

Olive oil mill effluents as a feedstock for production of biodegradable polymers

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Abstract

The aim of the present paper was to study the feasibility of using olive oil mill effluents (OMEs) as a substrate in biodegradable polymer production. OMEs were anaerobically fermented to obtain volatile fatty acids (VFAs), which are the most highly used substrate for polyhydroxyalkanoates (PHAs) production. The anaerobic fermentation step was studied both without pretreatment and with different pretreatments (i.e., centrifugation, bentonite addition, and bentonite addition followed by centrifugation) and at various concentrations (28.5, 36.7 and 70.4 g COD L⁻¹). During fermentation, VFA concentration was determined (7–16 g COD L⁻¹) as well as the corresponding yield with respect to initial COD (22–44%). At all initial concentrations, centrifugation pretreatment (with or without previous addition of bentonite) significantly increased the final VFA concentration and yield, whereas the addition of bentonite alone had no influence. Moreover, centrifugation pretreatment led to a different acid distribution, which affected the hydroxyvalerate (HV) content within the obtained copolymer poly β -(hydroxybutyrate-hydroxyvalerate) [P(HB-HV)]. OMEs were tested for PHA production by using a mixed culture from an aerobic SBR. Centrifuged OMEs, both with or without fermentation, were tested. PHAs were produced from both matrices, but with fermented OMEs PHA production was much higher, because of the higher VFA concentration. The initial specific rate of PHA production obtained with fermented OMEs was approximately 420 mg COD g COD⁻¹ h⁻¹ and the maximum HV content within the copolymer was about 11% (on a molar basis). The HV monomer was produced only until propionic acid remained present in the medium.

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1. Introduction

Bioplastics are attracting much interest as alternatives to traditional plastics, this is due to the fact that they are

biodegradable and can be formed from renewable resources. Among the biodegradable plastics polyhydroxyalkanoates (PHAs), and in particular the copolymer poly β -(hydroxybutyrate-hydroxyvalerate) [P(HB-HV)], are the most promising. P(HB-HV) has similar properties to polypropylene, it can be processed in the same way and it could have the same wide range of

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application (Lee, 1996; Carrasco et al., 2004). However, until now production of P(HB-HV) has proven to be much more costly than traditional oil-derived plastics and this has hindered its use becoming more widespread (Salehizadeh and van Loosdrecht, 2004). Hence, there is a potential for widening the market for PHAs, provided that their cost decreases.

One of the most relevant costs in the production of PHAs is the cost of the substrate (Lee, 1996; Choi and Lee, 2000), which is usually pure (e.g. glucose and propionate for P(HB-HV) production). In recent years, the use of organic wastes (such as swine waste liquor, palm oil mill effluents, and vegetable and fruit wastes) is being studied as an alternative substrate for PHA production (Hassan et al., 1996, 1997a,b; Meesters, 1998; Reis et al., 2003; Salehizadeh and van Loosdrecht, 2004).

Olive oil mill effluents (OMEs) can also be considered as an alternative, no-cost substrate for PHA production. OMEs cause serious environmental pollution due to their high level of production (about 30 million m³/year in Mediterranean countries) and COD content (100–200 g COD L⁻¹). Up to now, the processes used to treat OMEs are considerably diversified: combustion fluidized bed (Cliffe and Patumsawad, 2001), anaerobic filter (Borja and Banks, 1995), anaerobic digestion and codigestion (Andreozzi et al., 1998; Angelidaki and Ahring, 1997), UASB (Saatci et al., 2003), membrane technology (Ahmad et al., 2003), pond system (Chin et al., 1996), ozonation reactor (Andreozzi et al., 1998), and activated carbon bed (Galiatsatou et al., 2002).

From the point-of-view of PHA production, their high COD content can be an advantage due to the possibility of fermenting OMEs at high rates to produce volatile fatty acids (VFAs) (Beccari et al., 1996), which in turn can be used for PHA production. Indeed, the acidogenic fermentation step is not inhibited to a great extent by OME lipidic and phenolic substances, which, on the other hand, inhibit the further step of methanogenesis (Beccari et al., 1999). Another advantage of OMEs with respect to other organic wastes is that they are a liquid stream and can therefore be easily pumped and treated in slurry-phase bioreactors. There is a lack of experimental data on the feasibility of using fermented OMEs for PHA production, however.

A new process (Dionisi et al., 2004) was proposed for the production of biodegradable PHAs from wastes, by using a combination of anaerobic and aerobic steps. The proposed process has three sequential steps. In the first step, acidogenic fermentation transforms highly concentrated biodegradable waste into a mixture of organic acids. In the second step, an aerobically activated sludge process is operated at medium–high organic load by periodic feeding in a Sequencing Batch Reactor (SBR) in order to enrich and produce a sludge with a high storage response. The produced excess sludge has a high storage

response that is exploited in a third step, this is operated in batch but at a considerably higher organic load in order to saturate the sludge storage capacity. The PHA-rich sludge then flows downstream for processing for PHA extraction and purification. This process has only been previously studied with reference to steps 2 and 3, however, with only synthetic mixtures of organic acids being used as the feed (Dionisi et al., 2004). Experimental studies on applications with real waste matrices are therefore lacking.

The aim of this study was at to examine the production of PHAs from OMEs, with both the fermentation step (step 1) and the PHA production step (step 3) being investigated. In the fermentation step, VFA production rates and yields were studied for OMEs with and without different pretreatments (bentonite addition, centrifugation, or bentonite addition followed by centrifugation). The PHA production stage was investigated by means of batch tests performed by using a mixed culture enriched in a SBR fed with a mixture of organic acids (step 2, Dionisi et al., 2004). The production rates and the composition of the biodegradable polymer were also investigated in comparison with synthetic substrates to which the enriched biomass had been acclimated.

2. Experimental methods

2.1. OME characterization

Fresh OMEs were obtained from an olive continuous centrifuge processing plant. The OMEs were characterized as follows: pH = 5.2, total COD = 113.8 g L⁻¹, soluble COD (filtered at 0.22 μm) = 34.5 g L⁻¹, soluble polyphenols = 2.2 g L⁻¹, soluble carbohydrates = 3.1 g L⁻¹, Kjeldhal nitrogen = 2 g L⁻¹ and lipids = 11.1 g L⁻¹.

2.2. Pretreatment tests

The OMEs were brought to pH 6.5 by adding CaO. They were then used directly for fermentation tests (see Section 2.3) or pretreated according to three different procedures. The first type of pretreatment was carried out by the addition of bentonite (B-3378 Sigma) (up to 10 g L⁻¹, Beccari et al., 2001). The bentonite–OME slurry was magnetically stirred for 2 h, then it was left for 24 h. The bentonite–OME slurry was either recovered and used in its entirety for fermentation tests (OME–B) or it was pretreated further by centrifuging (5000 rpm for 15 min), and the supernatant was used in the fermentation tests (second type of pretreatment, OME–BC). The third type of pretreatment was the direct centrifugation of OME with no previous addition of bentonite (OME–C). The supernatant was recovered and used for fermentation tests, also in this case.

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