

Conversion of viticultural industry wastes into activated carbons for removal of lead and cadmium



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ABSTRACT

Many industrial activities generate large quantities of biomass wastes. The use of these to produce added value products or energy has become very important in recent years. Heavy metals as lead and cadmium are among the most toxic chemical water pollutants from natural or anthropogenic sources. This paper presents the studies carried out to assess the feasibility of preparing activated carbons from grape industrialization wastes of Cuyo Region, Argentina, grape stalk, lex and pomace, and their application for the removal of lead and cadmium. These materials were activated with steam. The activation conditions of each material were adjusted until the porosity and yield were acceptable. Products were characterized by their textural (BET area, porous volume) and physicochemical properties (proximate and elemental analysis, acid and basic surface groups, pH_{pzc} , FTIR). In order to determine the effectiveness of these products on lead and cadmium adsorption, kinetics and equilibrium assays were carried out. Adsorption data were fitted to Langmuir and Freundlich models.

All the adsorbents obtained were mainly microporous and showed a markedly basic character with pH_{pzc} values above 10. The study of the effect of pH over lead and cadmium adsorption showed that the maximum retention of metal is attained at pH 5.5 and 6, respectively. Removal percentages around 98% were reached when grape pomace activated carbons were used. The other adsorbents showed lower removal efficiency. Adsorbent textural properties did not show influence on cadmium and lead adsorption under the experimental conditions of this work. The pH of suspensions was a relevant variable in the adsorption of metals and their regulation was difficult. Consequently, the removal of lead and cadmium was attributed to the combined effect of adsorption and precipitation.

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Introduction

The increase of industrial, mining and agricultural activities affects the environmental quality if adequate cares are not brought into effect. For this reason, the regulations applied by states to preserve the environmental conditions of their countries are becoming more stringent. Furthermore the scientific investigations and technological developments that search and propose new prevention and remediation alternatives are acquiring great relevance.

Many industrial activities, particularly from agriculture, generate large quantities of biomass wastes. The use of these wastes to

produce added value products or energy has become very important in recent years [1,2]. Besides recovery for these uses, these technologies can lead to a substantial reduction in the overall waste quantities that require final disposal, improving their management in a controlled manner.

Among the alternative uses of agro-waste is the production of activated carbon, which is one of the most widely used materials because of its exceptional adsorbent properties. It is applied in a variety of purification and separation processes, in the abatement of hazardous contaminants, municipal and industrial wastewater treatments, as catalyst or catalyst support, in medicine, in hydrometallurgy for the recovery of gold and silver, etc.

In the last years, the industrial activities related with the exploitation of metal containing minerals have increased in San Juan-Región de Cuyo-República Argentina, which enhances the risks of contamination of surface and groundwater [3]. This situation promotes the development of regional alternatives to

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avoid or solve contamination problems. Heavy metals, such as lead and cadmium, are among the most toxic chemical pollutants in waters, which come from natural and especially from anthropogenic sources. Mining, industrial processes, domestic residues are important sources of contamination that contribute to the presence of heavy metals in waters. These pollutants cannot be removed from the aquatic systems by natural processes because they are not biodegradable [4].

Lead combines with the SH groups of the enzymes and cellular proteins, inducing nephrotoxicity, neurotoxicity, hypertension and damage in the central nervous system. Due to its size and ionic charge it can substitute calcium, accumulating in bones. This effect is particularly harmful in children [5,6]. Cadmium, which possesses high toxicity, is mainly absorbed in the breathing and gastrointestinal systems. It is considered a cumulative poison, remaining in the organism from 10 to 30 years. Poisoning with cadmium generally occurs by inhalation of powders and salts ingestion. Other diseases associated to this element are the hypertension and the itai-itai illness [4].

Several methods are used for the removal of heavy metals from water including oxidation, reduction, precipitation, ionic exchange, membrane technologies, electro-deposition, adsorption and solid phase extraction techniques [7]. These methodologies operate through different mechanisms such as ion-exchange, metal chelation, ion pair interaction, hydrogen bonding and other modes of binding. Among them, adsorption is considered highly effective and shows well-known advantages compared to other removal processes [8–14]. Activated carbon is the most used adsorbent for heavy metals removal due to its high versatility and effectiveness. This material exhibits a well developed porous structure and high internal surface area. Besides its textural properties, the surface chemistry is very important for specific applications [15].

