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Adsorbent properties of olive mill wastes for chromate removal

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ABSTRACT

The removal of chromate ions from aqueous solutions by adsorption onto two different olive mill waste materials was investigated using batch rate experiments. The solid material was obtained from olive mill wastes coming from two different extraction plants, two phase continuous, and discontinuous plant. The initial absence of chromium in the material was confirmed through scanning electron microscope equipped with Energy Dispersive X-ray analyzer. The adsorption analysis has demonstrated that both biomasses are able to adsorb chromate ions. An accurate analysis of polyphenols has highlighted that the presence of polyphenols does not interfere with the adsorption of chromate ions. A heterogeneous kinetics model provided the parameters of the adsorption kinetics within all the time ranges explored. For each biomass, a critical initial chromate concentration exists beyond which the adsorption process becomes independent of the initial chromate concentration. The results indicate that olive mill wastes may be reused as an adsorbent material for chromate ions removal by means of an ecologically friendly technology.

Keywords: Biomass; Olive mill waste; Chromate; Adsorption

1. Introduction

Ecologists have suggested that our age is the era of limits recognition. Indeed, modern agriculture has caused a series of environmental problems, such as erosion and chemical contamination of soils [1]. In this context, the disposal of olive mill wastes is a major concern for the Mediterranean countries where more than 30 × 10^3 m^3 both liquid and solids oil residues are produced during the short harvest period [2]. Because of their versatility, chemical physics methods are utilized for many applications, including environmental remediation, food chemistry, and a number of biotechnological processes [3–7]. In general, the oil separation from the olive paste is traditionally done with presses (traditional method) but nowadays, it is

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done by centrifugation and selective filtration (two-phase method). The traditional method requires the addition of water and yields a very high-quality olive oil. This procedure has the disadvantage of being a batch process and to require hard work for producing small quantities of oil. Conversely, the two-phase method is a continuous process that produces olive oil with low labor costs [8]. With this method, large amounts of olive mill wastewaters are produced [9]. Therefore, the amount of olive mill wastes and their composition depend on the kind of production process. Typically, this wastewater is characterized by an intensive dark brown to black color and strong acidic smell unique to olives. The high concentration of polyphenols, which are toxic to bacteria commonly used in biological oxidation plants, is an important negative property of olive mills wastewater. Indeed, olive mill wastes have a higher phenolic content than olive oil itself [10]. Furthermore, polyphenol antioxidants in olive oil are only 1–2% of the available pool of antioxidants in the olive fruit. The remainder is lost either in olive mill wastewaters or in pomace. Therefore, the recovery of phenolic compounds from olive mill wastewaters can be very valuable, not only from an environmental standpoint, but also because these compounds might be useful in pharmaceutical, food, and cosmetic industry [2,11,12]. If the wastewaters were discharged directly into natural waters, they would constitute a great risk for the aquatic ecosystem, while the direct discharge into the sewage could affect negatively the subsequent biological wastewater treatment. Therefore, guidelines to manage these wastes through technologies that minimize their environmental impact and lead to a sustainable use of resources are needed [13]. Recently, several authors have proposed the use of olive mill wastes as low-cost materials to adsorb heavy metals [14–18]. The methods suggested, however required vigorous chemical treatments of the material, discouraging producers of olive oil to use them in the production cycle [19,20]. In this paper, we show how it is possible to use olive mill wastes for detoxifying waters polluted by chromate ions, which is one of the most dangerous among heavy metals. The Agency for Toxic Substances and Disease Registry, classifies Cr(VI) as the 16th most dangerous substance known [21,22]. Hexavalent chromium compounds readily penetrate cell membranes via anion transport systems and therefore, they are known to be toxic to humans, animals, plants, and microorganisms [23]. In this paper, the sludge, coming from traditional method and the wet pomace from two-phase method, is used to adsorb the chromate ions. Moreover, to check the influence of biomass, surface characteristics and composition on the adsorption process was evaluated by washing treatments with water. This work aims to provide new tools to solve not only the problem of olive mill wastes disposal, but also the treatment of toxic effluents.

