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Biosorption of anthocyanins from grape pomace extracts by waste yeast: kinetic and isotherm studies

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ABSTRACT

The potential uses of two food industry by-products were analyzed in this study. The extraction optimization of anthocyanins from grape pomaces of different grape varieties and the application of waste brewery's yeast biomass as biosorbent of the anthocyanins in solution were evaluated. The biosorption capacity of the biomass was determined by pseudo-second order kinetic model and different isotherm models were used to describe the biosorption process. Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out to characterize the interaction of the biomass with anthocyanins. The biosorption process was also evaluated by HPLC analysis. Experimental data of the isotherm profile were adequately described by the Temkin model. The mean free energy (E) value from the model of Dubinin –Radushkevich suggested the occurrence of a chemical mechanism in the biosorption process. FTIR absorption spectrum of yeast biomass was complex. Significant changes in the intensity of yeast cell absorption bands and shifts of characteristic bands were observed after biosorption.

1. Introduction

Grapes are one of the most cultivated and profitable fruit crops in the world. The annual production of grapes in 2013 reached more than 77 million tonnes worldwide (FAOSTAT, 2013) and approximately 80% of the grapes are used in winemaking (Kammerer et al., 2004).

A large amount of residues **is** produced as a result of grape processing, especially by the winemaking industry. Grape pomace, which is a by-product that consists of skins, seeds and stems, is generally used as animal feed, fertilizer or simply disposed in the environment. However, this grape by-product is still a rich source of bioactive compounds that remain in the pomace due to incomplete extraction, increasing the array of possible applications. In fact, grape pomace is an expensive source of phytochemicals (González-Paramás et al., 2004), which may be useful in the food and pharmaceutical industries.

Anthocyanins are secondary metabolites of grapes and valuable compounds of grape pomace. Studies on different grape pomace varieties revealed anthocyanins 3-glucosides of the five most common anthocyanins: cyanidine, peonidine, delphinidine, petunidine and malvidine (González-Neves et al., 2012; Marquez et al., 2012). These flavonoids are widely known for their bioactive properties, with potential applications as natural antioxidants and antimicrobial compounds. Alternatively, anthocyanins can be used as natural food colorants in several food systems (Bordignon-Luiz et al., 2007). Considering that grape pomace is a cost-effective source of anthocyanins, the choice of a proper strategy of extraction and recovery of these multifunctional compounds is of great importance.

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The application of an adsorbent or biosorbent for recovery and concentration of anthocyanins is an interesting alternative (Scordino et al., 2004; Soto et al., 2011; Kohno et al., 2014). Only a few studies to date have focused on the recovery of these phytochemicals by biosorption (Jing et al., 2011; Mazzaracchio et al., 2012). Biosorption can allow the separation and concentration of anthocyanins from diluted solutions obtained from agro-industrial wastes. The process is attractive due to its relative simplicity, easy handling and low costs, especially if the biosorbent is cheap and highly available.

The biomass of the yeast *Saccharomyces cerevisiae* is the second most relevant byproduct of beer manufacturing. This surplus yeast is commercially used as animal feed (Ferreira et al., 2010). However, the valorization of this industrial byproduct could include the application in biosorption processes (adsorption) of several different compounds due to the fact that yeast cell walls contain proteins, lipids and polysaccharides, as basic building blocks with ion exchange properties, providing a series of functional groups which are capable of triggering adsorption (Aksu, 2005). In a recent study, phenolic compounds of teas were biosorbed into *S. cerevisiae* and an increase in antioxidant capacity after biosorption and digestion was noticed, suggesting that *S. cerevisiae* can act as a delivery system, increasing the bioaccessibility of the bioactive compounds (Jilani et al., 2015).

In this context, this research focuses on the extraction of anthocyanins from grape pomace of different grape varieties and the recovery of these compounds from the extracts by biosorption in brewer's yeast. For this, optimization studies were carried out for the extraction of monomeric anthocyanins from samples of Tannat, Merlot, Cabernet Sauvignon and Bordô grape pomace. Besides, batch biosorption experiments were performed and kinetic and equilibrium parameters of the process were obtained. High performance liquid chromatography (HPLC) was used to evaluate the biosorption process. Finally, the functional groups, usually involved in the biosorption process, were identified by Fourier Transform Infrared Spectroscopy.

