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Purification of sugar beet vinasse – Adsorption of polyphenolic and dark colored compounds on different commercial activated carbons

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Abstract

The adsorption on activated carbons of dark colored compounds contained in sugar beet vinasse was studied. Four commercial activated carbons with different properties (particle size, residual acidity and microporous properties) were respectively checked for efficiency at two temperature levels (25 °C and 40 °C) and at four pH levels (2, 3.5, 7, 10). The adsorption of organic molecules was determined by quantifying the amounts of total polyphenolic compounds and total organic carbon. The results showed that the adsorption capacity of dark colored compounds was enhanced by the decrease in both temperature and pH values of the solution. In this study, it is shown that this capacity depends on activated carbon characteristics which can be classified in the following order: particle size > residual acidity > microporous volume. Three models (Langmuir, Freundlich and Dubinin–Radushkevich) were tested from experimental data and compared. The Langmuir model provided the best correlation on all the activated carbons studied.

Keywords: Activated carbons; Adsorption; Vinasse; Polyphenolic compounds; Total organic carbon

1. Introduction

Sugar beet vinasse, a residue produced during the manufacturing of ethyl alcohol, is generally used as an additive for animal feed and as a fertilizer, but demand may be limited by strict environmental restrictions. Therefore, it has become of increasing interest to recover valuable components from distillery vinasse. For example, sugar beet vinasse dry matter contains around 15% of betaine (Caqueret, 2006). This compound possesses amphoteric surfactant properties which allow current industrial applications in toiletries and personal care products. The literature reports that betaine recovery is made by ion exchange (Giacobello et al., 2000; Heikkila et al., 1999), with strong cationic ion exchange resins. However, before obtaining pure betaine from a natural substrate like sugar beet vinasse, several operations of pretreatment need to be applied (Caqueret, 2006). Indeed, betaine is mixed with other molecules that damage the resin and reduce its properties (Zagonodni et al., 2002).

A multi-stage process for pure betaine recovery from vinasse was perfected in our laboratory (Caqueret, 2006) and it was shown that betaine was conveniently isolated in three steps: (i) removal of most insoluble compounds from the ethanolic medium, (ii) separation of most polyphenolic and other colored compounds, and (iii) purification of the betaine by ion exchange. In the second stage, it is difficult to remove the polyphenolic and colored compounds by oxidation with classic biological treatments and an adsorption process could be a good alternative to remove these compounds from agro-industrial residues (Ahmedna et al., 2000; Arslanoğlu et al., 2005; Bansode et al., 2004; Caqueret, 2006; Figaro et al., 2006; Garcìa-Araya et al., 2003; Pendyal et al., 1999; Satyawali and Balakrishnan, 2007).

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The purpose of this study was to find the best conditions for the discoloration of distillery vinasse by adsorption on activated carbons (ACs). To this aim, it was necessary to determine: (i) the main properties of the four commercial ACs used, (ii) the respective effects of temperature and solution pH on the removing of total polyphenolic compounds (TPP) first and then of total organic compounds (TOC), and (iii) the best adsorption model (Langmuir, Freundlich or Dubinin–Radushkevich (D–R)) that allows to estimate the ACs adsorption capacity and to determine the isotherm parameters.

2. Experimental

2.1. Characteristics of the distillery vinasse

The sample of distillery vinasse was supplied by a sugar refinery (La Vermandoise, Toury, France). The vinasse was first treated with ethanol in order to remove most of the proteins, pectins and other insoluble compounds (Caqueret, 2006). The content in protein (0.51 g kg^{-1} vinasse) was determined with the Bradford method by using a UV/Vis spectrophotometer (Jasco V-530). The determination of the pectins contents (24.50 g kg^{-1} vinasse) was carried out by "Laboratoire des Biopolymères Interactions Assemblages" (INRA Nantes, France) and the betaine content (204.20 g kg^{-1} vinasse) was determined by high pressure liquid chromatography (HPLC) (Zamarreno et al., 1997).The total organic carbon content (376.70 gC kg^{-1} vinasse) was determined by a TOC analyzer (Shimadzu TOC-V_{CSH}). The Folin–Ciocalteu method was used to estimate the amount of TPP within the vinasse. A calibration curve, obtained from caffeic acid with a spectrophotometer (Jasco V-530), gives the TPP content in equivalent caffeic acid (13.51 g_{eq} kg^{-1} vinasse). Systematically for all the experiments, TPP and TOC contents were determined before and after adsorption.

