909 Videotitrator, Copenhagen) under N<sub>2</sub> stream.

### 2.7. Analysis of the data

All the experiments were performed in triplicate and the relative standard deviation was lower than 3%.

## 3. Results and discussion

### 3.1. Characterization of the sorbents

Polymerin, which was recovered from OMW and chemically and spectroscopically characterized according to the procedure described by Capasso et al. [15], was confirmed to be a humic-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 present in polymerin.

Polymerin was coprecipitated with Fe to obtain an insoluble organo-mineral complex Fe(OH)<sub>x</sub>-polymerin, in order to study the influence of Fe(OH)<sub>x</sub> (a poorly crystalline Fe oxide) on the sorbing capacity of the biosorbent. The chemical and physico-chemical properties of these sorbents are reported in Table 1. Fe(OH)<sub>x</sub>-polymerin complex showed a slightly larger surface area (121 ± 2.8 m<sup>2</sup> g<sup>-1</sup>) than ferrihydrite (110.0 ± 3.0 m<sup>2</sup> g<sup>-1</sup>) attributed

**Table 1**  
Chemical and physico-chemical properties of polymerin and Fe(OH)<sub>x</sub>-polymerin.

Polymerin <sup>a</sup>	
Chemical composition (% w:w)	
Polysaccharide	43.07
Protein	22.40
Melanin	30.20 <sup>b</sup>
Phenol aromatic units	15.02 <sup>c</sup>
Non-phenol aromatic units	15.18 <sup>d</sup>
Metals <sup>e</sup>	Na (0.28), K (1.19), Ca (2.01), Mg (0.65), Fe(0.20), Total = 4.33
Rmw (relative molecular weight) (Da)	First peak: 3500 < rmw < 10,000 Second peak: 45,000
Carbon	45.96
COOH (mmol kg <sup>-1</sup> )	5826 ± 157.30
Phenolic OH (mmol kg <sup>-1</sup> )	3893 ± 109
Fe(OH) <sub>x</sub> -polymerin	
Metals (% w:w)	Fe (44.08)
Carbon (% w:w)	4.79

<sup>a</sup> The data relative to the chemical composition of this biosorbent are already cited by Capasso et al. [8] except for carbon, COOH and phenolic OH content.

<sup>b</sup> Determined by complement to 100 of the sum of the other components.

<sup>c</sup> Determined by chemical analysis.

<sup>d</sup> Determined by difference between b and c.

<sup>e</sup> The total metal composition of polymerin reported as mmol kg<sup>-1</sup> is 1226 [Na (120), K (300), Ca (500), Mg (270), Fe (36)].

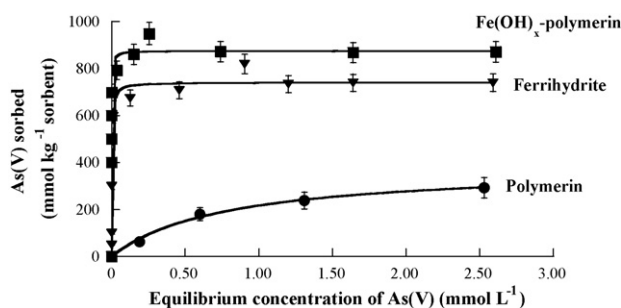
to the presence of polymerin sample coprecipitated with Fe which promoted the formation of an oxide of poorer crystallinity.

### 3.2. Sorption of As(V) or Cr(VI) on polymerin, Fe(OH)<sub>x</sub>-polymerin and ferrihydrite

The individual sorption data were analyzed according to the Langmuir and Freundlich equations.

The Langmuir equation can be written as follows:

$$x = \frac{x_m k c}{1 + k c} \quad (1)$$

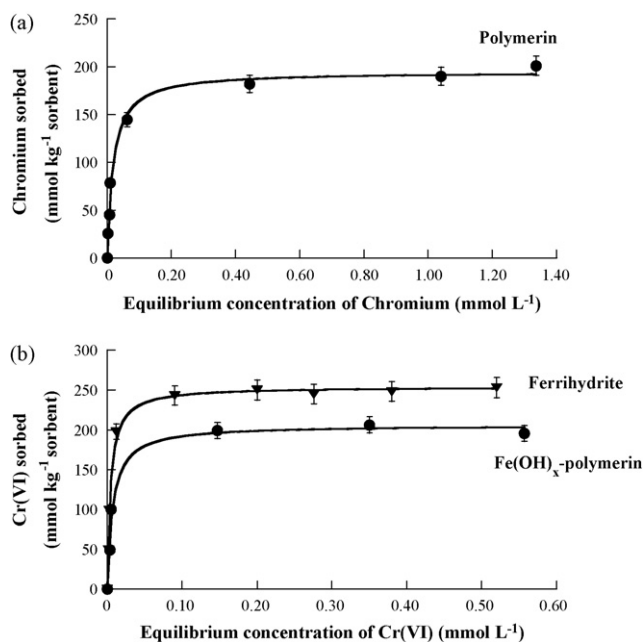


**Fig. 1.** Sorption of As(V) on polymerin, Fe(OH)<sub>x</sub>-polymerin and ferrihydrite.

**Table 2**  
Langmuir and Freundlich parameters for the sorption of arsenic and chromium on polymerin, Fe(OH)<sub>x</sub>-polymerin and ferrihydrite.

	Langmuir parameters			Freundlich parameters		
	$x_m$	$k$	$r^2$ <sup>a</sup>	$K$	$n$	$r^2$ <sup>a</sup>
<b>Arsenic</b>						
Polymerin	384.25	1.29	0.99	194	1.68	0.97
Fe(OH) <sub>x</sub> -polymerin	880.26	1102.78	0.99	1001.84	15.41	0.97
Ferrihydrite	743.02	391.57	0.99	781.27	16.27	0.95
<b>Chromium</b>						
Polymerin	194.78	54.32	0.99	218.0	3.42	0.96
Fe(OH) <sub>x</sub> -polymerin	205.91	136.43	0.99	238.12	6.37	0.96
Ferrihydrite	254.88	228.37	0.99	279.12	13.41	0.96

<sup>a</sup> Correlation coefficient.



**Fig. 2.** Sorption of chromium on (a) polymerin and (b)  $\text{Fe}(\text{OH})_x$ -polymerin and ferrihydrite. The chromium sorbed on polymerin was 75% as Cr(III) and 25% as Cr(V), while its occurrence in solution was only as Cr(VI).

where  $x$  is the amount of anion sorbed on the adsorbent ( $\text{mmol kg}^{-1}$ ),  $k$  is a constant related to the binding energy,  $x_m$  is the maximum amount of anion adsorbed ( $\text{mmol kg}^{-1}$ ) and  $c$  is the equilibrium concentration of anion ( $\text{mmol L}^{-1}$ ), according to Giles et al. [30].

The Freundlich equation is

$$x = Kc^{1/n} \quad (2)$$

where  $x$  and  $c$  are defined in Eq. (1), and  $K$  and  $n$  are the constants that give estimates of the adsorptive capacity and intensity, respectively.

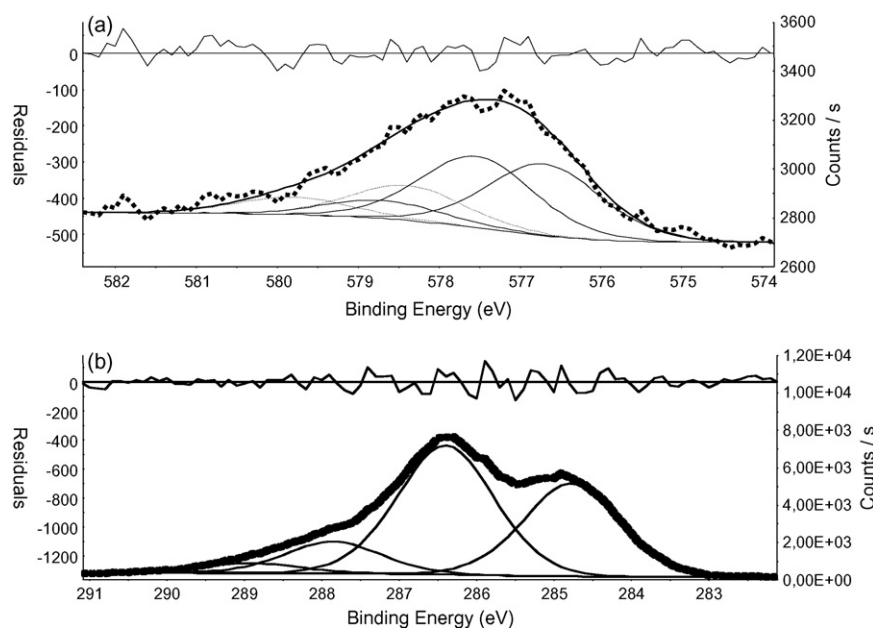
**Table 3**

Acquisition and curve fitting parameters of Cr2p signal for the polymerin–Cr XPS spectrum.