2. Materials and methods

2.1. Chemicals and reagents

Potassium chromate and 1,5-Diphenilcarbazide were from Carlo Erba Reagenti, Milan Italy. Reagent grade Caffeic acid (3-(3,4-Dihydroxyphenyl) 2-propenoic acid) was obtained from Acros Organics (Carlo Erba Spa, Milan Italy). Water was twice distilled in all quartz devices.

2.2. Biomasses

Two different kinds of biomass coming from a traditional olive mill and a two-phase extraction plant, respectively, were used to test their ability to adsorb chromium from aqueous solutions. The traditional olive mill uses hydraulic presses for the extraction of olive oil from olive paste. When applying pressure to diaphragms covered by a layer of olive paste, the liquid phase (oil and water) runs through the olive cake and it is a water-in-oil emulsion containing a solid residue as a thin particulate that stabilizes the emulsion. The biomass from the traditional olive mill comes from the final centrifugation/filtration step, also called racking of the oil. In this step, the initial water-in-oil emulsion or veiled olive oil is separated into oil and an aqueous semi-solid waste containing the sludge. This olive mill waste was collected from an oil mill and stored at 18˚C to prevent spoilage until use. Hereafter, this sample will be named biomass S. The second type of biomass derived from a two-extraction mini plant laboratory, with a capacity from 50 to 100 kg/h (OLIOMIO, Toscana Enologica Mori) that crushed the olives with a hammer crusher and gave as a result oil and olive pomace. The previous steps of washing and defoliation were made by hand, so it was possible that some leaves were crushed with olives and ended up in the olive pomace. This olive wet pomace is a pulpy material containing oil, water, small pieces of kernel, pulp debris, and pieces of leaves. It was stored at 18˚C straightaway until use. Hereafter, this sample will be named biomass WP. The olives used by both extraction plants were from different areas of Molise (Italy).

2.3. Preparation of adsorbent

Equal amounts of olive mill waste and olive wet pomace were centrifuged at 800 rpm for 20 min at room temperature to separate the liquid phase from the solid material. The solid material was treated with n-hexane to remove traces of oil and then was dehydrated by ethanol. These solid residues were stored in a dryer until constant weight. The separation yields of solid material (biomass) from the two different olive wastes were: 4 wt% for olive mill waste from the hydraulic presses (biomass S) and 30 wt% for Olive Wet Pomace, two-phase extraction (biomass WP).

2.4. Morphology and microanalysis

The scanning electronic microscope (SEM) images and quantitative X-ray analysis were obtained using Zeiss DSM 940 scanning electron microscope equipped with Link System inca Energy Dispersive X-ray analyzer (EDXRA). Scanning electron microscopy observation was made operating at 10 kV to monitor the morphology of the samples. Different samples of biomass were mounted and dried on aluminum stubs, and were performed at 20 kV using a working distance of 35 mm with a spot of 15 μm and applying the ZAF standard matrix correction procedure to convert X-ray into weight percentage.

2.5. Kinetics study of chromate ions adsorption

All measurements were carried out at 25˚C and chromate ions decrease was determined by recording absorbance change at $\lambda_{\max} = 540$ nm. The reactions were started by adding 500 mg of weighted biomass to 50 mL of solution containing potassium chromate. The samples were placed in a shaking water bath oscillating at 30 rpm. At regular time intervals, samples of solution were withdrawn from the reaction medium and spectrophotometrically analyzed. Chromate adsorption was determined from difference between initial and final solution concentrations with appropriate corrections based on blanks.

2.6. Analytical methods

A colorimetric method was used to measure the concentrations of chromate ions. The pink colored complex formed from 1,5-Diphenylcarbazide and Cr (VI) in acidic solution was analyzed with a Varian Cary 100 UV–vis spectrophotometer equipped with thermostated cells. The polyphenols content released in water by biomass when the experiments were measured using the Folin–Ciocalteau colorimetric method [24]. In a 25-mL volumetric flask, 0.5 mL of aqueous solution from adsorption experiments was mixed with 5 mL of Folin–Ciocalteau reagent diluted 1:10 with water. After 3 min, 5 mL of Na_2CO_3 10 wt% was added and the mixture was put in a water bath at 45˚C for 15 min. After this time, the mixture was taken to 25 mL with distilled water and then the absorbance was measured at 750 nm against a blank. The polyphenolic content was expressed as mg equivalent caffeic acid/kg using a calibration curve. All experiments were done in triplicate.