Activated carbon can be obtained from almost any material with high carbon content, including industrial wastes [16,17]. The kind of carbonaceous precursor used and the activation method selected strongly influences both, the product properties (surface area, pore size distribution, surface functional groups) and the activation process yield. The activated carbon production process can be performed by physical (or thermal) activation or by chemical activation. The first one involves a partial gasification of the carbonized raw material under carbon dioxide and/or steam atmosphere. Chemical activation involves the raw material impregnation with a chemical compound and thermal treatment, resulting in dehydration, carbonization and the development of the porous structure [18].

Grape industrialization is one of the main economic activities of Cuyo Region, Argentina, producing wines, concentrated musts, raisins, alcohols and oils. In 2012, about 2200 million kg of grapes have been industrialized [19]. These activities generate important volumes of residues, grape stalk, lex and pomace among them.

Grape pomace is the residue of the must production step. It constitutes 10% (w/w) of the grape processed and it is partially used to obtain alcohol and oil. Grape stalk is generated in wine, concentrated must and raisins industries. It represents 2.5–5.5% (w/w) of the processed fruit. Grape lex is the residue of press and solvent extraction of oil from grape seed.

In order to design adsorption treatment systems, kinetic and equilibrium data are essential. Kinetic data gives information about the rate at which the retention takes place and the minimum contact time required to reach the equilibrium. From the equilibrium experimental data, the adsorption isotherm is obtained, and the retention capacity of the adsorbent can be determined. Adsorption techniques become more attractive when low cost materials are used as adsorbent precursors [20–22].

This work presents the results of studies carried out to assess the feasibility of preparing activated carbons from viticultural industry

wastes, grape stalk, lex and pomace, and their application to remove lead and cadmium from water. These wastes were activated with steam, in order to promote adsorbent properties, and characterized by their textural and physicochemical properties. Kinetic and equilibrium assays for each adsorbate–adsorbent system were carried out. The influence of the adsorbents properties on their adsorption capacity and the differences found in their performances are discussed.

Materials and methods

Adsorbents preparation

The materials used to obtain the activated carbon were grape pomace and grape stalks, both provided by Callia Winery, and grape lex, given by Olivi Hnos.

These materials were carbonized by thermal treatment in the absence of oxygen in a stainless steel retort like reactor electrically heated. The heating rate was 1.4 K/min, from room temperature up to 773 K and kept at that temperature for 2 h.

Carbonized materials, particle size between 4 and 18 ASTM mesh, were subjected to an activation step with steam at high temperatures in a stainless steel reactor (30 mm internal diameter and 300 mm length), where the solid char was placed to form a fixed bed of about 150 mm height. The heating was performed in an electric furnace, from room temperature to the activation temperature, in a nitrogen atmosphere with a heating rate of 15 K/min. Activation conditions, which were adapted to the characteristics of each material to develop textural properties in the products, are summarized in Table 1.

Activated carbon samples were named as follows: GL-AC (grape lex activated carbon), GP-AC (grape pomace activated carbon) and GS-AC (grape stalk activated carbon).

Materials characterization

Raw materials were characterized by their proximate and elemental analysis. Proximate analyses were performed according to ASTM standards and elemental analysis in a Carlo Erba EA 1108 CHNS-O. For the last, samples were previously dried in oven at 378 K until constant weight.

The adsorbents obtained were characterized by their specific surface area (BET), from the adsorption–desorption nitrogen isotherms at 77 K using a Quantachrome Nova 2200 equipment. Total pore, mesopore and micropore volumes were also determined using the Gurvitch rule, BJH and Dubinin–Radushkevich methods, respectively.

The point of zero charge pH (pH_{pzc}) of the adsorbents was measured following the method proposed by Noh and Schwartz [23]. Three aqueous solutions of different initial pH were prepared from a 0.01 M $NaNO_3$, using 0.01 M $NaOH$ and HNO_3 for its regulation. Six vials containing different amounts of the adsorbent under study, between 10 and 2000 mg, were placed with 20 mL of solutions at different initial pH. The equilibrium pH was measured after 4 days in contact at room temperature.

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 contacted with 20 mL

Table 1
Physical activation parameters.

Material	Temperature (K)	Time (min)	Steam flow (g/g/h)	Yield (%)
Grape pomace	1073	105	1.0	36
Grape stalk	973	165	1.7	47
Grape lex	1153	105	1.7	45

of 0.05 N acid and basic solution. The containers were sealed and maintained under stirring for 48 h at room temperature. Suspensions were separated by centrifugation and the final concentration of the solutions was determined by titration.

