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Adsorption separation of 2-phenylethanol and L-phenylalanine on polymeric resins: Adsorbent screening, single-component and binary equilibria

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ABSTRACT

Eleven polymeric resin adsorbents were investigated for their potential to bind selectively 2-phenylethanol from solutions containing also L-phenylalanine. The capacity for single-component and the capacity/selectivity for binary adsorption of 2-phenylethanol and L-phenylalanine were determined to eliminate adsorbents with low performance. Single-component equilibrium data of both compounds were well described by the Langmuir equation for five selected adsorbents. Two most suitable adsorbents, which were both non-functionalised poly(styrene-divinylbenzene) resins with different pore structures, were then used in measurements of the binary adsorption equilibrium of 2-phenylethanol and L-phenylalanine. The modified competitive Langmuir equation and the LeVan–Vermeulen equation provided good description of co-adsorption of 2-phenylethanol and L-phenylalanine in a broad concentration range of both components when high capacity and selectivity for 2-phenylethanol binding was observed. In order to obtain data for characterization of desorption performance, adsorption isotherms of 2-phenylethanol were also determined for pure ethanol and ethanol/water solutions as solvents.

1. Introduction

2-Phenylethanol (2-PE) is an aromatic alcohol with a characteristic rose-like odour and it is one of the basic compounds of rose oil. Its annual production is approximately 10,000 t (Hua and Xu, 2011). Most of this production covers the needs of cosmetic industry; a smaller part is used for chemical synthesis and in food industry as aromas (Etschmann et al., 2002). The major part of 2-PE is still produced by chemical synthesis where harmful and dangerous materials and extreme operational conditions are used (Chaudhari et al., 2000; Etschmann et al., 2002). The main advantage of such production is the low price of about 5 USD/kg of 2-PE (Hua and Xu, 2011). A traditional alternative approach is based on the extraction of 2-PE from rose petals. Due to a very low concentration of 2-PE and high cost of the raw material, the price of the final product is rather high—about 1000 USD/kg (Hua and Xu, 2011).

Since flavouring substances are, in general, applied in very low concentrations, the expensive flavours of natural origin find their place in the food market. A significant group of consumers prefer their use. As far as foodstuffs are concerned, the European legislation allows to use the term natural flavouring substances only for substances obtained by physical, enzymatic or microbiological processes from a material of vegetable or animal origin (Council directive 88/388/EEC). The existence of such legislation and the increasing demand for natural products in the food industry encouraged remarkable efforts towards the development of biotechnological processes

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for the production of flavour compounds over the past few years (Longo and Sanroman, 2006).

This has also opened an opportunity for the production of 2-PE by a biotechnological process. 2-PE can be produced by biotransformation using yeasts such as *Saccharomyces cerevisiae, Pichia anomala, Pichia membranaefaciens, Kluyveromyces marxianus* etc. (Etschmann et al., 2003). To increase the production of 2-PE, L-phenylalanine (L-Phe) is added as a precursor to the fermentation broth. L-Phe is transformed to 2-PE via the Ehrlich pathway (Ehrlich, 1907), where the biotransformation of L-Phe into 2-PE is connected with the growth of yeasts on α-ketoglutarate acid. It means that 2-PE is produced only in the exponential phase of the microbial growth. One of the important problems during the fermentation, which has significant consequences for 2-PE recovery, is the product inhibition. 2-PE is rather toxic to all microorganisms used for its production (Etschmann et al., 2002). Total growth inhibition was observed already at the 2-PE concentration of 2 g l^{-1} for *K. marxianus* and 3.8 g l^{-1} for *S. cerevisiae*, respectively (Etschmann et al., 2002). The concentration of 3.8 g l^{-1} was also the highest one achieved for a fed-batch fermentation (Stark, 2001). A conventional 2-PE production process thus includes down-stream processing steps where this flavour compound is recovered from rather dilute biotransformation product mixtures.

To overcome the problem of low productivity of the biotransformation step, in situ product recovery techniques have often been investigated in the recent period. The concentration of 2-PE in the fermentation medium was maintained under the inhibition level using hybrid bioreactor/separator systems based on microcapsule extraction (Stark et al., 2003a), membrane extraction (Mihal et al., 2013) or adsorption (Gao and Daugulis, 2009; Mei et al., 2009). The integration of reaction and separation units either in a single equipment unit or in a recycle loop makes the whole process more complex. The implementation of hybrid systems on the production scale thus requires higher research/development costs and stricter process control. These requirements reduce the benefits of a higher volumetric productivity provided by the in situ recovery, for which the conventional biotransformation is still a preferred option.