3. Results and discussion

3.1. Morphology of biomass

From a macroscopic point of view, the biomass S appeared as a dark brown powder with uniform small particles. The biomass WP, instead, showed a more heterogeneous aspect with the coexistence of coarse particles (pieces of kernels) and fine particles with a general light brown color. By observing these two materials through SEM, some important differences can also be found and confirmed at the microscopic scale (Fig. 1).

In the biomass S (Fig. 1(A)), the particles are on average between 50 μm and below 1 μm. By having a look at the surface of these small particles, many pores are visible on a rough surface. Many pores are present also on the rough surface of the biomass WP particles but here the pores have larger size on an average, since the particles are larger in biomass WP, spanning from 200 μm to the order of mm (Fig. 1(B)). In Fig. 1(B), some tracheid structures are shown that give evidence of the presence of some leaves during the milling process. The porosity and roughness of the surface is a characteristic shared by both biomasses that can be accounted for the adsorption properties of these materials. The roughness increases the surface available for adsorption and this effect will be higher for smaller particles. In fact, the smaller the particles, the higher the surface to volume ratio and this fact may favor the absorption properties of the material. Other characteristics involved in the process of adsorption may be the presence of specific elements or chemical groups on biomass surface. The elemental composition was measured in different parts of the sample with EDXRA. The results are summarized in Table 1. It is worth noting the initial complete absence of chromium on both biomasses. Moreover, the two biomasses differ in some elements. The oxygen content is practically the same for both biomasses, while Mg is present only in the biomass WP. Finally, Cu is found only in the biomass S. The presence of Mg in biomass WP is due to the presence of shredded leaves containing chlorophyll. Conversely, the presence of Cu in the biomass S may be due to residues of copper antifungal treatments [25].

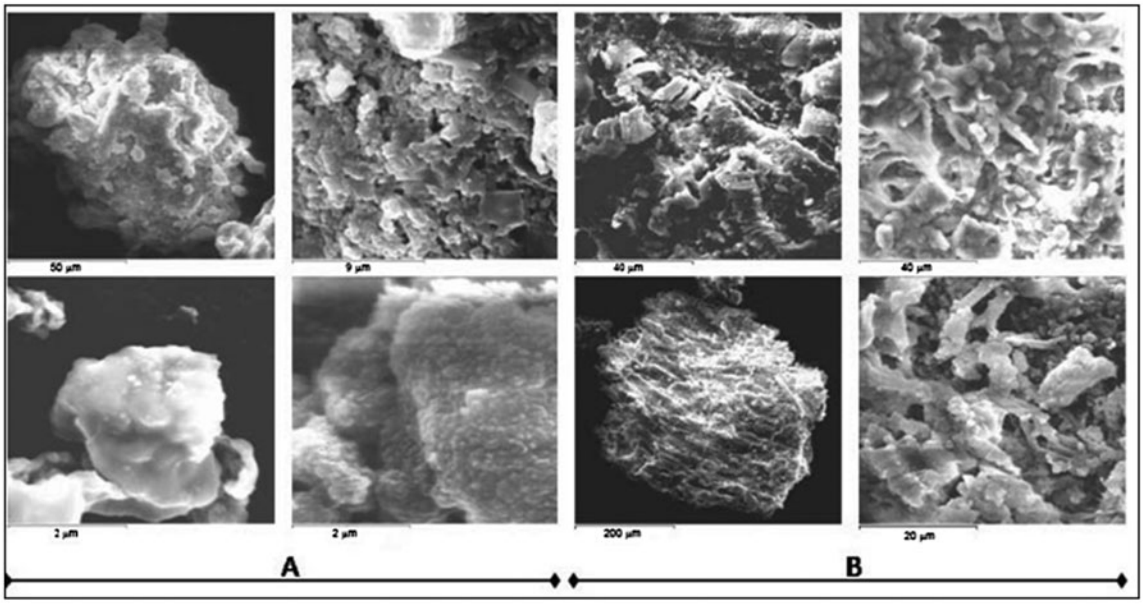

Fig. 1. Microphotographs obtained by scanning electronic microscopy at different magnifications, for biomass WP (A) and biomass S (B).