Surface functional groups were also studied by Fourier transform infrared (FTIR) spectroscopy, which were obtained using a Nicolet 380 equipment. Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 400/cm. The samples were previously placed in an oven at 60 °C for 72 h to remove any water present.

The morphological characteristics of the activated carbons surface was investigated by scanning electron microscopy in a JEOL JSM-6610LV (MEB) equipment. Samples were sputter coated with Au prior to the scanning.

Adsorption assays

To perform heavy metal adsorption assays, stock solutions were prepared by dissolving $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$ in deionized water.

In order to determine the best pH for the adsorption of the metals studied, assays at different pH values were performed. For this purpose 50 mg of adsorbent were placed in flasks with 84 mL of a 100 mg/L aqueous solution of metal at 293 K. Each suspension had a different pH value, ranging from 2 to 12, modified using NaOH or HNO_3 0.1 M. These suspensions were shaken for 2 h and centrifuged. Samples were taken from the liquid phase and metal concentration was determined by atomic absorption spectrometry, in a PerkinElmerAA-100, with hollow cathode lamp.

Cadmium and lead kinetic adsorption assays were performed in a Parr reactor at 294 K and atmospheric pressure. Adsorbent samples of 300 mg were placed in the reactor flask with 500 mL of a solution containing 100 mg/L of the metal under study. The experiments were carried out at a pH value of 6.0 ± 0.2 for cadmium, and at 5.5 ± 0.2 for lead adsorption assays, both determined from adsorption vs pH curves. The suspensions were stirred for 150 min and samples were taken at different contact time. The pH of the suspensions was measured at the beginning and at the end of each test. Metal concentrations were determined by atomic absorption spectrometry.

Adsorption isotherms were obtained contacting different quantities of the adsorbent, ranging from 10 to 200 mg, put in flasks with 50 mL of a 100 mg/L aqueous solution of the heavy metal, and shaken in a thermostatic bath at 293 K for the minimum contact time. All adsorption tests were carried out at the pH selected for kinetic studies, this is 5.5 ± 0.2 for lead, and 6 ± 0.2 for cadmium. Once equilibrium time was reached, samples were centrifuged and the metal concentration was determined in the liquid phase by atomic absorption spectroscopy (AAS).

Adsorption isotherms

Langmuir and Freundlich models were tested for equilibrium description. Langmuir equation, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface. It does not take into consideration interactions between adsorbed molecules. It can be represented by the equation:

$$q = \frac{Q_{\max} \times K_L \times C_e}{1 + K_L \times C_e}$$

where q is the amount of metal adsorbed at equilibrium (mg/g), C_e is the solute concentration (mg/L) in the aqueous solution after equilibrium was reached, and Q_{\max} and K_L are constants related to the maximum adsorption capacity (mg/g) and the adsorption energy (L/mg), respectively.

Table 2
Proximate and elemental analysis of raw materials.

Material	Proximate analysis (wt.%)				Elemental analysis (db ^a) (wt.%)			
	Moisture	Ash	Volatile matter	Fixed carbon	N	C	H	S
Grape pomace	29.4	8.3	48.7	13.6	1.98	52.22	5.80	0
Grape stalk	20.2	12.5	53.5	13.9	0.37	46.14	5.74	0
Grape lex	19.3	5.6	44.4	30.7	2.91	52.27	5.38	0

^a db: dry base.

Freundlich equation is an empirical model based on heterogeneous adsorption over independent sites and is given by:

$$q = K_F \times C_e^{1/n}$$

where K_F is related to the adsorption capacity of the solid and n is related to the intensity of adsorption.

Experimental data were fitted to Langmuir and Freundlich models by non linear regression using Matlab 7.6.

Results and discussion

Materials characterization

Table 2 presents the results of proximate and elemental analysis of the raw materials studied.

One relevant characteristic shown by these materials was the high ash content, especially for grape stalk and pomace. Another remarkable feature was the high fix carbon value of grape lex, an important feature to consider for industrial application.

In preliminary studies, standard activation conditions (1153 K, 1.7 g of steam/g of solid.h and 105 min) were applied to all the raw materials. Only grape lex yielded an adsorbent with a BET area near the commercially accepted limit. In the other two cases there was an almost complete gasification of the material, obtaining only ashes, due to the presence of alkali metals that catalyze the gasification reaction. For this reason, activation conditions were adjusted (see Table 1) until the porosity and yield, were acceptable.

