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A.C. Deiana[1,*], M.G. Gimenez[1], S. Rómoli[1], M.F. Sardella[1] and K. Sapag[2] *(1) Instituto de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional de San Juan, Avenida Libertador San Martín 1109 (Oeste) 5400 San Juan, República Argentina. (2) Instituto de Física Aplicada, Universidad Nacional de San Luis–CONICET, Avenida Ejército de los Andes, 950 (5700) San Luis, República Argentina.*

ABSTRACT: Adsorption studies (kinetic, batch and dynamic assays) were carried out for lead removal from aqueous solutions using wastes from the wine industry. The adsorbents used were obtained from grape stalk and pomace[#]. These materials were carbonized, briquetted and activated with steam. Addition of a leaching step before activation lowered the high ash content of the materials. The products were characterized by elemental and proximate analysis, point of zero charge pH, specific surface area, pore-size distribution, Fourier transform infrared spectroscopy and surface acidic and basic groups. Considering the physicochemical and textural properties of the adsorbents, a comparative analysis of the results was made. These solids showed a marked basic character; therefore, the pH was a very important variable in adsorption tests, and thus it was necessary to maintain the pH in a favourable range. Batch equilibrium assays showed that the tested adsorbents had good adsorption capacities, better than the ones reported previously for similar materials. In dynamic tests, the removal of lead by both activated carbon briquettes was good and attributed to the coupling of adsorption and precipitation as a result of the increase in the pH values, which could not be controlled.

1. INTRODUCTION

Treatment of water is essential for both the environment and the health of the population. Thus, several governments have implemented strict environmental regulations for water treatment, which has resulted in an increased number of studies focussing on developing efficient methodologies for water treatment.

Among the most relevant and frequent water contaminants are the heavy metals. These are the major pollutants of surface and groundwater and are an important constituent of industrial effluents (Nomanbhay and Palanisamy 2005). These metals are present as ions in water and are considered ecotoxic when their concentration exceeds certain limit because of their tendency to accumulate in vital organs of humans and animals (Üçer *et al*. 2006). Unlike the organic compounds, these heavy metal ions cannot be biodegraded or destroyed, and therefore there is a necessity to remove them (Çay *et al*. 2004). Industrial wastes, such as lead, cadmium, zinc, chromium and copper, are the major pollutants of natural waters.

In recent years, San Juan, República Argentina, has experienced a significant growth of industrial activities related to the exploitation of minerals, especially metallic ores. Large projects developed in Cordillera de los Andes, such as Veladero, Gualcamayo, Caspoco y Pascua-Lama, in

*Author to whom all correspondence should be addressed. E-mail: cdeiana@unsj.edu.ar (A.C. Deiana).
[#]The term 'pomace' refers to lex (Spanish), which is the residue from the solvent extraction of grape seed oil. The study used both pomace and grape stalk, another agricultural waste from the grape industry, as precursors of activated carbon.

addition to promoting economic activities in the area, release an increased amount of pollutants (heavy metals) to the surface water and groundwater. While extracting various minerals, a number of hazardous elements (especially lead) have also been obtained (Logan 1999). Biologically, lead is a worthless metal, because it is not required for the normal functioning of living organisms. However, exposure to lead causes a number of diseases, including mild mental retardation resulting from loss of IQ points, as well as increased blood pressure, anaemia and gastrointestinal effects. Children are more sensitive than adults to the effects of lead, and they encounter problems such as nephrotoxicity, neurotoxicity, hypertension and damage to the central nervous system. Lead poisoning has been linked to lower cognitive development in children exposed to even low levels of lead (Prüss-Üstün *et al*. 2004).

Several technologies have been applied for removing heavy metals from liquid streams, such as chemical precipitation, electrolysis, ion exchange and adsorption. Of these, adsorption is considered to be the best technology for removing heavy metals at low concentrations. Among the most suitable adsorbents, activated carbon is one of the most attractive and the most used adsorbent in various wastewater treatment industries (Kadirvelu *et al*. 2004; Roundhill 2004; Ayyappan *et al*. 2005; Machida *et al*. 2005a; Foo and Hameed 2011).

Activated carbons are carbon-rich materials synthesized by heat treatment of carbonaceous source materials. These materials have a well-developed porous structure, mainly consisting of numerous micropores. Because of their texture, activated carbons have very high specific surfaces, making them effective in adsorption. Although activated carbons can be manufactured from various carbonaceous precursors, various studies have focused on using low-cost and widely available lignocellulosic materials as precursors. The importance of the most suitable raw materials to produce activated carbon depends on several aspects such as potential for high-quality products, low content of inorganic materials, high availability and low cost, low degradation during storage and ease of activation (Bansal *et al*. 1988). The use of unconventional materials, with low cost and high availability, such as wastes from agricultural or industrial activities, is of special interest for the development of value-added materials that can have various technological applications (Namasivayan and Kardilevu 1999; Farinella *et al*. 2007).

Grape industrialization is one of the main economic activities in Región de Cuyo, República Argentina. It generates large volumes of wastes during the production of wine, concentrated grape must, raisins, alcohols and oils. Grape stalk and pomace are the main materials generated by these industries and these can potentially be applied as adsorbents.