Table 1
Quantitative X-ray analysis

Element	WP(%)	S(%)
O	71.0	72.0
Mg	0.6	0.0
Si	0.7	1.7
P	1.3	1.1
S	1.4	2.1
Cl	0.8	1.3
Cu	0.0	2.0
K	20.8	15.4
Ca	3.5	4.4

3.2. Uptake kinetics

Chromate ions adsorption is significantly affected by the initial concentration of ions in aqueous solutions. In the present study, the initial chromate concentration is varied from 2.5 to 250 mg/L, while maintaining the biomass dosage at 10 g/L and pH 5.5. Fig. 2 shows residual chromate ions concentration in aqueous solution as a function of the contact time with biomass S and WP. As it can be seen, the initial uptake of chromate ions is rapid for all experiments, but slow uptake continues up to 100 h, depending on the initial chromate concentration. This acute jump in the initial step of adsorption process may be considered as indicative of a fast initial external mass transfer step. However, such a fast rate of initial chromate ions removal may also be the result of chemical ion-surface interaction. Generally, the description of these processes is based on the solution of partial differential equations. If a well-defined shape for biomass particles is assumed, such approach provides an accurate representation for the chromate ions concentration *C(t)* during the adsorption process. Recently, we suggested that the parameter lifetime τ (the meaning of which emerges naturally from the Laplace transform domain representation of diffusion equation [26–28]) indicates the chemical affinity between the solute and binding sites, and thus represents a helpful tool for such kind of item. In particular, we showed that the function lifetime is a measure of the global rate of adsorption, while its initial contribution.

$$\frac{1}{\tau_I} = \lim_{t\to 0}\left(\frac{d}{dt}\frac{C(t)}{C_0}\right) \tag{1}$$

is related to the mass transfer of solutes on solid material. Eq. (1) indicates that the parameter τ_I^{-1} can be directly calculated from the slope at $t = 0$ of a plot of $C(t)/C_0$ vs. time, where $C(t)$ and C_0 are the chromate concentration at time t and the initial chromate concentration. To analyze the τ_I^{-1} (h^{-1}) course with the C_0 ($mg\,L^{-1}$), values calculated by means of Eq. (1) were plotted vs. C_0 Interestingly, by plotting $1/\tau_1$ vs. initial concentration, an estimation of the reaction order can

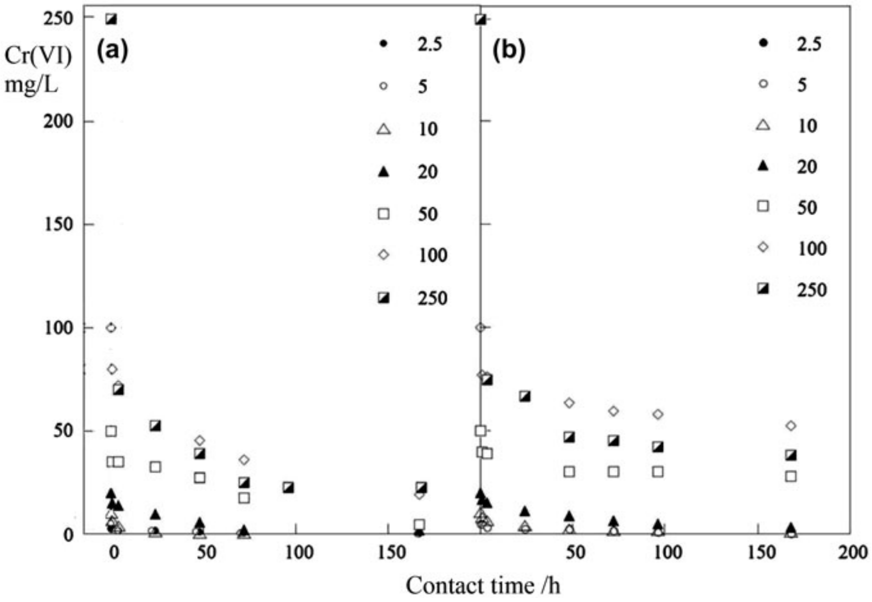

Fig. 2. Chromate ions concentration over time for biomass S (a) and biomass WP (b). The experiments were carried out at pH 5.5, mild agitation and temperature 25˚C. The numbers in the plots represent the initial concentration.