Table 3 shows the results of the textural characterization of the obtained adsorbents. These values show that only grape lex reached a well developed porous structure, while in the others the surface areas and pore volumes were low compared with those of commercial activated carbons. It can be observed that all samples showed micropore volume percentages above 75%.

The results of total acidic and basic groups and pH_{pzc} determinations are shown in Table 4. According to them, grape stalk activated carbon has the highest total content of surface chemical groups, showing a marked difference compared to the other two materials. In all cases the amount of basic groups exceeded that of the acids.

The pH_{pzc} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. When solution pH is below the pH_{pzc} the surface of carbon particles is positively charged. The pH_{pzc} is also related to the surface acidity, low acid surface group

Table 3
Textural characterization of activated residues.

Material	BET area (m ² /g)	V_{Total} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{micro} (cm ³ /g)
GP-AC	266	0.099	0.001	0.095
GS-AC	300	0.128	0.006	0.114
GL-AC	798	0.442	0.093	0.342

Table 4
Physicochemical parameters of activated residues.

Material	Basic groups (mEq/g)	Acidic groups (mEq/g)	Total groups (mEq/g)	pH _{pzc}
GP-AC	2.26	0.70	2.96	11.0
GS-AC	4.77	1.91	6.68	11.2
GL-AC	1.83	0.20	2.03	12.0

concentrations means high pH_{pzc} values. In this case, the pH_{pzc} values obtained for the adsorbents, which were around 11, confirmed their markedly basic nature.

Fig. 1 shows FTIR spectra for the three activated carbons, GP-AC, GS-AC and GL-AC. Some differences were observed between the spectra obtained, not only in the wave number of the peaks but also in the relative intensity. All samples exhibited bands at wave number below 900 cm⁻¹, which are attributed to C–H bonds in aromatic structures [24]. A peak at 1040 cm⁻¹, attributed to C–O stretching and OH bending of lactonic, ether, phenol, etc., was found in GS-AC spectra with greater intensity than in the other two materials [25]. This material also shows a peak at 1320 cm⁻¹, which may be associated to C–O stretching vibrations [26] and one at 1550 cm⁻¹ attributed to C=C of aromatic rings and amides [27]. Samples GP-AC and GL-AC exhibited bands between 1370 and 1430 cm⁻¹ attributed to OH bonds of phenolic groups, COO⁻ and –CH₃ [28]. Sample GP-AC shows a marked peak at 1620 cm⁻¹, attributed to C=O bond of carboxylic groups [27].

SEM images are exhibited in Fig. 2. The external surface of activated carbon from grape stalk (GS-AC), grape pomace (GP-AC) and grape lex (GL-AC) are shown in Fig. 2(a,c and e), respectively. These images show the different basic structure of the stalk and pomace, which can be well observed because these materials were processed as received and maintained their initial structures. Instead of this, the lex had to be agglomerated to allow its treatment in the activation reactor.

Fig. 2(b, d and f) exhibit a cross-section of the same samples. It can be seen that the longitudinal fibers of grape stalk basic structure were not altered, and that the pores retained the fibers cellular order (see Fig. 2(a and b)). The activation of pomace and lex produced a more randomized porosity distribution. Fig. 2(e and f) images show the presence of the binder, grape must, distributed in the basic matrix of lex. It can also be observed that the presence of

smaller pores distributed in the structure of this sample, corresponds to the further development of porosity in it.

Adsorption assays

The pH is one of the most important environmental factors influencing not only surface functional groups dissociation, but also the solution chemistry of metals. Fig. 3 presents the effect of pH on the removal of Cd and Pb by GP-AC. As the equilibrium quantities of adsorbed metal ions depend on the equilibrium pH, all the results are presented as a function of final (equilibrium) pH of the suspensions, and given in terms of percent metal uptake. It can be observed that the amount adsorbed increases sharply in a narrow pH range, between pH 3 and pH 5, reaching a maximum value at pH 5.5 for Pb and 6 for Cd. These values were similar for all the adsorbents studied in this work and are coincident with the ones found in the bibliography [20,29,30]. According to the speciation diagrams of these metals, the species present at the mentioned pH values are Pb²⁺ and Cd²⁺ respectively [30]. Very low pH values hinder the adsorption of the metals studied since protons compete for adsorption sites, while at pH values higher than the previously mentioned, precipitation of Pb(OH)₂ and Cd(OH)₂ occurs.