The two mainly ways to obtain activated carbons are (i) physical or thermal activation, in which the precursor material is pyrolyzed and then partially gasified in a stream of vapours and/or gases at high temperatures (approximately 900 °C); and (ii) chemical activation, in which the raw material is soaked in a solution of a dehydrating agent and subsequently activated at medium temperatures (approximately 450 °C; Rodriguez-Reinoso 2002).

Fixed-bed operations are widely used in pollution control processes such as the removal of ions or toxic compounds by adsorption (Goel *et al*. 2005). Industrial application of adsorption in fixed-bed column requires the implementation of different studies for the analysis of each adsorbent–adsorbate system. Kinetic studies, batch tests to determine equilibrium adsorption capacities and dynamic assays for obtaining the breakthrough curves in columns should be developed to obtain design parameters.

In this work, the kinetic, equilibrium and fixed-bed column studies of lead adsorption are presented. We used activated carbon briquettes (adsorbents) synthesized by thermal activation of grape stalk and pomace. The effects of design parameters, such as flow rate and pH on lead sorption have been examined.

2. EXPERIMENTAL ANALYSIS
2.1. Materials

Two agricultural wastes from the wine industry were tested. The first one is grape stalk, a residue generated in grape industrialization during the production of wine, grape must and raisins. It is the skeleton of the grape bunch, consisting of tissues that go through a lignification process with the progress of maturation (Deiana *et al*. 2009). The other one is pomace, which is a residue obtained during extraction of oil from grape seed by solvents. The stalks were provided by Callia Winery and pomace by OLIVI Hermanos.

All chemical reagents used were of analytical grade and deionized water was used to prepare solutions. $Pb(NO_3)_2$ was used for adsorption assays and $NaOH$ or HNO_3 for pH regulation and physicochemical characterization. $NaNO_3$ was used for point of zero charge pH (pH_{PZC}) determination.

2.2. Methods
2.2.1. Preparation of Activated Carbon Briquettes
2.2.1.1. Carbonization and Leaching

Wastes, as received, were heated in an inert atmosphere at a rate of 1.4 K/minute, from room temperature (298 K) up to 773 K and maintained at this temperature for 2 hours. This step was carried out in a stainless steel carbonization reactor that is electrically heated.

Each carbonized material was weighted and separated into two fractions. One of them was submitted to a leaching treatment with hydrochloric acid (5% w/w) at room temperature, and then the material was washed and dried at 378 K. The leaching treatment was included due to the high ash content of grape stalks, as detected in previous studies and confirmed by the proximate analysis performed on the material used in this work. Thus, the content of alkali metals (K, Na, Ca and Mg), which might interfere with the activation of this material is decreased (Deiana *et al*. 2009). For comparative purposes, this step was also applied to the carbonized grape pomace.

The other fraction was processed without acid treatment. Both fractions of each residue were crushed to particle sizes < 0.18 mm and subjected to further treatment.

2.2.1.2. Briquetting

Carbonized materials and those carbonized and leached were briquetted using concentrated grape must (collected from Cuyo Region, Argentina) as the binder. This product is a non-alcoholic by-product of viticulture, and is obtained by partial dehydration of grape juice. Although its composition is complex, its main components are glucose and fructose (approximately 860 g total sugar/l). The briquettes were made by mixing the aforementioned materials in a mortar with measured amounts of char and binder in a ratio of 4:1. One gram of the resulting mixture was submitted to pressures of 140 MPa for 6 minutes within a cylindrical stainless steel mould (10 mm height and 10 mm internal diameter), which was held in a hydraulic press. This step was carried out room temperature (Amaya *et al*. 2007).

2.2.1.3. Activation

Briquettes were activated under steam flow in a stainless steel tubular reactor (30 mm internal diameter and 300 mm length), and heated in an electric furnace with automatic temperature

control. The heating step, from room to activation temperatures, was carried out under flowing nitrogen gas at 15 K/minute. In all assays, the reactor was loaded with 15 g of briquettes, which were submitted to a steam flow of 1.7 g (g char)$^{-1}$ (h)$^{-1}$ at 1153 K for 105 minutes. Steam was generated in a heat exchanger, which was fed by the Masterflex peristaltic pump.

Once the activation step is completed, the activated briquettes were measured, weighed and stored.

2.2.2. Characterization of Raw Materials and Activated Carbons

The elemental analysis of the raw materials was carried out in Carlo Erba EA1108 CHNS-O equipment, and proximate analysis (moisture, ash, volatile matter and fixed carbon) was performed following ASTM standards (1994, 1995, 1998).

To evaluate the texture of the materials, adsorption–desorption isotherms of nitrogen at 77 K were carried out in a Micromeritics ASAP 2000 Model equipment. The specific surface area was calculated by the BET method, the total pore volume by the Gurvich rule at a relative pressure of 0.98 and the micropore volume was obtained using the t-plot method.

The pH$_{PZC}$ was measured following the method proposed by Noh and Schwartz (1989). Three aqueous solutions of different initial pH were prepared from a 0.01 M NaNO$_3$ solution, with 0.01 M NaOH and HNO$_3$ being used for regulating the solution pH. Six vials containing different amounts of the adsorbent under study were placed with 20 ml of solutions at different initial pHs. The equilibrium pH was measured after 4 days of contact at room temperature.