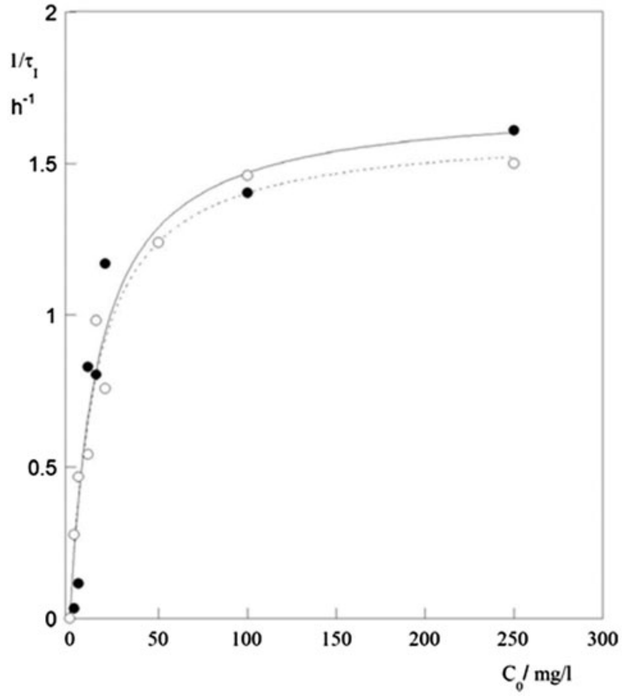

Fig. 3. Initial lifetime of the adsorption process, for biomass S (●) and WP (○), as a function of the initial chromate concentration.

be obtained (Fig. 3). The results gathered on both biomasses can be fitted by the following empirical equation:

$$\frac{1}{\tau_I} = \frac{(1.66 \pm 0.09)C_0}{(16 \pm 3) + C_0} \tag{2}$$

The term 16 ± 3 has units of concentration (mg/L). From Eq. (2) it is evident that at high initial concentrations, $C_0 >> 16$ mg/L, $1/\tau_1$ approaches the maximum ($1.66\ h^{-1}$). At this value, the biomass can be considered "saturated," i.e. the rate is independent of the initial concentration. Furthermore, as $C_0 << 16$ mg/L, the rate increases linearly with the initial concentration according to the $1/\tau_1$ = value ($0.10\ C_0\ h^{-1}$). The kinetic equation resembles that of enzymatic catalysis, so that, by similarity, we can denote the term 16 ± 3 mg/L as the "affinity" between biomass and chromate ions, while the coefficient $1.66 \pm 0.09\ h^{-1}$ is the maximum rate.

If adsorption occurs through external mass transfer during the first hours, then a straight line is observed. Interestingly, when we performed the analysis of the data of Fig. 3 (constant solid load), a saturation curve is found. Even more interesting is the fact that both the biomasses display the same general behavior although they have very different particle sizes.

The initial concentration has a strong effect on the initial rate of chromate removal. Indeed, a decrease of C_0 causes the value of $1/\tau_I$ to drop dramatically. From a kinetic point of view, the value of initial concentration (16 mg/L) is considered a critical value since it is exactly at that value that occurs at the transition from a first-order to a zero-order regime of the reaction.

Since the adsorbent material quantity, which is directly proportional to the external surface area of the adsorbent particles, is held constant, it is reasonable to assume an initial predominant mechanism of chemical nature rather than external film diffusion or mass transfer. Remarkably, this kinetics study highlights the fact that a unique chromate ions concentration value can be determined (16 mg/L) above which no further adsorption takes place and, considering that we have the same number for both the adsorbents the driving force of the absorption process is strongly related to the chemical nature of the molecules. Furthermore, this adsorption behavior is in accordance with what we found in a recent paper on the adsorption of chromate ions on a gelatin-composite material [26].

