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Preparation and analysis of high capacity polysulfone capsules

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ABSTRACT

Since the concept of solvent impregnated resins was introduced in the early 1980s, the technique has been applied to a limited amount of applications. The main disadvantage of the resins was that the amount of solvent inside was limited to approximately 1.5 ml/g polymer. A new generation of solvent impregnated resins is introduced. These capsules can contain up to 11.8 ml solvent/g polymer and were prepared using a modified dry impregnation technique. Due to the high solvent loading, the capacity per volume of capsule for extracting products from aqueous phases is therefore dramatically increased.

1. Introduction

Since Warshawsky [1] introduced the concept of Solvent Impregnated Resins (SIRs) the technology has gone a long way. SIRs are polymeric particles where an organic solvent is impregnated inside a polymeric matrix (see Fig. 1).

SIRs have been shown to be an effective way to remove aromatics [2–4], heavy metals [5–7], carboxylic acids [8,9] and zwitterions such as amino acids [10] from aqueous phases. In one of our previous articles it was shown that SIRs containing Cyphos-104 were able to remove phenol from fermentation broths [11]. The XAD-4 polystyrene polymer backbone, which was used for SIRs had a pore volume of 1 ml/g [12]. This limited the amount of solvent, which could be impregnated per volume of particle. Limiting the volume of the polymeric matrix of the SIRs in the fermentation broth can theoretically result in higher product capacities. Therefore, a high solvent to polymer ratio in the SIR can result in more efficient fermentations due to higher product removal capacities since the polymeric backbone has no influence on product removal [13]. These new SIRs will have more the appearance of capsules due to their higher pore volumes. Capsules also have been investigated quite thoroughly for various applications ranging from potential extracting tools [14–16] to perfume release agents [17]. In 2006, Gong et al. introduced new polysulfone capsules [18]. These capsules had the advantage of a void volume up to 90 vol% depending on the particle diameter. This feature gave the particles the potential of a very high solvent loading. However, in the described method only 1.186 ml/g solvent was impregnated with solvent losses in the process. More recently Gong presented a method to prepare uniform polysulfone capsules containing 1-octanol. The capsules had a maximum loading of 6.98 g octanol/g polymer and a potential to be used as a caprolactam extraction tool from aqueous phases [16]. In a review from Juang [19] it was described that there are generally four ways of impregnating a solvent in a resin phase, namely the dry, wet, modifier addition and dynamic column method. The most common method of impregnation is the so-called dry method. In this article we apply a modified dry impregnation technique which is able to load up to 11.8 ml solvent-phase in 1 g polysulfone polymer without solvent losses in the preparation process.

2. Materials and methods

2.1. Materials and chemicals

Cyphos-104 was purchased from Cytec and was used as received. Cyphos-104 (trihexyl(tetradecyl)phosphonium bis 2,4, 4-trimethylpentylphosphinate) is a viscous ionic liquid with a specific gravity lower than water (0.89 g/ml). It is colourless to pale yellow, has a negligible vapor pressure and is immiscible with water (H_2O solubility is 16 mg/l at 30 °C [11]). It is miscible with hexane, toluene, isopropyl alcohol, diethyl ether, tetrahydrofuran, and methanol [20]. Dimethylformamide (99.9%), methanol (99.8%), ethanol (>99.5%), XAD-4, phenol (99.9%), polysulfone (Typical M_n = 26,000, T_g = 190 °C) were bought from Sigma–Aldrich and were used as received unless indicated differently.

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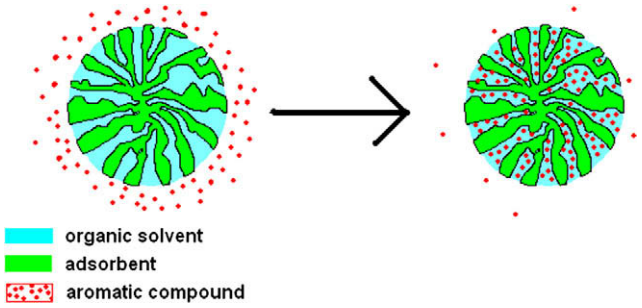

Fig. 1. Extraction of solutes from aqueous phase using SIRs.

2.2. Polysulfone capsule synthesis

Capsule synthesis consisted of preparing a polymer and anti-solvent solution similar to Gong's approach [18]. The same conditions were used as Gong [18] since capsule sphericallity is heavily influenced by nozzle distance to anti-solvent, anti-solvent composition and polymer concentration in the solvent. The polymer solution was prepared using a 1 g polysulfone/10 ml dimethylformamide ratio. Therefore, 30 g of polysulfone was dissolved in 300 ml of dimethylformamide at 50 °C, taking at least 2 h. Following this procedure, the polymer solution was then placed in a separation funnel where the nozzle had an inner diameter of 0.47 or 1.46 mm. The nozzle was at a distance of 7 cm from the top of the anti-solvent solution. The anti-solvent consisted of a 30 v/v% ethanol/water solution. The valve was opened in a way that there was a constant dripping of polysulfone/dimethylformamide droplets. In the anti-solvent bath the instantaneously formed droplets slowly precipitated due to the relatively high density of the polysulfone backbone. An overhead stirrer was used to prevent grinding of the newly formed capsules.