2. Materials and methods

2.1. Grape pomace

Samples of grape pomace were obtained from the process of winemaking. Three samples of grape pomace of the species *Vitis vinifera*, varieties Merlot, Cabernet Sauvignon and Tannat, and one sample of the species *Vitis labrusca*, variety Bordô, were used in the study. The grapes were cultivated, harvested and processed in the region of Toledo, PR, Brazil.

Samples were dried in an oven with forced air circulation (Tedesco turbo power expert) for 36 h, at 40 °C. After drying, they were ground in knife mills and conditioned in low density polyethylene plastic bags, vacuum sealed (VC 999 K-3, Switzerland) and stored in dark.

2.2. Biosorbent preparation

Residual biomass of *S. cerevisiae* was obtained from the alcoholic fermentation process of Pilsen beer-type production by the microbrewery Bier Hoff, Curitiba, PR Brazil. Samples of surplus yeast were washed in distilled water and dried in an oven with forced air circulation (Tedesco turbo power expert) for 24 h at 40 °C. Dry biomass was then ground in a knife mill, conditioned in low density polyethylene plastic bags, vacuum sealed (VC 999 K-3, Switzerland), stored in dark, and used as biosorbent in the experiments.

2.3. Optimization of the extraction of anthocyanins from grape pomace

An experimental design was used for the optimization of the extraction of anthocyanins from grape pomace. Effect of three independent variables of the extraction process (temperature, solid–liquid ratio and concentration of solvents – water and ethanol) on the dependent variable (anthocyanins concentration) were evaluated. A central composite rotational design (CCRD) with eight factorial points, six axial points and five replications at the central point, totaling 19 experiments, was employed for experimental design.

2.4. Quantification of anthocyanins

The amount of total anthocyanins in the samples (grape pomace and yeast) was calculated by the pH differential method of Giusti and Wrolsted (Giusti and Wrolstad, 2001).

2.5. Biosorption kinetics

Kinetic studies were carried out in 125 mL Erlenmeyer flasks with 50 mg of *S. cerevisiae* biomass (dry weight) and 12.5 mL of a solution rich in anthocyanins obtained from the hydro-alcoholic extraction of grape pomace (in the optimized region). The experiments were performed until 400 min. At 120 min the equilibrium was already reached. Erlenmeyer flasks were agitated on a shaker (Tecnal TE-421) at 140 rpm and 25 °C. Samples were removed at regular intervals, over a period of 120 min, to analyze the anthocyanin concentration in solution and evaluate the amount biosorbed by the yeast. Samples were centrifuged at 5000 rpm for 30 min prior to anthocyanin quantification in the supernant.

The amount of anthocyanin biosorbed on yeast biomass (qt), in mg g^{-1}, was determined by mass balance, following the Equation (1):

$$q_t = \frac{(C_0 - C_t)}{M} V \tag{1}$$

where, q is the sorption capacity (mg g^{-1}), C_0 and C_t are concentrations (mg L^{-1}) of anthocyanins in the initial solution and after biosorption, respectively, V is volume of the aqueous phase (L) and M is the amount of biomass (g).

Kinetic modeling of the experimental data was performed by pseudo-second order mathematical model (Equation (2)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where, q_t and q_e are the sorption capacity (mg g^{-1}) at time t and at equilibrium, respectively, and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order model (Ho and McKay, 1999).

2.6. Isotherm studies

Biosorption equilibrium isotherms were performed in Erlenmeyer flasks with 50 mg of yeast biomass in 12.5 mL of a solution of anthocyanins at different concentrations and agitated at 140 rpm for 120 min in a shaker at 25 °C. Langmuir (equation (3)) (Langmuir, 1916), Freundlich (equation (4)) (Freundlich, 1906), Temkin (equation (5)) (Temkin and Pyzhev, 1940) and Dubinin–Radushkevich (equation (6)) (Dubinin and Radushkevich, 1947) models were utilized to describe and evaluate the experimental data.