The basic and acid surface functional groups were determined by titration with hydrochloric acid and sodium hydroxide, respectively. Samples of 200 mg from each adsorbent were treated with 20 ml of 0.05 N acid and basic solutions in flasks that were sealed and maintained under constant stirring for 48 hours at room temperature. Suspensions were separated by centrifugation and the final concentration of the solutions was determined by titrating with NaOH and HCl.

Surface functional groups were also studied by Fourier transform infrared (FTIR) spectra, which were obtained using a spectrometer (Nicolet 380). Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 400 cm^{-1}. The samples were previously placed in an oven at 60 K for 72 hours to remove water.

2.2.3. Lead Adsorption Assays

To evaluate the adsorbent properties of activated carbons, kinetic, batch and dynamic assays were performed. For these tests, Pb(NO$_3$)$_2$ solutions were prepared using deionized water.

2.2.3.1. Batch Adsorption Studies

First, the influence of pH on lead adsorption was determined in order to obtain the optimal value of this parameter for the adsorbate–adsorbent systems under study. Tests at different pH values were performed by treating 30 mg of adsorbent with 50 ml of a 100 mg l^{-1} aqueous solution of lead at 293 K. Each suspension had a different pH value, ranging from 2 to 12, which was regulated by adding 0.1 M NaOH or HNO$_3$. These suspensions were shaken for 2 hours and centrifuged. Samples were taken from the liquid phase and metal concentration was determined by an atomic absorption spectrometer (Perkin ElmerAA-100 with a hollow cathode lamp). A blank test, without adsorbent, was carried out to consider other effects, such as precipitation.

Lead kinetic adsorption assays were performed in a Parr reactor at 293 K and atmospheric pressure. Adsorbent samples of 300 mg were placed in the reactor flask with 500 ml of a 100 mg l^{-1} solution

of metal. The suspensions were stirred for 150 minutes and samples were taken at different contact times. The experiments were carried out at a pH value of 5.5 ± 0.2, which was obtained from adsorption assays at different pH.

From these assays, the best pH value and the minimum contact time necessary to reach adsorption equilibrium were obtained.

To obtain adsorption isotherms, 30 mg of grape stalk and pomace were added into flasks containing 50 ml of $Pb(NO_3)_2$ solutions at several concentrations (30, 45, 60, 75, 90, 100 and 120 mg l^{-1}). The mixture was shaken in a thermostatic bath at 293 K for the minimum contact time. Once the equilibrium time was reached, samples were centrifuged and the metal concentration was determined in the liquid phase by atomic absorption spectrometry. The pH for all adsorption tests was adjusted to 5.5 ± 0.2.

Lead uptake (q) was calculated from the mass balance equation as follows:

$$q = V\,(C_0 - C_f)/M \tag{1}$$

where V is the solution volume (l) and M is the weight of activated carbon (g) used. The parameters C_0 and C_f are the initial and final concentrations of Pb (mg l^{-1}), respectively.

The Freundlich and Langmuir isotherms were used to describe lead adsorption from bulk solution onto activated carbon briquettes, assuming no interaction among adsorbed molecules.

The Freundlich isotherm is expressed as follows:

$$q = K \times Ce^{1/n} \tag{2}$$

where q is the amount of metal adsorbed per unit weight of adsorbent (mg g^{-1}) and Ce is the equilibrium concentration of the adsorbate (mg l^{-1}). The parameters K and n are the model constants related to the adsorption capacity of the solid and the intensity of adsorption, respectively.

The Langmuir isotherm is expressed as follows:

$$q = \frac{Q_0 b C_e}{1 + b C_e} \tag{3}$$

where Q_0 is the monolayer adsorption capacity (mg g^{-1}) and b is the Langmuir constant (l mg^{-1}).

2.2.3.2. Fixed-Bed Column Studies

Dynamic tests were carried out in a glass column of 14-mm inner diameter and 250-mm length, supplemented with cooling jacket. The adsorbent, with a grain size between 0.7 and 1.7 mm, was packed in a bed with 150-mm height. A 100 mg l^{-1} $Pb(NO_3)_2$ solution was flown through the fixed bed with an upstream flow of 4, 10 and 20 ml $minute^{-1}$, driven by a Cole-Parmer peristaltic pump. The temperature was set at 293 K.

The experimental data were fitted using the Thomas model, which is one of the most widely used models and is applicable in systems with a constant flow rate and no axial dispersion and whose behaviour matches the Langmuir isotherm (Trgo *et al*. 2011).

$$C/C_0 = 1/\{[1 + \exp(k/Q)\,(q_m - C_0 Q_t)]\} \tag{4}$$

where C_0 and C are the influent and effluent concentrations (mg l^{-1}), respectively; k is the Thomas rate constant [l (mg minute)$^{-1}$]; q is maximum capacity of adsorption (mg g^{-1}), m is the quantity of adsorbent in the column (g), Q is the feed flow (ml minute^{-1}) and t is time (minutes).

3. RESULTS AND DISCUSSION

The results of elemental and proximate analysis of unprocessed grape stalks and pomace are shown in Table 1.