Taking into account these results, kinetic adsorption assays for cadmium and lead were developed adjusting the suspensions initial pH to 5.5 ± 0.2 for lead and 6 ± 0.2 for cadmium.

Figs. 4 and 5 show the kinetic curves obtained for cadmium and lead adsorption assays using grape stalk, lex and pomace activated carbon.

In all cases removal process equilibrium was achieved in less than 40 min, except for GL-AC in lead adsorption that took more than 100 min. For this reason the equilibrium time used for all batch adsorption assays was set in 120 min.

From Fig. 4 it can be observed that GP-AC removed almost 99% of the cadmium initially present, while GS-AC and GL-AC achieved 60% and 55% removal, respectively. Fig. 5 shows that GP-AC had also a good performance in lead adsorption. In this case, GS-AC and GL-AC showed an improved performance in lead adsorption, reaching 95% and 80% of metal removal respectively.

It is apparent that the porous structure has little influence over the metal retention process, because the better adsorbent is the one with the lowest BET surface area. Differences in surface chemical groups of activated carbons, obtained by FTIR studies, would be the cause of the better performance of grape pomace activated carbon. Other important aspect of these assays is that the final pH of the suspensions was always higher than the initial, reaching in all cases values close to 8 and exceeding that at which insoluble species begin to appear.

Data from batch adsorption assays were used to obtain cadmium and lead adsorption isotherms, which are shown in Figs. 6 and 7. As in kinetic adsorption assays, the best adsorbent for both metals was GP-AC, followed by GS-AC. The adsorbent obtained from grape lex, GL-AC, was the less effective for metal retention. All adsorbents showed a better performance for lead removal, achieving adsorption capacities three times greater than those obtained for cadmium. Due to the basic nature of the adsorbents, that led the pH of the suspensions to high values, the contaminants removal is attributed to the combined effect of precipitation and adsorption phenomena. This aspect is more important for lead removal because, in accordance with the speciation diagram of both metals, insoluble species appear at a lower pH [30].

Another factor that should be considered for this analysis is the ash content of the adsorbents. It is known that the ashes of these materials have alkaline oxides in their composition which have an

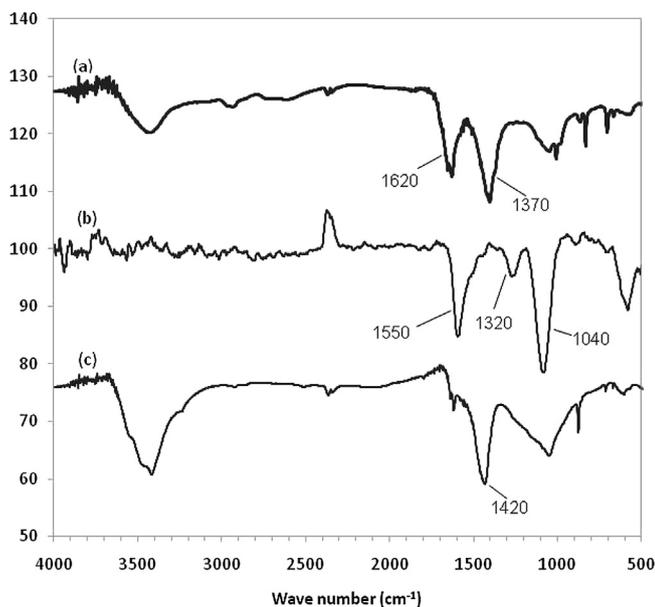


Fig. 1. FTIR spectra of activated carbons from grape (a) pomace, (b) stalk and (c) lex.