To shed light on the chemical molecules involved in this adsorption process here, it should be remembered that the chromate reactivity is affected by speciation and solubility [29]. In aqueous solution, chromium exists in the form of H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, and $Cr_2O_7^{2-}$ depending on both the solution pH and the total chromate concentration. The relative amount of these species is the result of multiple equilibria.

$$H_2CrO_4 \rightarrow H^+ + HCrO_4^- \quad pK_1 = -0.08 \tag{3}$$

$$HCrO_4^- \rightarrow H^+ + CrO_4^{2-} \quad pK_2 = 6.52 \tag{4}$$

$$2HCrO_4^- \rightarrow H_2O + Cr_2O_7^{2-} \quad pK_3 = -1.55 \tag{5}$$

$$HCr_2O_7^- \rightarrow H^+ + Cr_2O_7^{2-} \quad pK_4 = 0.07 \tag{6}$$

These equilibria, at room temperature, determine the equilibrium concentration of all species. With the aid of these equilibrium constants we calculated, at pH 5.5, the concentration of each species acts as a function of the total concentration of chromate. For concentrations ranging from 0.05 to 5 mM, $HCrO_4^-$ is the predominant species. At pH 5.5, the surface of biomass is slightly positive and this promote the binding of the negatively charged $HCrO_4^-$ ions.

The $HCrO_4^-$ species are more easily exchanged with OH^- ions, as shown in Eq. (7):

$$BmOH + HCrO_4^- \rightarrow H^+ + BmHCrO_4 + H_2O \tag{7}$$

where Bm symbolizes a free binding site in the biomass. This mechanism is comparable to that suggested for the adsorption of chromate ions on sawdust [30]. The most important feature of this adsorption mechanism is that, in order for the uptake of chromate to occur, the liquid solution has to contain enough protons to effectively push the equilibrium of Eq. (7) to the right. According to this mechanism, the disappearance of ions should reduce the acidity, so that the solution pH is expected to change. Nevertheless, solution acidity did not vary during adsorption experiments yielding the pH 5.5. This means that the biomass releases and/or uptakes protons as a bulk.

3.3. Kinetics of polyphenols release

The eventuality of a contribution of polyphenol contained in the biomass on the chromate removal process from aqueous solution was studied by means of the following experiments. Firstly a polyphenol released from the biomasses was followed. Release from biomass in water (10 g biomass/L) was followed by measuring polyphenol content at different time interval and constant temperature of 25°C (Fig. 4). As shown, the release of polyphenol appears higher for the S biomass than for the WP biomass. From a kinetic point of view, the data were reported in terms of the parameter $t_{0.5}$, the release half-life, i.e. the time needed for the biomass to release half of the maximum amount. For the biomasses under investigation one finds $t_{0.5}^{S}$ = 16 h and $t_{0.5}^{WP}$ = 12 h. The second step is to verify if the presence of polyphenols that could be involved in the adsorption process was performed by washing the content of polyphenols from the biomasses. Briefly, polyphenols contained in the biomass were completely extracted, by successive washes with water, and their concentration measured. We found 61.76 and 76.90 mg caffeic acid equivalents/L solution, for biomass WP and S, respectively. Further,

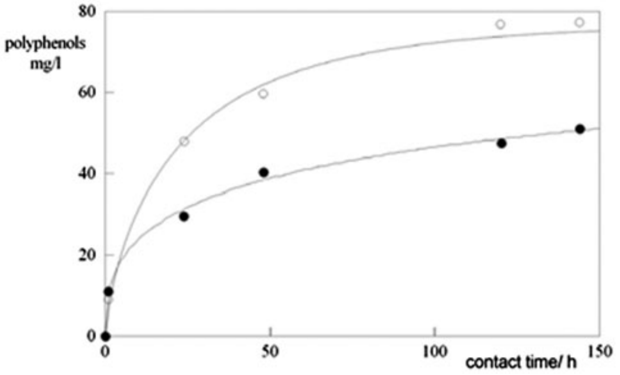

Fig. 4. Release of polyphenols from biomass S (○) (●) in water at 25°C as function of contact time between biomass and water solution.

we performed the adsorption process (in a 10 mg/L solution of chromate ions, at pH 5.5 and 25°C), by addition of caffeic acid (70 mg/L) in the presence of washed and unwashed biomasses. Data collected in Fig. 5 show some interesting features: (i) under the experimental conditions adopted, the percentage of chromate ions adsorbed within 1.5 h exceeds 90% for both biomasses and (ii) the presence of added caffeic acid in both biomasses samples does not modify the amount of chromate adsorbed. These results highlighted that the presence of polyphenol molecules does not affect the adsorption process.