The isolation and purification of both natural and synthetic 2-PE were considered primarily in patent literature. Distillation of 2-PE alcoholic or aqueous/alcoholic solutions is a typical purification step (Hopff et al., 1958; Nienhaus and Hopp, 1990; Savina et al., 1999). Liquid–liquid extraction or adsorption are suitable isolation processes for the recovery of 2-PE from raw materials. For example, the extraction by hexane is the conventional process of obtaining 2-PE from rose petals (Baser and Buchbauer, 2009). Adsorption on polymeric resins was applied for the recovery of 2-PE from alcohol distillation residues (Savina et al., 1999) or from a biotransformation product mixture (Subbiah, 1999). Desorption was done using ethanol or methanol, respectively. The latter patent includes also a comparison of the adsorption recovery process with the liquid–liquid extraction by hexane, ethyl acetate and butanol (Subbiah, 1999). The performance of the adsorption process was better in regard to the 2-PE yield and concentration when using methanol. For 2-PE aqueous solutions, the adsorbent capacity is higher than the extractant capacity (Gao and Daugulis, 2009). On the contrary, the selectivity of 2-PE to L-Phe is higher for the extraction process because L-Phe is insoluble in organic solvents (Mihal et al., 2012a,b). This drawback of lower selectivity in the adsorption phase can be eliminated by a choice of suitable desorbent. L-Phe can then be completely separated from 2-PE in the desorption phase.

Few equilibrium and kinetic characteristics of 2-PE and L-Phe adsorption, which are prerequisites for engineering design of separation equipment, are available in the cited works. Mei et al. determined a single value of adsorption capacity for each tested macroporous resin (Mei et al., 2009). Only one of these resins provided the 2-PE adsorption capacity higher than 100 mg per gram of adsorbent dry mass. This is not a high value for low-molecular compound adsorption even if it is considered that the corresponding liquid-phase equilibrium concentration was relatively low—about 1 g l^{-1}. Moreover, the adsorption capacity of L-Phe was quite high for this particular adsorbent, about 80 mg g^{-1}, which indicated not a good selectivity for the separation of 2-PE and L-Phe.

Gao and Daugulis used a hydrophobic thermoplastic elastomer Hytrel 8206, which has an infinite value of selectivity because it does not bind L-Phe (Gao and Daugulis, 2009). They achieved a 2-PE partition coefficient of about 80 for the liquid-phase equilibrium concentrations of about 1 g l^{-1} and lower. Drawbacks of this adsorbent appear to be the absence of regular pores at low water content (up to 30%) and large particle size (over 2 mm) which must result in a significant mass transfer resistance. This slow kinetics probably caused that, in a semi-continuous operation investigated by these authors, the total volume of three packed bed adsorbers used was very high; about 50% of the fermentation medium volume.

The overall objective of our research activities in this area is to make a systematic design and optimisation of 2-PE separation from post-biotransformation solutions. This particular work was focused on the investigation of equilibrium properties of suitable adsorbent(s). Our search started with a group of commercial polymeric resins from two major world producers of adsorbents. In order to evaluate their capacity for 2-PE and the selectivity of 2-PE and L-Phe, batch adsorption experiments were carried out using single-component and binary aqueous solutions, respectively. A broad range of concentration values and different ratios of 2-PE and L-Phe were used in these experiments to determine single-component and binary adsorption isotherms for selected adsorbents.

2. Materials and methods

2.1. Chemicals and resins

2-Phenylethanol and L-phenylalanine were purchased from Merck Schuchardt OHG (Hohenbrunn, Germany). All other chemicals were of analytical grade and they were purchased from local vendors. Milli-Q-grade water was used for the preparation of all solutions. The solutions used for HPLC analysis were filtered through a 0.45 μm cellulose nitrate membrane filter.

The tested adsorbents were different types of Amberlite (Dow Chemical Company, Michigan, USA) and Macronet resins (Purolite, Philadelphia, USA). The list of the adsorbents together with their properties, such as the surface area and pore size are shown in Table 1. Before use, the adsorbents were conditioned in a 96% ethanol aqueous solution for 24 h. They were then gently stirred and rinsed with redistilled water.

2.2. Measurement of adsorbent dry mass

Adsorbent slurry was filtered through a 0.45 μm cellulose nitrate membrane filter. In this way, the water outside the