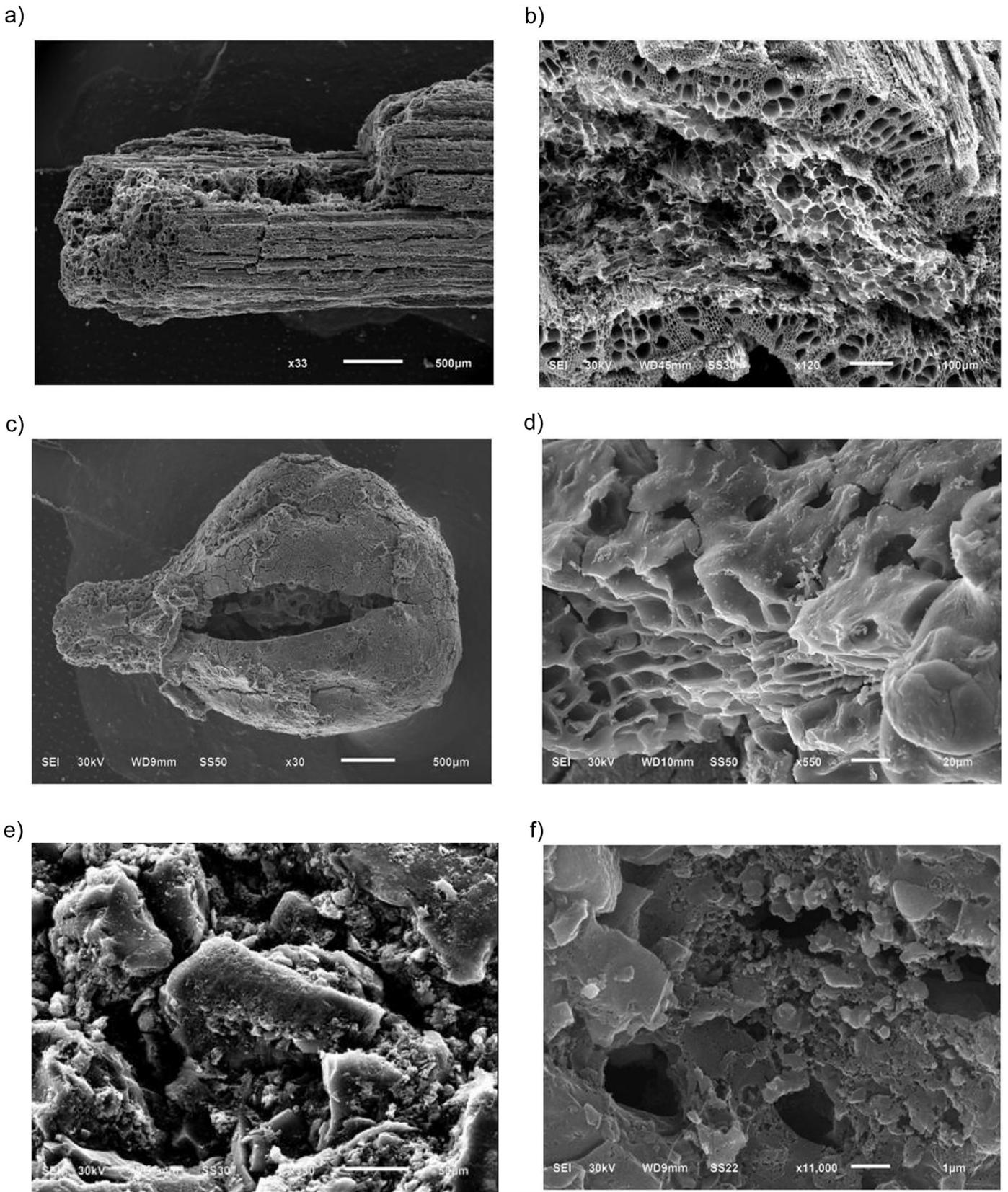


Fig. 2. SEM images of activated carbons obtained from (a) grape stalk (GS-AC), (b) grape pomace (GP-AC) and (c) grape lex (GL-AC).

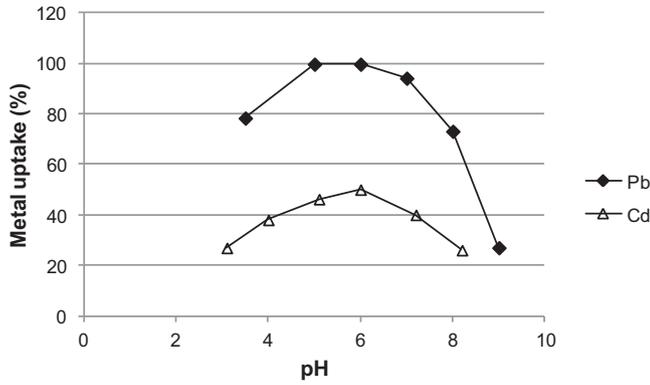


Fig. 3. pH influence on Cd and Pb uptake on grape pomace activated carbon.

