



Research article

Grape stalk application for caffeine removal through adsorption

Rodrigo Portinho^{a, *}, Odivan Zanella^b, Liliana Amaral Féris^a^a Federal University of Rio Grande do Sul, Department of Chemical Engineering, Laboratory of Separation and Unity Operation (LASOP), R. Eng. Luiz Englert, s/n. Campus Central, CEP: 90040-040, Porto Alegre, RS, Brazil^b Federal Institute of Rio Grande do Sul, Laboratory of Separation Process, Rodovia RS 135, Km 25, CEP: 99170-000, Distrito Eng. Luiz Englert, Sertão, RS, Brazil

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ABSTRACT

Concern over emerging pollutants presence in water resources is growing, justifying the search for alternative or additional techniques to those applied in conventional water treatment processes. Use of adsorption with agricultural wastes directly as adsorbents or as precursors for activated carbon synthesis is a viable method, combining removal efficiency, low cost and biodegradability of the material applied. This study investigated the employability of grape stalk, a waste from grape industrialization process without effective use, in caffeine removal from aqueous solution. Grape stalk was used in three different forms: raw with only grain size adjustment (GS), modified by phosphoric acid action (MGS) and as activated carbon (GSAC). In the first two cases parameters pH, residence time and adsorbent concentration were varied in order to find optimum batch process conditions. For GSAC, on the other hand, caffeine removal percentages were high even for the least amount of adsorbent that could be measured with acceptable accuracy, which did not justify concentration parameter variation. Better adsorption capacities were observed in acidic solutions, with optimum pH values being considered as 2.0 for GS and MGS and 4.0 for GSAC. Optimum residence time and adsorbent concentration were 40 min and 25 g L⁻¹ (GS), 30 min and 15 g L⁻¹ (MGS) and 30 min (GSAC). Moreover, equilibrium was evaluated through adsorption isotherms construction, which were best represented by Sips model, displaying determination coefficients R² equal to 0.994, 0.999 and 0.987 and maximum adsorption capacities equal to 89.2, 129.6 and 916.7 mg g⁻¹. Adsorbents particular characteristics such as specific surface areas and micro-pore volumes were also determined, resulting in 6.23, 4.21 and 1099.86 m² g⁻¹ and 0.003, 0.002 and 0.568 cm³ g⁻¹ for GS, MGS and GSAC, respectively.

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1. Introduction

Many organic compounds from different origins contribute to the pollution of urban, industrial and agricultural wastewater. In this context, pharmaceutical compounds are highlighted, since they are characterized as emerging contaminants, i.e., they have been recently recognized as an environmental problem and are not present in any regulatory list of pollutants (Villaescusa et al., 2011).

After application, pharmaceuticals are excreted through urine and feces both by people and animals, being unchanged or in the form of metabolites. Additionally, inappropriate disposal of outdated drugs or surplus from a treatment can also contribute to

those contaminants appearance in wastewater. According to Fatta-Kassinos et al. (2011), pharmaceutical compounds have been detected in a great variety of samples, such as sewage, surface water and groundwater, with concentrations ranging from traces to parts per billion. Main polluting sources are hospital (Kümmerer, 2001; Langford and Thomas, 2009) and municipal (Yuan et al., 2014) effluents.

A problem associated with pharmaceuticals lies in the fact that many of them are not completely removed using conventional wastewater treatment methods. This entails the entry of these compounds in the environment and their appearance even in potable water (Santos et al., 2009).

Caffeine, a nervous system stimulant, is sometimes classified as a pharmaceutical, which may be explained by its wide use as an adjuvant in analgesic combinations of drugs. It can be found in cold medicines and analgesics, besides anorectics, stimulants and cosmetics with transdermal uptake (Benowitz, 1990; Oestreich-

* Corresponding author.

E-mail addresses: rodrigo_portinho@hotmail.com (R. Portinho), odivanzanella@yahoo.com (O. Zanella), liliana@enq.ufrgs.br (L.A. Féris).

Janzen, 2016).

Caffeine metabolism in human body is high and fast, where only a small quantity is excreted. Additionally, it is biodegradable, requiring three to six weeks to be naturally mineralized (Oestreich-Janzen, 2016). Even so, this component appears in many studies about surface water and wastewater (Deblonde et al., 2011; Loos et al., 2009; Pereira et al., 2016; Santos et al., 2009), being also used as an anthropogenic marker.

A possible explanation for caffeine notable presence in water matrices is due to the great consumption of this component. Fredholm et al. (1999) state that caffeine is the most consumed behaviorally active substance worldwide, with an average of 70–76 mg per person per day. Humans ingest caffeine through beverages produced from plants that have this substance, such as coffee, tea, mate and cola, besides soft drinks, in which it is artificially added. Furthermore, some foods as chocolate also contain caffeine and drugs that have this component in their formula often do not need medical prescription, being sold without restrictions and in large volumes.