Signal	Binding energy (eV)	FWHM (eV)	Atomic concentration (%)
Cr(III) total: 75.52%			
CrIII	576.7	1.72	$33.60 \pm 0.84$
CrIII	577.5	1.72	$33.38 \pm 0.66$
CrIII	578.7	1.72	$8.54 \pm 0.23$
Cr(V) total: 24.47%			
CrV	578.4	1.72	$16.31 \pm 0.18$
CrV	579.8	1.72	$8.16 \pm 0.23$

The sorption isotherms of As(V) on polymerin,  $\text{Fe}(\text{OH})_x$ -polymerin and ferrihydrite (Fig. 1) fitted the Langmuir equation. The shapes of the isotherms were different and were distinguished by the initial slope. The sorption of As(V) on polymerin increased slowly when the oxyanion equilibrium concentration increased. These findings might be attributed to a weak affinity for each other. Very probably, arsenate binds 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  $\text{Fe}(\text{OH})_x$ -polymerin and ferrihydrite (Fig. 1) indicated a high affinity behavior, the sorption being characterized by a rapid rise at low As(V) equilibrium concentration. In fact, at a  $0.25 \text{ mmol L}^{-1}$  equilibrium concentration of As(V), the amount of sorbed oxyanion significantly increased from  $60 \text{ mmol kg}^{-1}$  on polymerin to  $700$  and  $820 \text{ mmol kg}^{-1}$  on ferrihydrite and  $\text{Fe}(\text{OH})_x$ -polymerin, respectively; therefore, the amount of As(V) sorbed on the three sorbents followed the order  $\text{Fe}(\text{OH})_x$ -polymerin > ferrihydrite > polymerin. This trend was confirmed analyzing the values of the Langmuir constants,  $x_m$  and  $k$ . The data also fitted the Freundlich equation, as supported by the high values of  $r^2$  (Table 2).

The high sorption of As(V) on ferrihydrite is attributable to the formation of inner-sphere complexes. It is well known that the arsenic mobility in natural systems is controlled primarily by sorption onto metal oxide surfaces [31–34] involving surface complexation reactions in which the oxygen moiety of the As(V) displaces an hydroxyl group on the metal oxide surface to generate an inner-sphere complex [21]. Arsenate may form



**Fig. 3.** Curve fittings of (a)  $\text{Cr}(2p_{3/2})$  and (b)  $\text{C}1s$  Shirley background subtracted spectra. The thick solid curves represent the best fit to the spectral data and residuals are shown in the upper region of both figures. (a) The thin solid curves represent the Cr(III) multiplet peaks and the dotted curves represent the Cr(V) (see Table 3). (b) The thin solid curves represent the peaks of the several carbonaceous species (see Table 4).



**Table 4**  
Acquisition and curve fitting parameters of C1s signal for the raw polymerin and polymerin–Cr XPS spectra.

Signal	Binding energy (eV)	FWHM (eV)	Atomic concentration %
<b>Raw polymerin</b>			
CH (–CH <sub>3</sub> , –CH <sub>2</sub> , –CH)	284.8	1.53	36.27 ± 0.90
C–(O, N) (ether and amino acid bindings)	286.4	1.53	48.01 ± 1.05
(C=O)	287.8	1.53	11.97 ± 0.27
O=C–O	288.9	1.53	3.75 ± 0.075
<b>Polymerin–Cr</b>			
CH (–CH <sub>3</sub> , –CH <sub>2</sub> , –CH)	284.8	1.57	31.27 ± 0.75
C–(O, N) (ether and amino acid bindings)	286.3	1.57	48.95 ± 0.88
(C=O)	287.7	1.57	14.08 ± 0.35
O=C–O	288.9	1.57	5.70 ± 0.11

three different surface complexes on inorganic soil components: a monodentate complex, a bidentate–binuclear complex, and a bidentate–mononuclear complex in different proportions, depending on surface coverages [35,28]. The higher sorption of As(V) on Fe(OH)<sub>x</sub>–polymerin compared to ferrihydrite, although slight, is consistent with the larger surface area of the former sorbent, as previously reported (121 ± 2.8 and 110 ± 3.0, respectively).

The individual sorption of Cr(VI) on the three sorbent systems selected was characterized by the corresponding isotherms (Fig. 2a and b), which fitted the Langmuir and Freundlich equations (Table 2). In particular, the sorption isotherm of chromium on polymerin appeared as a L-form (Fig. 2a). However, XPS and DRIFT investigations showed that on polymerin Cr(III), mainly, and Cr(V) were the effective sorbed chromium forms which formed by the redox reaction at pH 4.0 of Cr(VI) with the CH<sub>2</sub>OH groups of the polysaccharide moiety of this sorbent.