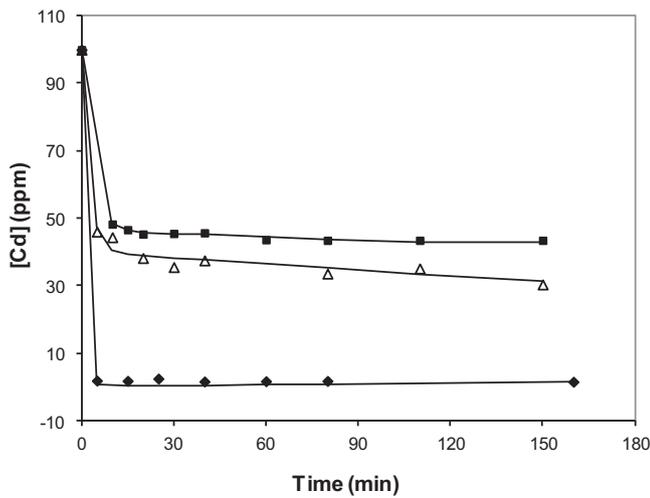


Fig. 4. Kinetic curve of Cd adsorption on grape lex (Δ), pomace (\blacklozenge) and stalk (\blacksquare) activated carbons.

important affinity for heavy metals [31]. Considering that these materials have notable quantities of ashes in their composition, this could be another contributing factor for metals retention.

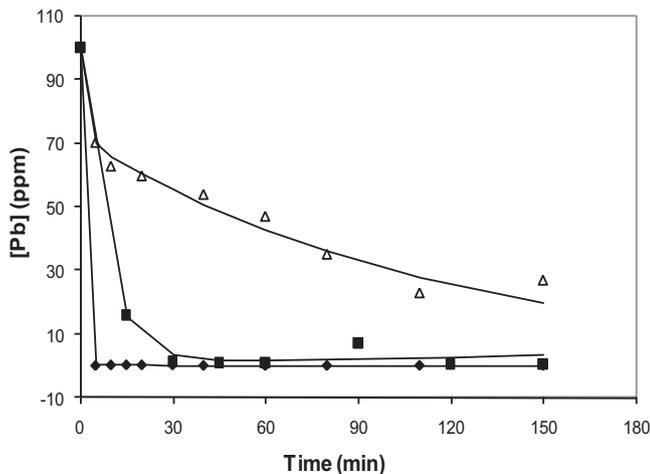


Fig. 5. Kinetic curve of Pb adsorption on grape lex (Δ), pomace (\blacklozenge) and stalk (\blacksquare) activated carbons.

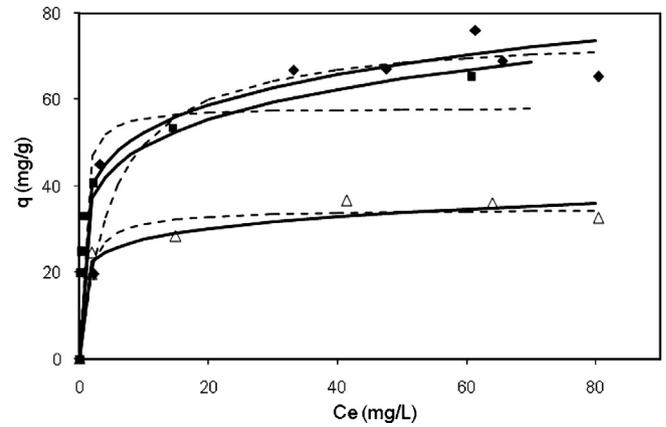


Fig. 6. Cd adsorption isotherms on grape lex (Δ GL-AC), pomace (\blacklozenge GP-AC) and stalk (\blacksquare GS-AC) adsorbents with Langmuir (dotted line) and Freundlich (continuous line) models.

Adsorption isotherms

Tables 5 and 6 show Langmuir and Freundlich parameters obtained for the removal of cadmium and lead respectively.

A comparative analysis shows that data fitted better to the Freundlich model. Higher values of the adsorption capacity, 1.93 mmol Pb/g and 0.67 mmol Cd/g, show the better behavior of GP-AC.

A comparison with parameter values reported in the literature shows that the results obtained in this work are markedly high, as can be seen in Table 7 [32–39]. This is attributed to the coupled effect of adsorption, precipitation and retention on the ashes of activated carbons, which made metal removal more efficient. It is difficult to obtain simple relationships between the removal capacity and each specific effect; the impact of these properties as a whole must be taken into account.