As shown in Table 1, grape stalk has high ash and low fixed carbon content compared with pomace. According to previous studies, this is due to the presence of elements such as K, Na, Ca, Mg, which hinders the activation of this material under standard conditions. To reduce this hindrance, a leaching step before activating the sample was introduced. This step removes approximately 80% of the elements Na and K, and 50% of Ca, which are the major minerals in the stalk (Deiana *et al*. 2009). Thus, the solid matrix of the stalk is modified and can be activated under standard conditions, that is, at those conditions that are adequate to activate materials with similar characteristics (as mentioned in the 'Preparation of Activated Carbon Briquettes' section). Grape pomace showed a low ash content. Although this material can be activated without any hindrance, a leaching step was added for comparative purposes.

The results of the textural properties, specific surface area (S_{BET}), total pore volume (V_{tot}) and volume of micropores (V_{micro}) and mesopores (V_{meso}) of the activated briquettes, with and without leaching, are shown in Table 2. The values of the first and second column correspond to activated briquettes of grape stalks without leaching (ASB) and leached (ASBL), and the third and fourth column to activated briquettes of grape pomace without leaching (ALB) and leached (ALBL), respectively.

As shown in Table 2, the addition of the leaching step produces significant improvements in the textural properties of stalk briquettes. This is due to the removal of mineral elements present in this material, obtaining products with higher porosity. As expected, owing to its low ash content,

TABLE 1. Proximate and Elemental Analysis of Grape Stalk and Grape Pomace

	Proximate analysis (%)				Elemental analysis (db) (%)			
Material	Moisture	Ash	Volatile material	Fixed carbon	N	C	H	S
Grape stalk	20.2	12.5	53.5	13.9	0.37	46.14	5.74	0
Grape pomace	19.3	5.6	44.4	30.7	2.91	52.27	5.38	0

db = dry base.

TABLE 2. Textural Properties of Activated Carbon Briquettes

Property	Sample			
	ASB	ASBL	ALB	ALBL
S_{BET} (m^2/g)	285	723	795	669
$V_{\mu p}$ (cm^3/g)	0.10	0.25	0.27	0.22
V_{Tp} (cm^3/g)	0.13	0.37	0.40	0.35
V_{mp} (cm^3/g)	0.03	0.12	0.13	0.13

the application of the leaching step on grape pomace did not produce significant changes on these properties. The pore volumes in all samples are similar, except for non-leached stalk briquettes, which were all mainly microporous.

Table 3 shows the results of the determination of acidic and basic properties and the pH_{PZC} of the materials. For comparative purposes, values of only charred grape stalk and pomace were included.

The surface chemical properties indicate that activated carbon briquettes of both materials have basic character. Raw wastes possess greater amount of acidic groups, but the addition of the processing steps (carbonization and activation) increases the ratio of basic to acid groups. The incorporation of the leaching stage, which lowers the alkaline metal content in the materials, reduces this ratio. Briquetting also causes a reduction of this ratio in both materials, which is due to the addition of grape must as binder, a material with acidic character.

The minor differences in the pH_{PZC} values, between leached and non-leached materials, are attributed to the low concentration of HCl used in the leaching step, which is not enough to substantially change the basic nature of activated carbon briquettes.

Figure 1 shows the FTIR spectra of activated carbon briquette samples, ASB, ASBL, ALB and ALBL. All samples exhibited bands of very low intensity at wave numbers below 900 cm^{-1}, which are attributed to the C–H bonds in aromatic structures (Giraldo and Moreno 2008). This signal was stronger in samples ALBL and ALB. A peak at 1040 cm^{-1}, attributed to C–O stretching and OH bending of the lactonic, ether and phenol groups, was found in samples ASBL and ALB with greater intensity than in the other two materials (Dantas *et al*. 2011). A peak at 1420 cm^{-1}, attributed to OH bonds of phenolic groups, COO^{-} and $-CH3$ was found in ALB (Ioannidou *et al*. 2010). The same band can be observed as a shoulder in ASB and ASBL. All samples showed a small peak at 1620 cm^{-1}, attributed to the C = O bond of carboxylic groups (Amir *et al*. 2010). All spectra showed a strong wide absorption band at 3600–3200 cm^{-1} with a maximum at approximately 3420 cm^{-1} due to surface hydroxyl groups and chemisorbed water. The position of the band is characteristic of the stretching vibration of hydroxyl compounds, whereas broadening of the band indicates a high degree of association due to hydrogen bonding (Puziy *et al*. 2005). Thus, it is expected that the investigated carbons contain hydroxyl groups from carboxyls, phenols