Interestingly, here it is important to note that chromate compounds are strong oxidizing agents and Cr(VI) has the tendency to be reduced to Cr(III) in the presence of biological matrices [31]. On the other hand, biomass contains poliphenolic antioxidants, such as hydroxytyrosol, tyrosol, therefore it is reasonable to assume that polyphenolic compounds could also be responsible for an *in situ* reduction of Cr(VI).

3.4. Adsorption isotherms

Isotherms for S and WP biomasses are drawn on the basis of chromate ions disappearance from solution. The experiments carried out at pH 5.5 and 10 g/L solid load were found to obey the Freundlich adsorption isotherm (Fig. 6). This is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved [31,32]. In this case, Freundlich adsorption isotherm correlates the amount of chromate adsorbed per unit mass of adsorbent, q_e, with the concentration of the chromate at equilibrium, C_e.

$$q_e = k_F {C_e}^{1/n} \tag{8}$$

where k_F and n are Freundlich constants, characteristics of the system. The log–log plot of q_e vs. C_e, as shown in Fig. 6, displays a linear trend with adsorption capacities (k_F) calculated as 0.315 and 0.450 g/kg and adsorption intensities (n) equal to 1.35 and 1.77 for S and WP, respectively. Since the higher the value of k_F the, higher the biomass affinity for chromate, it can be concluded that biomass WP is more effective as adsorbent material with respect to biomass S. The degree of heterogeneity of adsorption surface was also measured from the $1/n$ values. According to

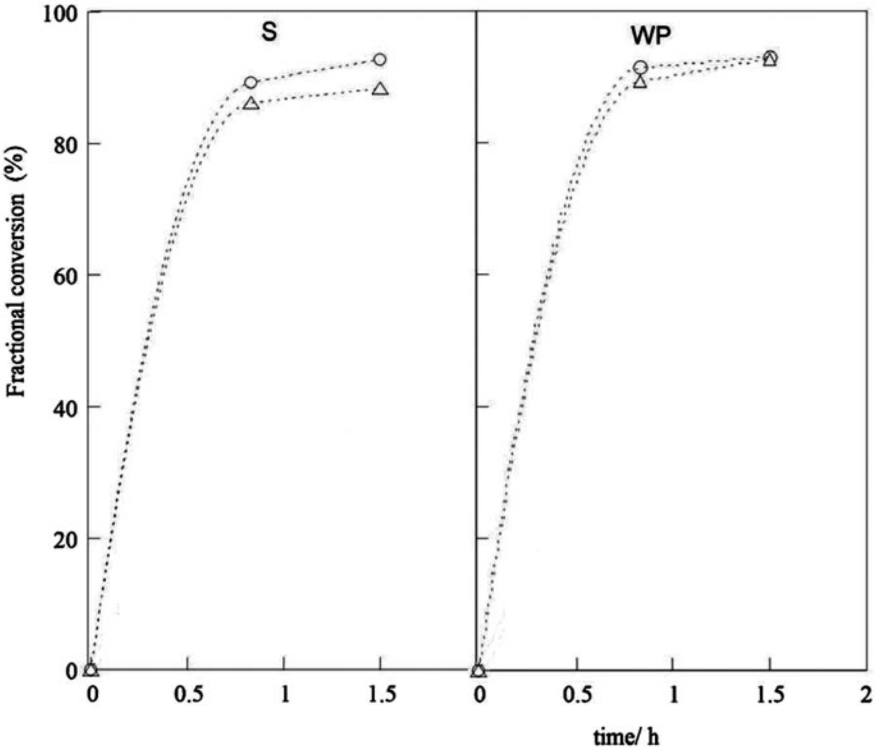

Fig. 5. Percentage of chromate ions adsorbed in the control experiment. Sample with 10 mg/L of chromate, 70 mg/L of caffeic acid, and 10 mg/L of biomass unmodified (○) and washed (Δ).