In order to evaluate the adsorbents performance for lead and cadmium remotion in a real situation, adsorption studies using sewage wastewater were carried out. This effluent was centrifuged to separate suspended solids and then contacted with activated carbons samples for 150 min under the experimental conditions applied for batch adsorption studies. Initial lead concentration was 1.31 mg/L, while cadmium was under the detection limit. The results indicated lead removals around 50% for GP-AC and GS-AC, while for GL-AC was only 11%.

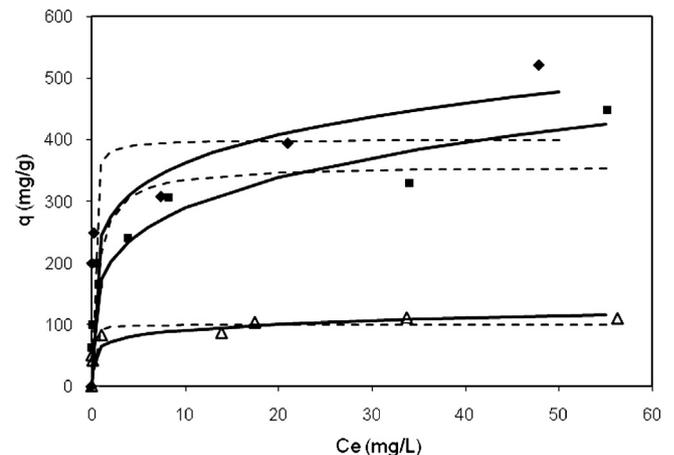


Fig. 7. Pb adsorption isotherms on grape lex (Δ GL-AC), pomace (\blacklozenge GP-AC) and stalk (\blacksquare GS-AC) adsorbents with Langmuir (dotted line) and Freundlich (continuous line) models.

Table 5
Langmuir and Freundlich parameters for cadmium adsorption.

Materials	Langmuir model			Freundlich model		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F	n	R^2
GS-AC	2.12	58.20	0.88	33.03	5.81	0.97
GP-AC	0.19	75.61	0.98	35.93	6.10	0.94
GL-AC	0.89	34.65	0.81	20.68	7.93	0.83

Table 6
Langmuir and Freundlich parameters for lead adsorption.

Materials	Langmuir model			Freundlich model		
	K_L (L/mg)	Q_m (mg/g)	R^2	K_F	n	R^2
GS-AC	1.49	358.10	0.88	172.8	4.44	0.94
GP-AC	9.38	399.50	0.83	244.30	5.81	0.87
GL-AC	11.18	99.77	0.80	65.32	7.06	0.88

Table 7
Langmuir and Freundlich parameters for other adsorbents.

Heavy metal	Activated carbon source	Langmuir model Q_m (mg/g)	Freundlich model K_F	Reference
Pb ²⁺	Van apple pulp	17.77	6.60	32
	Pine cone	27.53	12.53	33
	Phaseolus aureus hulls	21.80	7.50	34
	Alkali pyrophyllite	87.92	9.32	3
Cd ²⁺	Commercial carbons modified with egg shell wastes	7.66	0.195	36
	Ceiba pentandra hulls	19.59	8.32	37
	Rice husk	20.24	4.192	38
	Sulfurized activated carbon from nut shells	142.86	15.793	39

Conclusions

The study results showed that is feasible obtaining adsorbent materials from viticultural industries wastes, grape stalk, pomace and lex, and can be utilized to remove heavy metals such as lead and cadmium. Removal percentages above 95% were reached in some assays.

Adsorbents textural properties did not show important influence over metals removal under these experimental conditions. Grape pomace activated carbon presented the better performance despite this material had the lowest BET area. FTIR analysis showed some differences in the surface chemistry of these materials which would explain these results.

The basic nature of the adsorbents led the suspensions equilibrium pH to values around 8, which is in the range where insoluble species such as Pb(OH)₂ and Cd(OH)₂ appear. Therefore, the removal mechanism is attributed to the coupled effect of adsorption and precipitation. Furthermore, alkaline earth oxides present in the ashes of these materials may contribute to the removal process sorption. The adsorbents obtained by steam activation of viticultural industry wastes showed a remarkable performance in lead and cadmium removal, compared with other adsorbents obtained from industrial wastes reported in the literature.

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