



## Batch and fixed bed column studies on phenolic adsorption from wine vinasses by polymeric resins



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### ABSTRACT

The adsorption of phenolic compounds from wine vinasses onto non ionic resins was investigated with the goal of recovering antioxidant components from the effluent. Batch studies showed that the kinetic data fit to a pseudo-second order kinetic model. Dynamic adsorption studies with macroporous resins packed columns were also conducted to analyze the effect of initial phenolic concentration, the elution speed and the length of the packed bed on breakthrough curves. The experimental data showed that with increased column bed depth from 10 to 20 cm, breakpoint time ( $t_b$ ) increased from 19.6 to 25.6 min. The breakthrough curve was simulated well by Bohart-Adams, Yoon-Nelson and Thomas models. Bohart-Adams model was the only effective to fit the initial part ( $1-t_{1/2}$ ). The maximum removal capacity ( $q_{Th}$ ) calculated by Thomas model reached 98.3 mg/g at a flow rate of 5 mL/min.

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## 1. Introduction

Wine industry is one of the most important agro-industrial activities in the world generating huge amounts of effluents, which contain mainly grape pomace (stems, seeds and peel wastes), lees, filtration aids, cleaning products and racking effluents (Rodrigues et al., 2006).

These wastes have a considerably high concentration of toxic phenolic component, responsible for a significant environmental problem in the production areas. However, these streams are also considered as a source of various valuable compounds useful in cosmetic, food and pharmaceutical applications (Rubilar et al., 2007; Soto et al., 2012).

Grape pomace generated in the pressing stage, which is performed to produce the must, is a widely studied source of antioxidants, mainly catechins, flavonols, benzoic and cinnamic acids (Saura-Calixto, 1998; Bonilla et al., 1999; Torres and Bobet, 2001). In the wine industries that produce spirits the pressing pomace is processed in the distillation stage and the distilled pomace is the final residue of the plant.

The direct utilization of the distilled pomace offers operative, environmental and economic advantages, since: i) the distilled pomace can be valorized, ii) the solvent extraction of a wet solid is

not required, and iii) the final agricultural reuse of the pomace would be favored since the phenolic content becomes reduced.

From a nutritional point of view, polyphenols are the most important constituents of grape pomace. In toxicological studies, polyphenol extracts from winery by-products have been shown to be safe (Bentivegna and Whitney, 2002; Pereiro et al., 2011).

A simple alternative to recover polyphenols from distilled grape pomace, consisted on the adsorption of this effluent onto activated charcoal, but in this option, polyphenols could not be desorbed and eluted (Soto et al., 2008). However, the reversible adsorption of these grape polyphenols onto resins was observed (Díaz-Reinoso et al., 2010). Nonetheless, to the best of our knowledge the recovery of polyphenols compounds from wine distillery effluent in a continuous sorption process in a fixed bed column packed with non-ionic resin has not been thoroughly studied.

Macroporous adsorption resins are highly crosslinked polymers with large surface area and numerous permanent pores. In last years numerous surveys have proved the resin efficiency on the adsorption-desorption processes of bioactive compounds owing to their advantages including high adsorption capacity, low operational expenses, and easy regeneration (Soto et al., 2012).

There have been increasing numbers of studies on the application of macroporous resins to recovery and/or purify various pharmacologically-active natural products, e.g., polyphenols, alkaloids, and carotenoids, from natural sources as products and byproducts of the food industry, i.e. citrus peel and molasses (Grohmann et al., 1999), apple and grape pomace (Kammerer et al.,

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2005; Kammerer and Carle, 2008; Cardona et al., 2009; Kammerer et al., 2011), mango peel (Geerkens et al., 2015) or for solvent extracts from autohydrolysis liquors of grape pomace (Conde et al., 2011).

The aim of the present work is to explore the possibility of utilizing macroporous resins in a fixed bed to recovery polyphenols from white wine vinasses (WV). The adsorption process in column was evaluated by modifying the system variables (polyphenols concentration, flux, and bed height). The shape of the breakthrough curve was analyzed to correlate the compounds uploading and the time and volume of elution. Bohart-Adams, Yoon-Nelson and Thomas models were used to predict the column performance.

## 2. Materials and methods

### 2.1. Materials

White wine vinasses (WV) from Cooperativa do Ribeiro (Ribadavia, Ourense, Spain), years 2007–08, were collected and processed to separate the solid and liquid fractions. The drained liquid stream was centrifuged at 4500 rpm to remove suspended solids, diluted with tap water and stored at 4 °C until use. The total phenolic compounds in the centrifuged and diluted vinasses stream were 3.0 g (expressed as gallic acid equivalents)/L. The antioxidant characterization reports a DDPH radical scavenging capacity, expressed as EC<sub>50</sub>, of 0.216 g/L and a Trolox equivalent value of 58.4 mM.