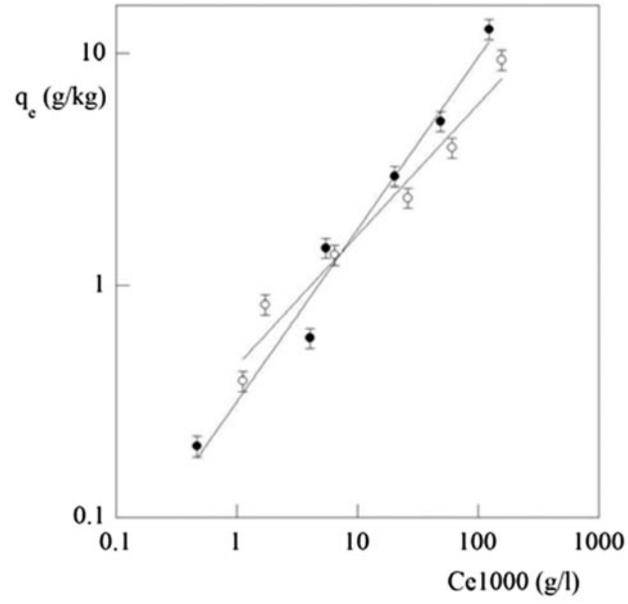

Fig. 6. Freundlich plot for adsorption of Cr(VI) on biomass S (○) and WP (●) at pH 5.5 and adsorbent dosage 10 g/L.

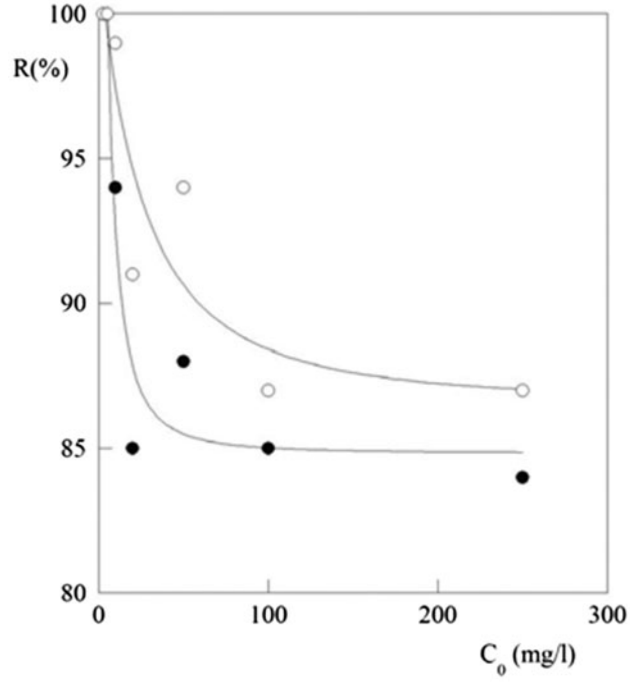

Fig. 7. Adsorption percentage of biomass WP (●) and S (○) as a function of initial chromium concentration. The experiments were carried out at pH 5.5, mild agitation and temperature (25°C) and adsorbent dose 10 g/L.

Freundlich equation, the slope (1/n), ranging between 0 and 1 is a measure of surface heterogeneity [33]. Surface becomes more heterogeneous as 1/n values get closer to zero. Based on this, biomass WP with (1/n) = 0.565 presents a more heterogeneous surface respect to biomass S exhibiting (1/n) = 0.741.

As regards the adsorption of chromate ions, we analyzed the percentage of adsorption, R(%), as a function of the initial concentration of chromate. We demonstrated that the chromate ions removal efficiency decreases with the increase in initial chromate concentration up to reach a plateau (Fig. 7). From the data shown in Fig. 7, we can conclude that for each biomass, a critical initial chromate concentration exists beyond which the adsorption process becomes independent of the initial chromate concentration.

4. Conclusions

A solid material was obtained from the sludge of a traditional olive mill and from wet pomace obtained from a two-phase continuous plant after simple washing/separation steps. These materials, named S and WP, respectively, were tested for their adsorption activities toward chromate aqueous solutions. The investigations carried out by means of SEM microscopy showed that the two biomasses differ in both the morphological structure and the elemental composition. Moreover, an important feature of both materials is a residual content of polyphenols, and no correlation was found between the polyphenols molecules and the adsorption process. With this respect, a critical initial chromate concentration was found beyond which the adsorption process can be considered to follow a zero-order kinetic. Interestingly, the kinetics of the two processes can be explained by the same model of heterogeneous kinetics by means of stretched exponentials. By taking into consideration the fact that the continuous systems of extraction of olive oil are replacing the old traditional system of extraction by presses, these results may provide new ideas to a sustainable reuse of the solid waste material from modern olive mills.

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