Note. Vinegar Decolourization by Re-Activated Carbon

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This paper describes a batch-system for the decolouring of vinegar with modified activated carbons. The carbon was modified using controlled oxidation with a mixture of Ar/air at a temperature of 350°C. The porosity and functionality of the carbon obtained was studied by nitrogen physisorption and FTIR. The BET area increased from 625 to 1126 m²/g and the functionality also increased, giving new bands around 1700, 1200, 1450 and 1550 cm⁻¹, which contain most of the information about the functionality assignments of the activated carbons. The decolouring efficiency (DE) of a modified pelleted activated carbon (85.9 ± 2.2%) increased with respect to nonmodified pelleted activated carbon (14.1 ± 4.2%). This increase in DE is related to the increase in both the BET area and the functionality.

Key Words: vinegar, activated carbon, decolouring, polyphenols

INTRODUCTION

Phenolic compounds need to be removed during the production of certain foods as molasses, fruit juices and vinegars (Bento, 1990; Lyndon, 1996; Noomhorm et al., 1998). At high concentrations, these phenolic compounds, which provide besides the colour, astringency and a bitter taste, may give rise to oxidative reactions which are detrimental to the initial quality (Shahidi and Naczk, 1995). Therefore, the excess of phenolic compounds needs to be removed to increase the chemical stability and increase the shelf life of the product. The adsorbent that is most commonly used to remove these compounds is powder activated carbon in discontinuous operation, which makes automation difficult.

Vinegar can be produced from a variety of raw materials (malt, cider, alcohol, etc.) however wine vinegar is greatly appreciated in wine producing countries such as Italy and Spain, where it is made almost exclusively from wine. Because of this, both countries are interested in emphasising the quality of their product, which is obtained from a raw material of considerable commercial value. This added value makes it necessary to define quality parameters, and the vinegar maker needs to be able to control the final characteristics of the product, one of which is colour. It is common practice in the vinegar industry to decolour a fraction of vinegar, and blend it with nondecoloured vinegar to obtain a standard final product, thus maintaining the product’s characteristics and quality.

Activated carbon is used to decolour vinegar, the method used consists of mixing the powder activated carbon with the vinegar, stirring and then separating the activated carbon by filtration or settling. This process is a semicontinuous operation and small producers generally separate activated carbon by settling, which generates a considerable loss of vinegar and solid wastes. The settling process normally requires about 48 h, then the vinegar is filtered to remove the remaining residues of activated carbon. The decolouring process uses as much as 10–20 g/L of activated carbon, which increases production costs.

It is generally accepted that oxidation of carbons produces oxygen-containing functional groups at the edge sites of the graphitic planes. Furthermore, the surface oxygen functional groups are mainly at the entrance to micropores (Franz et al., 2000). It is well known that the adsorption capacity of activated carbons is related to their functionality.

The goal of oxidizing AC is also to modify its structural characteristics: BET surface area, pore volume and pore distribution. There are many studies on how different treatments affect the physical characteristics of activated carbon. The oxidation of activated carbon with steam increases the BET surface area, the external surface area, the total pore volume and the micropore volume (Petrov et al., 2000; Juang et al., 2001). In the wet
oxidation of AC, the BET surface area normally decreases and the pore diameter normally increases, while the micropore volume increases or decreases depending on the acid used for the treatment (Mangun et al., 1999; Moreno-Castilla et al., 2000; Nevskaia and Guerrero-Ruı´z, 2001). Furthermore, the oxidation with air increases the BET surface area, the pore diameter, the micropore volume and, more clearly, the pore size distribution (Mangun et al., 1999; Franz et al., 2000; Moreno-Castilla et al., 2000; Petrov et al., 2000). As a result of the treatment with air, more mesopores and many more micropores are generated on the activated carbon. Alternatively decolouring vinegars using cationic exchange columns is viable on a laboratory scale in continuous operation (Achaerandio et al., 2002).

The aim of this paper is to improve the adsorptive properties of a granulated activated carbon using air oxidation, and compare the efficiency of the modified and non-modified activated carbons in removing polyphenols from coloured vinegars.

**MATERIAL AND METHODS**

The activated carbons obtained from coconut shells were provided by Quimivita, S.A., Sant Adrià del Besós (Spain). The rosé wine vinegar was supplied by Badia Vinagres S.L., Mollerusa (Spain).

**Methods**

**Vinegar Characterisation**

The colour of the vinegar samples was characterised with modified colour intensity (MCI), which is the sum of the absorbance at wavelengths of 420, 520 and 620 nm (1-cm pass). These wavelengths were measured on a Hitachi U-2000 spectrophotometer. To normalise the values for vinegars, the decoloring efficiency (DE) was defined as:

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DE = 100(MCI_0 - MCI)/MCI_0
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where MCI\(_0\) is the MCI of vinegar before it is treated in batch studies or before it enters the column in continuous studies.

The polyphenol content was measured by the total polyphenol index (TPI) defined by the absorbance at 280 nm in 1-cm pass. The polyphenols were determined by liquid chromatography (chromatograph Hewlett-Packard 1050) with UV detector (diode array UV–visible HP 1059M). The column system consisted of a Tracer Nucleosil column (reverse phase) C\(_{18}\)120 (25 × 0.4 cm) with a particle size of 5 μm and a Guard-column of the same material. The oven temperature was 40 °C. The mobile phase was acetonitrile/acidulated water in a ratio of 80:20 v/v. The ratio of components of the acidulated water was 27:1000 v/v (acetic acid:Milli-Q water). The injection volume was 100 μL and the flow rate was 1.5 mL/min. Measurements were taken at 280, 320 and 365 nm.