TABLE 3. Surface Chemical Properties of Activated Carbon Briquettes

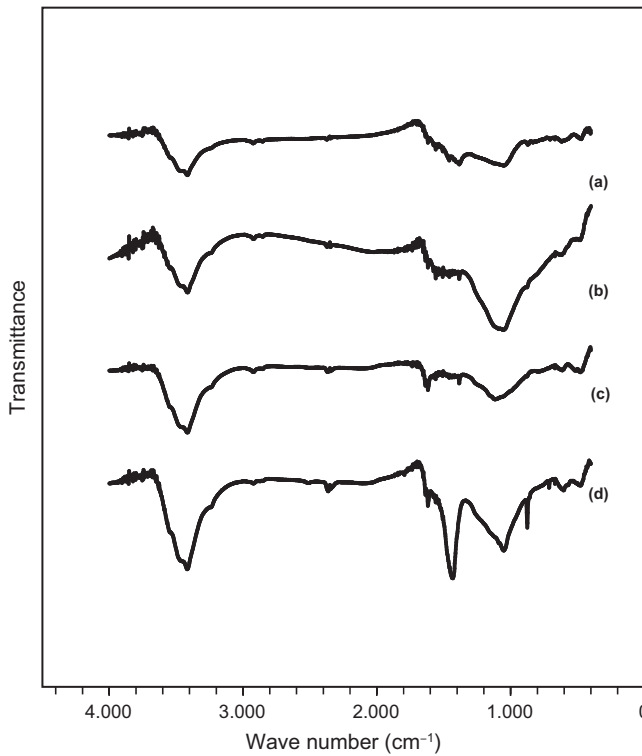|	Basic groups (meq/g)	Acid groups (meq/g)	Total groups (meq/g)	pH_{PZC}
Raw grape stalk	0.45	3.05	3.50	4.59
Carbonized grape stalk	2.81	0.75	3.56	9.76
Granular grape stalk AC	4.85	0.00	4.85	11.19
ASB	1.72	0.16	1.88	10.22
ASBL	0.86	0.82	1.68	10.02
Raw grape pomace	0.06	3.47	3.53	4.25
Carbonized grape pomace	1.63	1.05	2.68	9.55
Granular grape pomace AC	2.53	0.21	2.74	12
ALB	1.75	0.21	1.96	12.03
ALBL	1.23	0.63	1.86	11.42

AC = activated carbon.

Figure 1. IR spectra for grape stalk and pomace briquettes: (a) ASB; (b) ASBL; (c) ALBL; (d) ALB

or alcohols. It can be observed that samples ASBL and ALB are the most functionalized, bearing higher contents of surface chemical groups that enhance metal uptake.

The complete characterization of each material, which comprises textural and physicochemical properties, reported in Tables 2 and 3, showed that activated carbons of leached grape stalk and pomace without leaching have the best features as adsorbent materials. Based on these results, the leached grape stalks briquettes (ASBL) and grape pomace briquettes (ALB) samples were selected for lead adsorption tests.

3.1. Batch Adsorption Studies

Figure 2 shows lead adsorption versus pH curves for grape stalk and pomace, which were used to obtain the proper pH value for adsorption tests. This was obtained by subtracting the values of Pb concentration versus pH curve corresponding to blank assays (no adsorbent) and the values of the curve from the test with the adsorbent added. It can be observed that at very low pH values (i.e.<4) the adsorption is low, which is attributed to the competition between metal and protons present in solution for adsorption sites. At pH > 6 adsorption decreases, which is attributed to the appearance of an insoluble lead species [$Pb(OH)_2$]. Therefore, a pH value of 5.5 was considered to be suitable for carrying out adsorption tests to avoid the appearance of insoluble species. This value has also been reported as optimal by other authors and confirmed by lead speciation diagram for 100 mg l^{-1} solution (Machida *et al*. 2005b; Giraldo and Moreno 2008).

Figure 3 shows the curves corresponding to kinetic assays of lead adsorption by activated carbons obtained from both wastes. Because of the basic nature of the adsorbents, tests were
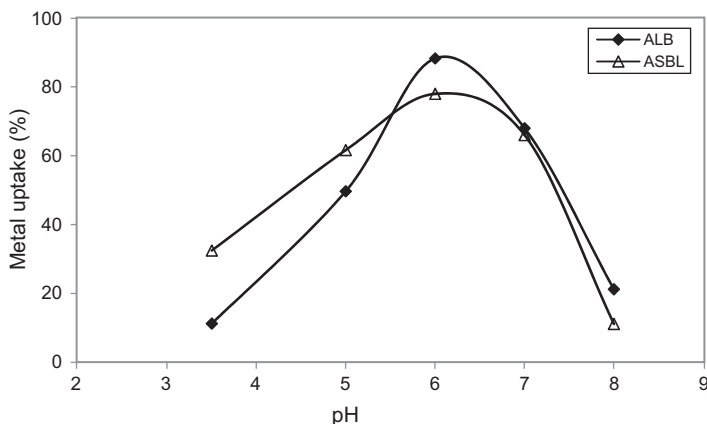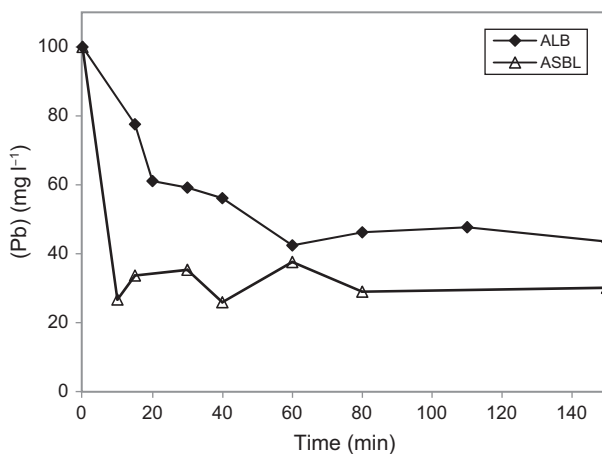
Figure 2. Lead uptake versus pH.