2.2. Characterization of the activated carbons

Three of the commercial ACs used (Picachem 150, 120P and 120PN) were supplied by Pica (Vierzon, France) and the fourth (CXA) by Ceca (Parentis, France). These ACs were used as received from the supplier without further treatment. The porosity of these ACs was characterized through conventional nitrogen adsorption isotherm at −196 °C (77 K) by Promes (UPR 8521, Perpignan, France) using a Micromeritics ASAP 2000 M. The samples were previously degassed at 250 °C for 24 h under a residual vacuum of less than 10^{-4} Pa. The nitrogen adsorption isotherms were analyzed according to the Dubinin theory (Stoeckli, 1996). Both the specific microporous volume (W_0 in cm^3 g^{-1}) and the mean pore size (L_0 in nm) were estimated from the linear part of the Dubinin–Radushkevich (D–R) plot (Stoeckli, 1996; Stoeckli et al., 2001). Besides, the Sing α_S plots (Sing et al., 1985) were used to determine the external specific surface (S_{ext} in m^2 g^{-1}) and assuming that for slit-shaped micropores the specific surface of micropores (S_{micro} in m^2 g^{-1}) could be estimated using the specific microporous volume and the mean pore size (Stoeckli, 1996).

2.3. Adsorption isotherms and analysis

All the isotherms were carried out with TOC initial concentrations expressed in gC L^{-1} ranging from 7.5 to 113 gC L^{-1} for TOC and 0.27 to 4.4 g_{eq} L^{-1} for TPP concentrations, which correspond to dilution factors ranging from 3 to 50 with deionised water. The adsorption isotherm experiments were carried out by adding 4 g of AC to 200 mL of the sorbate solution for different TOC concentrations, under mechanical stirring at 150 rpm, in a thermostated multi-agitation apparatus (Vankel Vanderkamp 600).

It was first verified that the adsorption equilibria at 25 °C were reached in less than 3 h for TOC and TPP adsorptions for all the ACs used (Caqueret, 2006). The results presented in Fig. 1 shows that the TOC adsorption capacity becomes stable after a contact time of 150 min for Picachem 150, 120 min for Picachem 120PN, 100 min for Picachem 120P and 60 min for Acticarbone CXA. Thus, a contact time of 180 min was chosen for all the experiments. Moreover, it was proved that hardly any betaine was adsorbed on ACs (<1%) in these experimental conditions (Caqueret, 2006). At the end of the contact time, the reactor medium was filtered through a 0.45 μm membrane filter. The TOC content of the liquid-phase was analysed by Shimadzu TOC-V_{CSH} and the total phenolic compounds content was determined with the Folin–Ciocalteu method. For all four ACs, two adsorption temperatures were studied (25 °C and 40 °C) and the influence of pH was checked on the neutral AC (120PN), by adding HCl (37 wt%) or NaOH (2.5 M) until the expected pH was reached.

2.4. Isotherms models

It is well known that the Langmuir equation is used for a monolayer adsorption (Langmuir, 1918). The linear

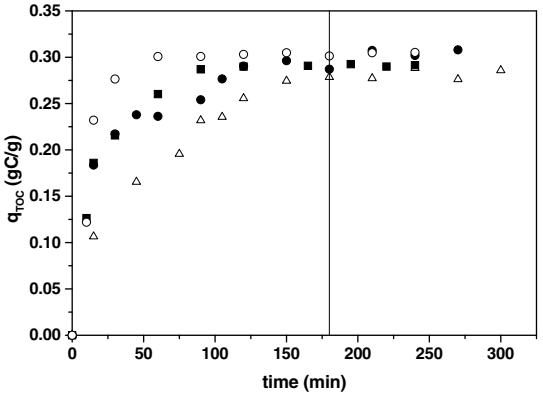

Fig. 1. Evolution of TOC adsorption in sugar beet vinasse as a function of the contact time for the different ACs used in the process at 25 °C (150 (△), 120PN (●), 120P (■) and CXA (○)).