**Batch Experiments**

The batch experiments were conducted at room temperature. Samples of 50 mL vinegar were mixed with 1.0 g of activated carbon (dose of 20 g/L in accordance with a prevision work, Achaerandio et al., 2001) for 72 h. The amber flasks containing the vinegar and the activated carbon were placed in a shaker and agitated at 150 rpm. The performance of the activated carbons was evaluated in batch experiments. Before analysis, the samples were filtered through a 0.22 μm Millipore membrane of cellulose acetate. All experiments were carried out in triplicate to ensure accuracy, and control samples were used.

**Sample Preparation**

Modified pelleted activated carbon (MPeAC) was prepared by placing 100 g of pelleted activated carbon (PeAC) in a tubular quartz glass reactor under a flow of equimolar Ar/air (5 mL/s) and heating at a rate of 5 °C/min to 350 °C, which then remained stable for 2 h.

**BET Surface Areas and Pore-Size Distributions**

The surface area of activated carbon were calculated using the Brunauer, Emmett and Teller Method (BET). The BET surface areas were calculated from nitrogen adsorption isotherms at 77 K with a Micromeritics ASAP 2000 surface analyser. The value for the area covered by a nitrogen molecule was 0.162 nm\(^2\). The same equipment calculated the distribution of pore sizes for diameters between 17 and 3000 Å using the Barrett, Joyner and Halenda’s method, BJH (Barrett et al., 1951).

**FTIR Measurements**

The IR measurements were performed in a Bruker Equinox 55. The discs were prepared by mixing 1 mg of activated carbon with 500 mg of KBr, and subsequent pressing at 106 kPa for 5 min. with a hydraulic press. After preparation, the discs were oven-dried at 50 °C for 1 h to remove water. The FTIR spectra were recorded in the 400–4000 cm\(^{-1}\) range of wave numbers, at a resolution of 4 cm\(^{-1}\) and with 30 scans per sample. A previously recorded background spectrum was subtracted automatically from the spectrum of each sample.
RESULTS AND DISCUSSION

Characterisation of Activated Carbon

The characteristics of the activated carbons showed that after treatment the BET area and pore volume of the MPeAC were practically twice those of the PeAC and that the average pore diameter decreases from 4.4 to 3.2 nm (Table 1). However, the pore-size distribution (amount micro/meso) was practically the same. This was due to the reaction of oxygen with carbon surface, that gave CO₂ and produced more micro- and mesopores.

The functionality of modified activated carbon increased according to the FTIR spectra (Figure 1). The bands around 1700, 1200, 1450 and 1550 cm⁻¹ contained most of the information about the functionality assignments of the activated carbons (Politou et al., 1990a,b). The most important functions found on the surface of the activated carbon have been ascribed as follows: the band around 1700 was assigned to the C=O stretching vibration in lactone and quinones (Boehm 1994; Gómez-Serrano et al., 1994); the bands around 1550 and 1450 cm⁻¹ were assigned to the asymmetric and symmetric aromatic carboxylic acid stretching vibrations (Davydov, 1984); the band around 1450 cm⁻¹ may be assigned to the C=O single bond stretching vibrations from γ- and δ-lactone functions, there were bands around 1200, 1450 and 1550 cm⁻¹ in the PeAC, while in MPeAC the bands around 1200 and 1550 were higher, the small band around 1450 cm⁻¹ disappeared and a new band around 1700 cm⁻¹ appeared. These results confirmed that the functionality of MPeAC has increased.

Adsorption Equilibrium

Colour removal was maximum with powder activated carbon (99.9%). Pelleted activated carbon gave a DE of 14.1%, while the modified pelleted activated carbon was 85.9% (Table 2). TPI reduction had the same tendency as DE but, for the PeAC, TPI reduction (60.3%) was higher than DE (14.1%). This difference was due to the analytical method, because simple phenolic compounds have absorption maxima in the 220–280 nm region (Shahidi and Naczk, 1995).

Two main groups were identified by HPLC: phenolic acids (gallic, p-coumaric, caffeic, p-coumaric,caffeyltartaric, and 2-S-glutathionyl caftaric [SGC]) and flavonoids (catechin and epicatechin). All the polyphenols identified were removed by the powder activated carbon, PoAC (Table 3).
The adsorption mechanism of phenolic compounds took place between the aromatic rings and the active sites of carbon. The steric hindrance in the more complex polyphenols did not allow the interaction of the phenol rings with the carbon surface (Nevskaia and Guerrero-Ruiz, 2001). The carbon modification increased the functionality, and favoured the adsorption by hydrogen bonds. Simple polyphenols such as gallic, p-coumaric, and caffeic acids were totally removed with PeAC and MPeAC, while p-coumaric and caffeoyltartaric acids were almost totally removed by both activated carbons. Catechin and epicatechin are practically removed with both activated carbons, but 2-S-glutathionyl caftaric acid (SGC) was reduced more with MPeAC than with PeAC. Removal of SGC in PeaAC was 72%, but in MPeAC was complete due to the increase of its functionality.

The considerable difference in the DE of PeAC (14.1%) and MPeAC (85.9%) was probably not due to the increase in surface area (about double) but to the increase in functionality. However, the highest DE was for PoAC, because the particles were smaller than PeAC, which minimised diffusion problems. The particle size of PeAC made it difficult for large molecules with steric hindrance to reach the active points on the pores. However, in the PoAC they could reach the active points more easily. The MPeAC and PeAC particles were the same size but the considerable increase in functionality may explain the large rise in decolouring efficiency.

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