In fact, X-ray photoelectron spectroscopy analyses (Fig. 3 and Table 3) performed on polymerin sorbed with chromium (polymerin–Cr) confirm the presence of Cr(III) species on the sorbent. Curve fitting of Cr(2p<sub>3/2</sub>) Shirley background subtracted XPS spectrum (Fig. 3a), which were carried out using curve fitting parameters as reported in Table 3, indicated the presence of chromium mainly as trivalent form (75% atomic concentration). A smaller amount of chromium sorbed onto polymerin according to XPS results was likely to be present as Cr(V) (25%). Furthermore, XPS results (Fig. 3b and Table 4) also showed an increase of carboxylate groups (O=C–O signal, 5.70%), as well as a decrease of the

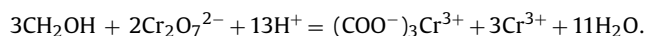
CH<sub>2</sub> groups (C–H signal, 31.27%) in polymerin–Cr compared to the raw polymerin (3.75 and 36.27%, respectively). The potentiometric analysis performed on polymerin–Cr confirmed the increase of COOH groups (6326 mmol kg<sup>–1</sup>) with respect to the raw polymerin (5826 mmol kg<sup>–1</sup>, Table 1).

The transformation of Cr(VI) into Cr(III) form sorbed on polymerin at pH 4.0 was confirmed by the DRIFT spectrum (Fig. 4b) of this sorption system. In fact, the band at about 1072 cm<sup>–1</sup>, attributed to the stretching of alcoholic C–OH binding of polysaccharide moiety of polymerin at pH 4.0 [8] was strongly reduced, as compared to the raw polymerin spectrum registered at pH 4.0 (Fig. 4a), as a consequence of the oxidation of the CH<sub>2</sub>OH groups into COO<sup>–</sup> groups. In fact, two characteristic bands appeared in the spectrum of Fig. 4b centered at 1612 (more intense) and 1397 cm<sup>–1</sup> and were to be mainly attributed to the respective asymmetric and symmetric stretching of carboxylate ion, as inferred by our previous researches on the salified polymerin [8]. In addition, the correlated bands occurring in the spectrum of polymerin (Fig. 4a) centered at 2920, 1720, 1433, 1348 and 1245 cm<sup>–1</sup>, due to the carboxymethyl groups [8], appeared strongly reduced in the spectrum of polymerin–Cr (Fig. 4b). This finding clearly suggested the previous groups to be hydrolyzed in the presence of protons and Cr(III), which in turn bound to the liberated corresponding COO<sup>–</sup> groups. This behavior is also confirmed by the decrease of –CH<sub>3</sub> groups detected by XPS analysis of raw- and Cr–polymerin (see Table 4).

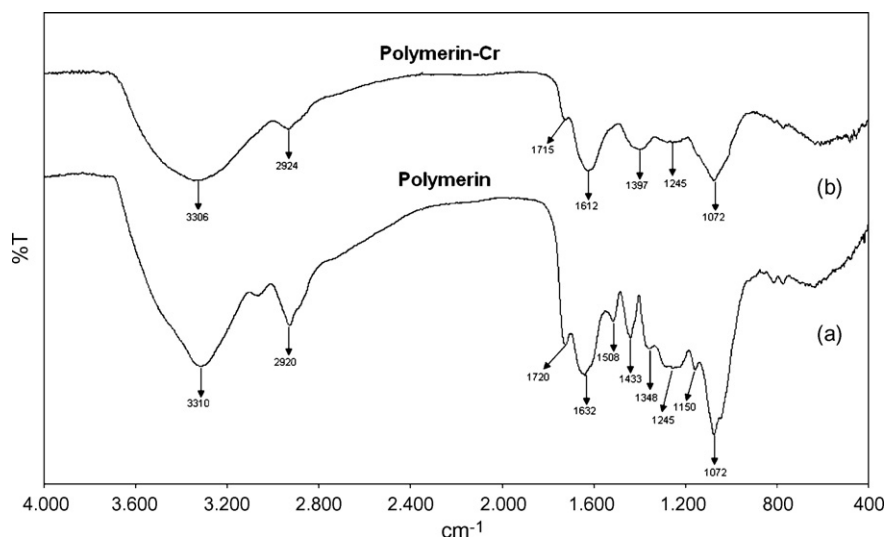
The specific colorimetric analysis of Cr(VI) [29] indicated the only presence of this chromium form in the supernatants, its amounts being coincident with the total amount 1.20 mmol L<sup>–1</sup> detected by AAS. These findings suggested that Cr(VI) present in the supernatant to be the remaining part of unreacted oxyanion.