2.3. Loading of solvent in polysulfone capsules

The particles were washed with 2 l of water, 3 times in order to remove the dimethylformamide/ethanol from the particles. The capsules, which contained water, were placed in contact with a Cyphos-104/methanol mixture. This was ultrasonified for 1 h to equilibrate the water/methanol/Cyphos-104 phases. The volume of added Cyphos-104 was never more than the void volume of the capsules otherwise this will result in leakage of the Cyphos-104. The solution and particles were then placed in a roto-evaporator and continuously rotated (approximately 60 rpm) at 78 °C. As a result the methanol and water were vaporized from the particles/solution. Furthermore, the high temperature resulted in a higher viscosity of the Cyphos-104 facilitating impregnation. Due to the capillary forces the Cyphos-104 was absorbed in the capsules. After impregnation the capsules were cooled down to room temperature resulting in a lower density of the Cyphos-104 phase. Therefore, the remaining Cyphos-104 that was on the outside layer of the polysulfone shell was taken up in the porous structure. Using Karl-Fischer (870 KF Titrino plus; Metrohm) the mass% of water in saturated Cyphos-104 was measured. The results showed that 13.1 mass% of the solvent-phase consisted of water. This corresponded well with literature values found by Martak et al. [21], which was 14.4 mass%. Before use the particles were washed 3 times with 1 l of demineralised water.

2.4. Preparation XAD-4 solvent impregnated resins

XAD-4 (100 g) was washed three times with a total of 200 ml demineralised water to remove salts and organic impurities. This was performed in a beaker, which was placed in an ultrasonification bath for 1 h. XAD-4 was subsequently immersed three times in 200 ml methanol for 15 min each cycle for removal of trace organics. Finally, the washed adsorbent was put in the oven overnight (100 °C) for removal of the methanol/H_2O mixture. The SIRs were prepared using the dry impregnation method described by Juang [19]. Cyphos-104 was selected as the solvent-phase since it had a favorable phenol partition coefficient and a negligible vapor pressure. The low vapor pressure prevents solvent losses during the impregnation procedure. Cyphos-104 of 84.0 g was first dissolved in approximately 30 ml methanol to decrease the viscosity. XAD-4 (84.0 g) was then immersed in the diluted solvent and subsequently put in an ultrasonification bath for 1 h. This resulted in impregnation of the adsorbent. After ultrasonification, the SIRs were put in an oven (80 °C) for 4 h to dry the SIRs and remove the methanol.

2.5. Uptake rate of SIRs and capsules

A 200 ml aqueous solution containing 11.6 mM phenol was placed in contact with 5.00 g of solvent impregnated resin or capsule. The test was performed at room temperature and mixing was performed using a magnetic stirrer at 800 rpm. Samples of 100 μl were drawn and aqueous phenol concentrations were determined using a spectrophotometer (Ultrospec plus; Pharmacia LKB) at 270 nm.

2.6. Capacity of SIRS, capsules and pure extractant

Isotherms were measured of pure L–L extractant (Cyphos-104), SIRs and empty/loaded capsules. A 50 mM phenol solution was

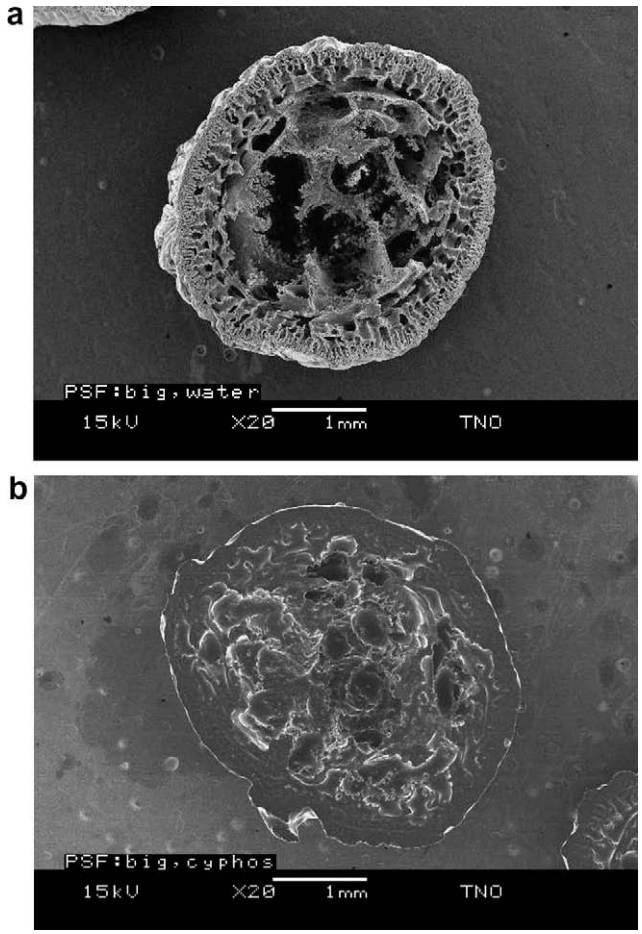

Fig. 2. (a and b): Empty and fully loaded capsule.