Figure 3. Kinetics of lead adsorption by activated carbons synthesized from grape pomace and stalks.

carried out under strict pH control and taking into account the other conditions specified in the 'Lead Adsorption Assays' section.

It was observed that the adsorption kinetics is faster for ASBL and the amount of lead ions removed at the same time is increased. This is in agreement with the textural characterization of the adsorbents, where ASBL showed a more developed porous structure. Besides, in both cases, it was found that 120 minutes would be sufficient to achieve equilibrium conditions in batch testing. This time value was used to develop the equilibrium tests.

Data from equilibrium batch assays were used to construct the lead adsorption isotherms for the materials studied, which are shown in Figure 4. Experimental data were fitted to the Langmuir and Freundlich models. The corresponding curves are also shown in the figure. The parameters of both models were estimated by non-linear regression and are presented in Table 4.

Experimental data obtained for ASBL were better fitted with the Freundlich model while for ALB the Langmuir model was found to be better suitable, although the R^2 values were close.

According to the Langmuir model, adsorption capacities in the monolayer (Q_0) for ASBL and ALB are 105.02 and 76.87, respectively, while the adsorbate–adsorbent affinity (b) is higher for
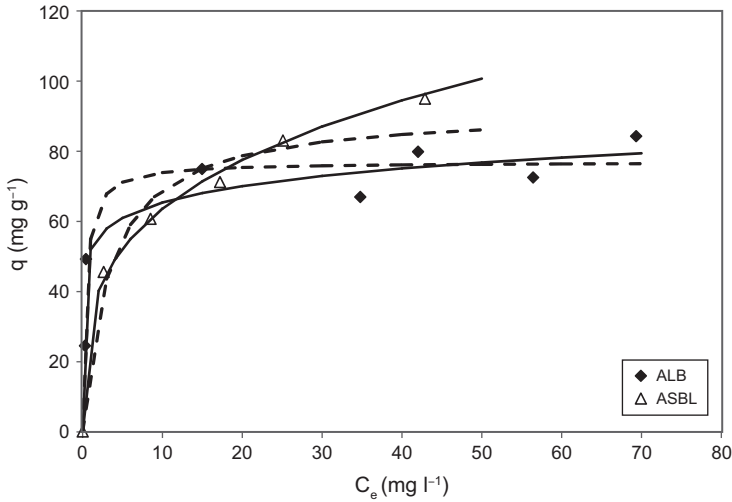
Figure 4. Lead adsorption isotherms on activated carbons from grape pomace and stalks. The isotherms were fitted to the Langmuir (dotted lines) and Freundlich (continuous lines) models.

TABLE 4. Freundlich and Langmuir Parameters

Isotherm model	Parameter	ASBL	ALB
Freundlich isotherm	K	33.31	44.65
	$1/n$	0.281	0.143
	R^2	0.998	0.927
Langmuir isotherm	Q_0	105.02	76.87
	b	0.190	2.687
	R^2	0.953	0.950

ALB. These results are in accordance with the textural properties of the adsorbents and are appropriate compared with those reported by other authors for monolayer adsorption capacity (Q_0) of the Langmuir model for similar materials (Table 5). It can be seen that grape stalk renders an adsorbent with a remarkable performance, showing an adsorption capacity higher than all the ones reported.

The essential characteristic of the Langmuir isotherm model can be described by the separation factor, R_L, which is represented as follows:

$$R_L = 1/(1 + b \times C_0) \qquad (5)$$

The values obtained for the ASBL and ALB samples were 0.095 and 0.007, respectively. Values of R_L between 0 and 1 indicate that the adsorption is thermodynamically favourable (Ahn *et al.* 2009).

3.2. Fixed-Bed Column Studies

As the adsorbate solution passes through the column, the adsorption zone (where the bulk adsorption takes place) starts moving out of the column and the effluent concentration begins to

Table 5. Lead Adsorption Capacity of Activated Carbons from Different Materials

Activated carbon source	Adsorption capacity, Q_0^* (mg g^{-1})
Apricot stone (Kobya *et al*. 2005)	22.85
Pecan shell (Bansode *et al*. 2003)	64.20
Palm shell (Issabayeva *et al*. 2006)	95.20
Coconut shell (Kikuchi *et al*. 2006)	76.66
Mature pods of *Moringa oleifera* containing seeds (Nadeem *et al*. 2006)	19.20
Eichhornia crassipes (Shekinah *et al*. 2002)	16.61
Date pits (Abdulkarim and Al-Rub 2004)	30.70
HCl-treated commercial coconut shell (Song *et al*. 2010)	17.19
Pine cone (Momcilovic *et al*. 2011)	27.53
Phaseolus aureus hulls (Rao *et al*. 2009)	21.80

