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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.

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