It is important to emphasize that caffeine consumption in moderate quantities do not cause significant adverse effects on human health, leading to the conclusion that it is not necessary to evaluate the influence of small concentrations shown in the mentioned studies and other papers in literature, which range from ng L^{-1} to $\mu\text{g L}^{-1}$. However, should always be taken into account the effect that the component may have on other forms of life present in water media and possible synergic toxic effects when combined with other pollutants commonly found.

Caffeine and other pharmaceutical compounds removal from water media may be guaranteed utilizing advanced technologies, such as ozonation (Ternes et al., 2003) and advanced oxidative processes (Afonso-Olivares et al., 2016; Trovó et al., 2013), reverse osmosis (Sui et al., 2010; Urtiaga et al., 2013), membrane filtration (Mahlangu et al., 2015) and adsorption (Mestre et al., 2014; Nam et al., 2014; Sotelo et al., 2012a, 2012b, 2014; Villaescusa et al., 2011). Among these, Margot et al. (2013) indicate ozonation and adsorption onto activated carbon as methods with potential to large scale application, taking into account efficiency, cost and energy requirement of those processes. On the other hand, both techniques may present disadvantages, such as possibility of forming toxic byproducts, in the case of ozonation, and reduction of activated carbon efficiency caused by natural organic matter presence in water, leading to the need of spending larger adsorbent quantities.

In adsorption processes the cost of commercial activated carbons may be limiting, creating necessity to develop new materials with lower investment. An alternative is the utilization of agricultural residues directly as adsorbents or as precursors to activated carbon synthesis, since these materials are inexpensive, or even free, available in large quantities and renewable, besides the fact that they present high carbon content together with low inorganic matter percentage (Yahya et al., 2015).

Grape stalk, which corresponds to the woody part of the bunch, has already been studied as adsorbent in the removal of metallic ions (Fiol et al., 2008; Martínez et al., 2006; Villaescusa et al., 2004) and pharmaceuticals (Nurchi et al., 2014; Villaescusa et al., 2011). Additionally, Deiana et al. (2009) and Ozdemir et al. (2014) used this material as precursor in activated carbon synthesis, along with different oxidizing agents (phosphoric acid and zinc chloride, respectively). Stalk is a residue of grape industrialization process, being available in large quantities and having no current practical application. Basically, it is applied as a fertilizer due to potassium and other minerals presence, such as calcium and magnesium. However, its slow biodegradability and possibility of altering soil chemical composition turns stalks into a low quality fertilizer.

Moreover, its low nutritional value and high moisture content makes application as food in livestock industry or as fuel not feasible (Deiana et al., 2009; Prozil et al., 2012).

Based on facts mentioned, the present study intends to evaluate grape stalk application in caffeine removal through adsorption. For such, the material was used as an adsorbent in three different forms: *in natura* with only granulometric adjustment, modified through phosphoric acid action and in activated carbon form. For all adsorbents, optimum conditions for batch operation process were determined and adsorption equilibrium isotherms were constructed.

2. Materials and methods

2.1. Precursor preparation

Grape stalk from *Vitis Vinifera* species, including varieties *Cabernet Sauvignon*, *Tannat*, *Merlot*, *Chardonnay*, *Pinnot Noir* and *Cabernet Franc*, was used as precursor material in adsorbent synthesis. This material was kindly provided by a wine industry from Bento Gonçalves, Brazil.

Preparation process consisted in a series of steps. First, raw precursor was severely rinsed with distilled water until no solid particles were observed in residual water. Thereafter, stalk was dried at 110 °C during 24 h in a kiln. Preparation process was concluded with the material grinding in a knife mill and sieving between 4 and 12#.

2.2. Adsorbents

Three different adsorbents were developed and tested in the present study: grape stalk (GS), modified grape stalk (MGS) and grape stalk activated carbon (GSAC).

2.2.1. GS

Knife mill was used again for this adsorbent synthesis, although with a reduction in distance between rotatory and fixed blades in order to transform the precursor into a powder. Particle size was homogenized by sieving, resulting in an average particle size of 0.7 mm.

2.2.2. MGS

Prepared precursor was separated in 10 g portions. These quantities were adequately put into 250 mL Schott glass flasks, completing with enough 85% phosphoric acid (Sigma-Aldrich) to reach 4.22:1 impregnation ratio. A pre-mixture was done with a glass rod aid to prevent solid concentration on solution surface, ensuring a good contact between solid and activating agent. Thereafter, flasks were put into a Marconi MA563 shaker, where 25 °C and 30 rpm parameters were set. Contact time allowed was 24 h.

Resulting solid from previous step was drained to remove phosphoric acid excess and dried at 110 °C in a kiln for 24 h. Then, the material was washed several times until residual water pH reached a neutral value, which was measured with an OHAUS Starter 3100. Synthesis process was concluded with another drying step in the same conditions as before.

Granulometric adjustment was done through grinding with crucible and pistil and sieving. Average particle size obtained was 0.7 mm.

2.2.3. GSAC

GSAC synthesis process was based on Deiana et al. (2009) work, where authors obtained better specific surface areas and micro-porous volumes when phosphoric acid concentrations were raised

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