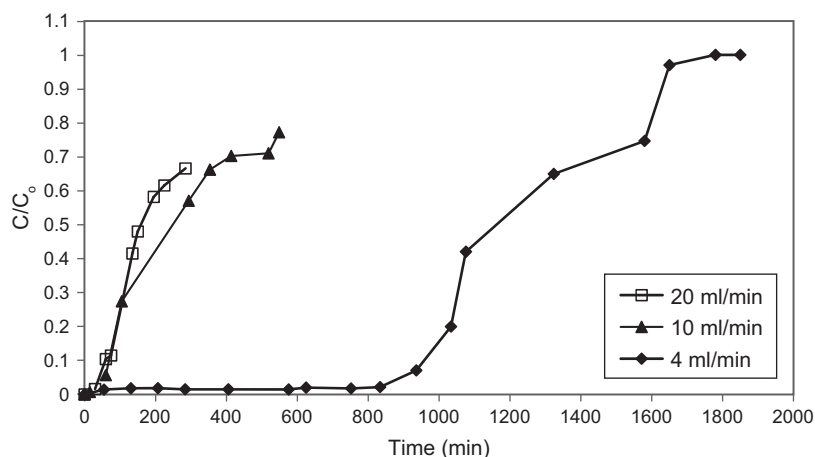* Monolayer adsorption capacity of the Langmuir model.

Figure 5. Breakthrough curves of Pb removal by grape pomace briquettes (sample ALB) at different flow rates.

rise with time. The time taken for the effluent concentration to reach a specific breakthrough concentration of interest is called the breakthrough time. The breakthrough curve is a plot of the concentration measured at a fixed point in the column, usually at or near the outlet, versus time (Singh and Pant 2006).

Figure 5 shows the breakthrough curves obtained from dynamic lead adsorption assays, which were carried out in a fixed-bed column at different flow rate for grape pomace briquettes (sample ALB). The column experiments were conducted with 100 mg l^{-1} Pb(II) solutions at bed depths of 150 mm, maintaining a constant flow rate of 4, 10 and 20 ml minute^{-1}. It can be observed that the time required to reach the breakthrough point decreases with the increase in flow rate. This effect is most likely attributed to the decrease in the residence time of the metal ions in the bed at higher flow rates, which leads to a weak distribution of the liquid inside the column and lower diffusivity of the solute among the particles of the adsorbent (Yin *et al*. 2009). Singh and Pant (2006) explained that the decrease of breakthrough capacity of adsorbent due to increase in flow rate was caused by breakage of adsorption film surrounding adsorbent particles, thereby reducing the adhesion of adsorbate to the adsorbent particle. Therefore, a flow rate of 4 ml minute^{-1} was adopted for further assays.

The S-shaped breakthrough curves obtained for stalk and pomace activated briquettes (ASBL and ALB) developed at a constant flow rate of 4 ml minute^{-1} are shown in Figure 6. Breakthrough times and the exhaust times, corresponding to $C/C_0 = 0.1$ and 0.9, respectively, were 540 and 1120 minutes for ASBL, and 850 and 1550 minutes for ALB.

Experimental data were fitted using the Thomas model, which was performed by non-linear regression using MATLAB software. In Table 6, parameters of Thomas model, namely, k and q, and R^2 are shown.

It can be seen that the model fits well to the experimental values, yielding adsorption capacities of 43.91 and 47.45 mg/g for the grape stalk and pomace briquettes, respectively.

During these assays it was difficult to maintain pH values close to 5.5, which is the optimal value for adsorption. The basic character of the adsorbent increased the pH in the first hours of each test, despite the acidic character of the adsorbate solution. Figures 7 and 8 show the trend exhibited by the pH throughout the fixed-bed adsorption studies. Values increased drastically from influent pH of 5.5 to effluent pH higher than 10 initially, which gradually decreased to pH less than 6 and approaches towards influent pH. This behaviour is probably caused by the high availability of adsorption sites on AC at initial stages, which facilitates high adsorption rates of the metal and H$^+$ ions, increasing OH$^-$ proportion and pH values in the bulk solution. As the experiment progresses, adsorption sites on AC get relatively saturated resulting in reduced H$^+$ adsorption and lower effluent pH (Yin *et al*. 2009).
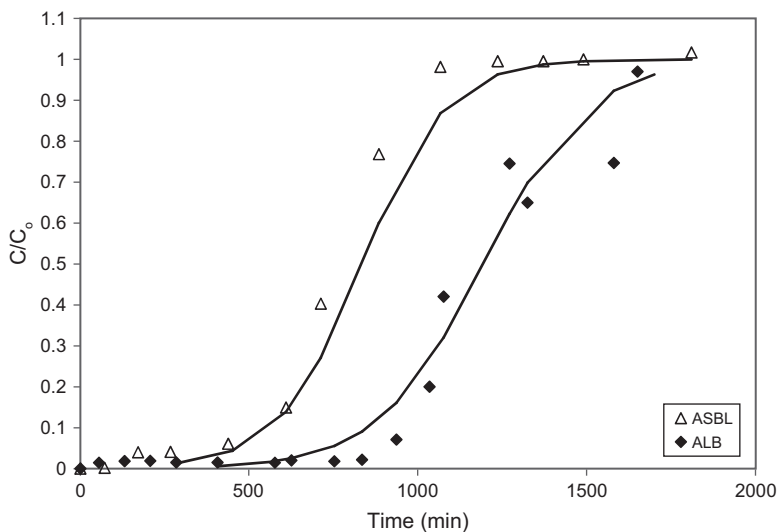