The maximum sorption capacity of chromium [Cr(III) and Cr(V)] is 200 mmol kg<sup>–1</sup>, corresponding to 100 mmol kg<sup>–1</sup> of Cr(VI) (i.e. 21.60 g kg<sup>–1</sup>). This latter amount was almost comparable to that (35.00 g kg<sup>–1</sup>) reported by Dupont and Guillon [36], for the sorption of the same oxyanion on a lignocellulose substrate, where it proved to be analogously transformed into Cr(III) in acidic medium.

Therefore, the sorption of Cr(III) on polymerin should be derive by the following reaction:



Cr(III) in part bound to the new COO<sup>–</sup> groups, i.e. deriving from the oxidation of –CH<sub>2</sub>OH, in remaining part bound to those deriving from carboxymethyl groups. Each Cr(III) was probably in turn



**Fig. 4.** DRIFT spectra of (a) polymerin and (b) polymerin–Cr.

chelated by three OH groups of polymerin polysaccharide moiety, forming exa-coordinated very stable structures. No investigation was performed on the mechanism of formation of Cr(V) from Cr(VI). However, it could be deriving from an incomplete reduction of Cr(VI) rather than an intermediate reaction.

As regards to the sorption of Cr(VI) on ferrihydrite and Fe(OH)<sub>x</sub>-polymerin, the isotherms reported in Fig. 2b fitted the Langmuir and Freundlich equations (Fig. 2b and Table 2). Sorption of chromium on both sorbents increased slowly with increasing metal equilibrium concentration, according to a L-form. Furthermore, the amount of Cr(VI) was lower on Fe(OH)<sub>x</sub>-polymerin compared to ferrihydrite, despite the larger surface area of the former. This behaviour could be explained considering on ferrihydrite the occurrence of positively charged groups (–OH<sub>2</sub><sup>+</sup>) capable to bind the dichromate ions [Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>] by electrostatic binding. The decrease of the sorbed chromium on Fe(OH)<sub>x</sub>-polymerin is attributable to the presence of organic component (polymerin) that partially covers the positive available sites of the Fe(OH)<sub>x</sub> species. Finally, the only chromium specie present in the previous system is Cr(VI), very likely because of the presence of a very low amount of polymerin (see Table 1), and therefore a scarce involvement of this organic component in the redox reaction with Cr(VI).

#### 4. Conclusions

Among the three sorbent systems investigated for the sorption of As(V), the most convenient for the potential removal of this oxyanion from wastewater proved to be Fe(OH)<sub>x</sub>-polymerin ( $x_m = 880.26 \text{ mmol kg}^{-1}$ ), as compared to ferrihydrite ( $x_m = 743.02 \text{ mmol kg}^{-1}$ ) and polymerin ( $x_m = 384.25 \text{ mmol kg}^{-1}$ ). Instead, polymerin proved to be the most convenient one for the removal of Cr(VI), even if in this latter form it was sorbed to a lesser amount ( $100 \text{ mmol kg}^{-1}$ ) compared to ferrihydrite ( $x_m = 254.88 \text{ mmol kg}^{-1}$ ) and Fe(OH)<sub>x</sub>-polymerin ( $x_m = 205.91 \text{ mmol kg}^{-1}$ ). In fact, Cr(III) was the main effective form fixed on polymerin ( $200 \text{ mmol kg}^{-1}$ ), which was produced by the redox reaction of Cr(VI) with this sorbent, as explained above. The remaining sorbed form Cr(V) could be also transformed to Cr(III) by desorbing the chromium from polymerin–Cr and retreating the desorbed heavy metal with new raw polymerin. Analogously, the unreacted Cr(VI) could be transformed into Cr(III) by cyclic sorption on polymerin renewed at each cycle, applying the same procedure previously described for the purification of waters contaminated with Cr(III) [8]. The final advantages should be the purification of waters contaminated with the strongly toxic Cr(VI) and recover a less toxic Cr(III) which is also of considerable biological [9] and industrial interest [23]. As an example of a possible application in environmental technology processes, polymerin could be potentially utilized to re-generate Cr(III) from Cr(VI) formed in the oxidation process of some tannery plants, before these wastes are discarded.

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