### 2.2. Resins

PS-DVB copolymers with different hydrophobicity, Sepabeads SP700 supplied by Resindion S.R.L. (Mitsubishi Chemical Corporation) and Amberlite XAD16HP supplied by Sigma Chemical Corporation, were used. The physicochemical characteristics of these resins are summarized in Table 1.

The resins were activated by contact with 2.5–5 cm of excess methanol. Resins and methanol were blended gently by shaking one minute and then the mixture was stirred at 175 rpm and 25 °C during 15 min. Before use, they were rinsed with deionized water at a L:S ratio of 5 (w:w). The moisture content of the resins was determined by drying the beads in an oven at 70 °C up to constant weight, and adsorption experiments were carried out utilizing known amounts of resins.

### 2.3. Batch adsorption

Batch experiments were carried out for equilibrium studies by contacting the centrifuged and diluted WV and in batch mode with weighed quantities of hydrated resins in sealed Erlenmeyer flasks at 25 °C in an orbital shaker at 175 rpm.

After the selected contact time, the suspension was filtered through cellulose nitrate membranes (0.45 μm), and the total phenolic concentration was determined. The concentration of phenolics adsorbed at time,  $t$ , onto a mass unit of wet resin ( $q_t$ , mg/g) was measured as gallic acid equivalents and calculated by the equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of phenol in the aqueous solution (mg/L) at the initial stage and at  $t$  time, respectively,  $V$  is the volume of the solution (L), and  $W$  is the weight of the wet resin (g). Experiments were performed in triplicate.

### 2.4. Adsorption kinetics of phenolic compounds

The time course of adsorption from WV was experimentally assessed to estimate the contact time needed to reach equilibrium. The assays were performed in 25 mL Erlenmeyer flasks, with 5 mL of liquor sample and 3 g of wet resins at an initial pH 4.0, at 25 °C for up to 3 h. The content of each flask was filtered through a 0.45 μm membrane filter and the liquid phase was analyzed. The experimental data obtained, the total phenolics adsorbed measured by variable  $q_t$ , and expressed as mg of GAE/g wet resin, were fitted to the pseudo-first and to the pseudo-second order models.

The pseudo-first order rate equation of Lagergren assumes that the rate of solute uptake is proportional to the gradient in saturation concentration and in its linearized form is described by equation (2),

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where  $q_t$  and  $q_e$  are the amount of phenol adsorbed (mg/g) at contact time  $t$  (min) and at equilibrium,  $k_1$  is the pseudo-first order rate constant (min<sup>-1</sup>).

For adsorption systems following the pseudo-second order kinetics, the adsorbate was assumed to get adsorbed onto two surface sites. Thus the sorption kinetics following pseudo-second order kinetics can be represented as per the rate law described by equation (3) integrated for boundary conditions  $t = 0$  and  $t = t$  and  $q = 0$  and  $q = q_e$  gives the integrated rate law for pseudo-second reaction:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t \quad (3)$$

Where  $t$  is the contact time,  $q_t$  and  $q_e$  are the concentrations of phenolics adsorbed (expressed as mg/g) at the considered time and at the equilibrium respectively,  $K_2$  is the pseudo-second order kinetic parameter (g/mg min).

The initial sorption rate,  $h$  (mg/g min), as  $t \rightarrow 0$  can be defined as

$$h = K_2 q_e^2 \quad (4)$$

Eq. (3) can be linearized to at least four more different linear forms as shown in Table 2. A type 1 expression was reported by Ho (2006), this equation is valid at low and high times of sorption. At  $t \rightarrow \infty$ ,  $q \rightarrow q_e$  and at  $t \rightarrow 0$ ,  $q \rightarrow 0$ .

The experimental kinetic data obtained were fitted to the five different linearized forms of pseudo-second order model given in Table 2. The pseudo-second order kinetic constant ( $K_2$ ) and the theoretical  $q_e$  by a type 1 pseudo-second order expression can be calculated from the plots of  $t/q$  versus  $t$ . Similarly the pseudo-

**Table 1**

Physicochemical characteristics of the commercial resins used for the recovery of phenolic compounds from white wine vinasses (WV).

Resin name	Structure	Surface area (m <sup>2</sup> /g)	Pore radius (Å)	Porosity (mL/g)	Particle size (mm)	Density (g/mL)
XAD16HP	PS-DVB	800	100	1.82	0.25–0.84	1.02
SP700	PS-DVB	1200	90	2.3	0.25–0.70	1.01

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