Figure 6. Breakthrough curves for grape stalk and pomace briquettes at a flow rate of 4 ml minute^{-1} fitted to the Thomas model (continuous lines)

Table 6. Thomas Model Parameters for Activated Carbon Briquettes from Grape Stalk and Pomace

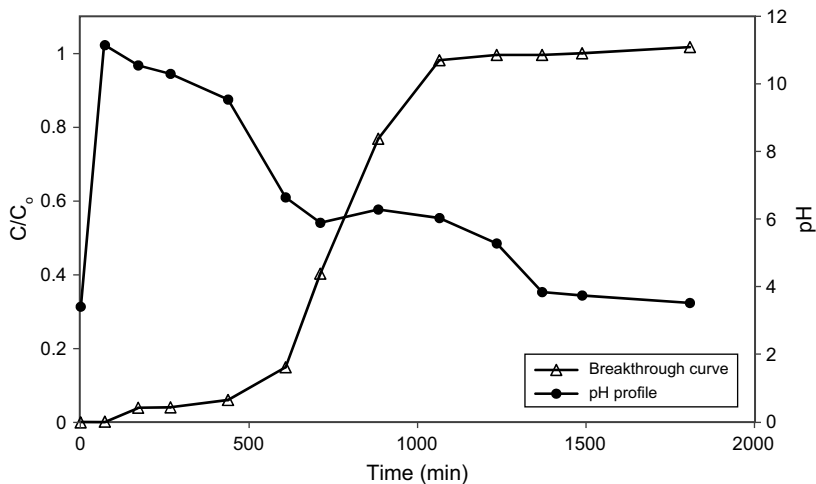| Model	Parameter	ASBL	ALB
Thomas	k (l/mg minute^{-1})	8.12×10^{-5}	6.43×10^{-5}
	q (mg g^{-1})	43.91	47.45
	R^2	0.995	0.931

Figure 7. Breakthrough curves for grape stalk briquettes and pH profile during the assay.
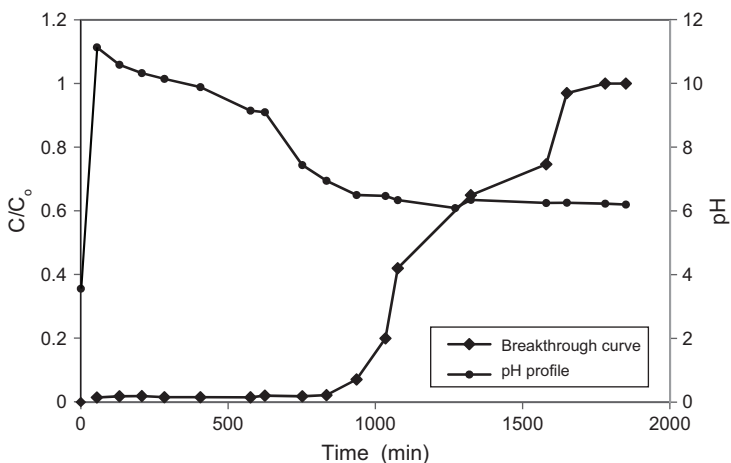

Figure 8. Breakthrough curves for grape pomace briquettes and pH profile during the assay.

As a consequence of the increase in pH values during the adsorption in the column, precipitation of the insoluble lead species [Pb(OH)$_2$] was observed by the appearance of the characteristic white precipitate of this compound. This effect enhances metal retention, improving the performances of the removal systems.

By analyzing the behaviour of both materials, the higher breakthrough and exhaust times obtained for ALB sample can be attributed to the pH profile, which remained at higher values (>6) throughout the test. This resulted in a better removal caused by the greater impact of precipitation in this adsorbate–adsorbent system.

It is important to highlight that Pb(OH)$_2$ precipitation was only detected in the column tests, due to the impossibility of controlling the pH during each dynamic test. This does not happen in the batch equilibrium trials, because this parameter could be effectively controlled, and the studied porous solids showed high adsorption capacities.

Anyways, it can be said that the removal of lead by the activated carbons briquettes, obtained from grape stalks and grape pomace, is good. In systems where pH cannot be controlled, as in the fixed-bed column, lead retention is produced by the coupling of adsorption and precipitation.

4. CONCLUSIONS

The results of the studies showed that the wastes from the wine industry, namely, grape pomace and stalks, can be used as precursors of activated carbon and can be applied to the removal of lead from aqueous solutions. Grape stalks present high ash content, which hinders the activation process. For this reason, a leaching step must be incorporated.

The addition of the processing steps (carbonization and activation) on the wastes increased the amount of basic groups on the surface of the materials. The incorporation of the leaching stage reduces the basic-to-acid group ratio and leads to significant improvements in the textural properties of grape stalk briquettes. Anyways, the adsorbents presented a marked basic character and very high pH_{PZC} values. Therefore, the control of the pH variable was very difficult.

Static assays showed that the adsorbents had good adsorption capacities, higher than the majority of the ones reported in the literature for similar materials. In dynamic tests, the removal of lead by both activated carbon briquettes was good and attributed to the coupling of two phenomena, namely adsorption and precipitation, caused by the increase in the pH values, which could not be controlled.

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