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Continuous predispersed solvent extraction process for the downstream separation of 2,3-butanediol from fermentation broth

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ABSTRACT

2,3-Butanediol (BDO) offers the possibility of expanding the list of value-added chemicals produced from the biorefinery platform. However, a major challenge and technical bottleneck for an efficient biological production in a large scale is the separation of BDO from the fermented broth system. The use of colloidal liquid aphrons (CLAs) in pre-dispersed solvent extraction (PDSE) is considered as an emerging technique for the recovery of bio-based compounds. Herein, we describe the application of an environment friendly PDSE system using CLAs for the recovery of (BDO). Continuous mode of countercurrent extraction employing CLAs is demonstrated for the extraction of synthetic as well as fermented BDO in a bubble column apparatus. For the first time, the use of centrifugal contactor (CCS) is established for the formation of stable CLAs. The optimum system parameters required for the CLA formation using CCS method were: 0.25 wt% sodium dodecyl sulfate (SDS) as ionic surfactant, 0.5 wt% Tween 80 as non-ionic surfactant in butanol–water system having a flow ratio of 2 with agitation of 2000 rpm. Compared to the traditional liquid–liquid extraction (LLE) process, PDSE method provided 35–85% increase in mass transfer coefficient and about 30% reduction in overall solvent loading. In the presence of CLAs, the distribution coefficient (K_d) of BDO was found to be similar for all the concentrations of BDO. The results of this work open up the scope of PDSE–CLAs for the downstream processing of other biorefinery products.

1. Introduction

There has been an increasing interest in renewable bio-based products generated through the optimal utilization of biorefinery. The bio-based molecules obtained from the biorefining technologies provide sustainability not only for biofuels production but also create additional secondary economic benefits. This is because the bio-based products or the platform molecules, like products from the petroleum refinery, find applications in various chemical and biochemical industries. Most of the bio-based products are prepared by an optimal combination of chemical, physical, thermal and biological processes. Consequently, the biochemical production of 2,3-butanediol (BDO) from various feedstock such as starch residues, sugarcane or sugar beet, as well as lignocellulosic biomass residues, has gained significant attention recently [1–3]. The reason for the wide attention of BDO is due to its application in manufacturing of printing inks, perfumes, fumigants, moistening and softening agents, explosives, and plasticizers [4]. BDO has also main applications in asymmetric synthesis and fuel additives [5]. Recently, BDO has received a greater attention for its use as an intermediate in the production of bio-butadiene. Another area where BDO requirement is highly desired is for the production of green methyl ethyl ketone (MEK), an industrial solvent used for many applications [6].

The large scale production of BDO via biochemical routes is still in its early phase, but the growth prospects are showing enormous promise [6]. Recently, several articles have demonstrated that a variety of microbes can be used for the fermentation of sugars to BDO [4,6,7]. Toward that end, some of these studies reported biochemical production of BDO from a variety of first generation and second generation lignocellulosic biomass feedstock. Various feedstocks that have been explored include synthetic sugars, starchy materials, sugarcane juice, sugarcane beet and various lignocellulosic biomass hydrolysates [8]. All these studies have indicated that one of the major challenges associated with the production of BDO is the cost effective recovery of BDO from the fermentation broth [9,10]. This is because the use of different feedstock results in the complexity of fermentation broth, making the process of BDO separation and recovery a difficult task. Furthermore, the low concentration of BDO in the broth combined with its high boiling point

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(BP 182 °C) poses great challenges for the downstream operations. The recovery of BDO through distillation is expensive as well as energy intensive. Therefore, for successful large scale production of BDO efficient downstream processing is essential.

In the literature, various downstream processes are reported for the separation of BDO. Amongst various separation methods employed, solvent extraction or liquid–liquid extraction (LLE) was suggested as promising and low-energy intensive method [11]. The potential of LLE for BDO separation have been highlighted in various recent articles [12–14]. Toward that end various polar, non-polar, and ionic liquids were screened and a few promising extraction solvents were identified [15–18]. Although some organic solvents show good promise toward extraction, the amount of solvent used in the conventional LLE is fairly large and the recovery of the solvent poses an economical and environmental challenge. Added to this there is a growing concern with respect to the environmental impact and safety issues related to use of volatile organic solvents. Therefore, there is a need to replace or to minimize the use of solvents in downstream separation operations.

Within the domain of solvent extraction of BDO there are no experimental reports that have tried to address and overcome limitations encountered in traditional solvent extraction. In fact, there is paucity in literature concerning alternative methods to reduce solvent loading. In addition, there are also little data and details on mass transfer characteristic, particularly for a continuous LLE process. Therefore, to overcome the problems encountered in the conventional solvent extraction or LLE and to improve mass transfer characteristic for BDO extraction, this work utilizes predispersed solvent extraction (PDSE) method. In principle, PDSE is an intensified LLE technique in which the solvent phase used for the extraction is predispersed in the form of biliquid foam called polyaphrons. These polyaphrons discovered by Sebba et al. [19] form individual colloidal liquid aphrons (CLAs) when dispersed in water. CLAs are surfactant stabilized droplets of solvents providing a large interfacial area and thereby increasing the mass transfer in extraction systems [20,21]. CLAs have application in PDSE, enzyme immobilization, soil and water purification [22]. The use of CLAs in PDSE has the potential to overcome the problems encountered in traditional solvent extraction such as capital cost of mixer settlers, the power required for solvent dispersion, large solvent inventories and potential toxicity problems [23]. In addition, the use of CLAs provides higher extraction efficiency, shorter equilibrium time and lower toxicity as compared to conventional liquid–liquid extraction. Previous investigations reported in literature on CLAs include the screening of surfactant types and concentration for CLA formation and its influence on CLA stability [24–26]. The application of CLAs in PDSE is reported for compounds such as metals, antibiotics, antioxidants, organic dyes, and organic acids [27–34]. Only very few studies on mechanism of CLA mass transfer are investigated in the literature [35,36].

The use of CLAs in PDSE has been proposed for the recovery of lactic acid and succinic acid [33,34]. These reports have only explored the synthetic aqueous solutions and not the real fermented systems. Majority of bio-based chemicals generated in the biorefinery are produced via fermentation routes involving aqueous solutions and little is known about the role of CLAs in biorefinery separations. Hence, the use of CLAs can provide new alternative method for the development of LLE technology, possibly toward greener separation process. In this paper, we demonstrate the use of CLAs for the extraction of synthetic as well as fermented BDO in a continuous mode of countercurrent extraction. Additionally, a unique method is employed for generation of CLAs using centrifugal contactor (CCS). The formation of aphrons using CCS is a continuous method of preparation of CLAs which differs from the earlier methods reported [37,38]. The advantages of using CCS over other reported methods are low energy consumption [39], continuous method and easily scalable. For continuous countercurrent extraction of BDO using CLAs, bubble column apparatus is used due to its ease of operation, lack of mechanically operated parts inside, the low maintenance and the low operating cost [40,41]. Selection of solvent was done based on our previous studies on thermodynamic solvent screening which resulted in highest distribution of BDO in *n*-butanol solvent [42]. Therefore, *n*-butanol was used as solvent for LLE and PDSE of BDO carried out in this work. A recent literature article which was published in relation to the survey of solvent selection guides suggest that *n*-butanol comes under the classification of preferred and recommended solvent for various large scale applications [43].

In this work, we focus mainly on investigating the effect of CLAs on mass transfer characteristics of continuous BDO extraction in bubble column. Using CLAs as solvent system, the mass transfer characteristics such as distribution coefficients, mass transfer coefficients, number of theoretical stages and extraction efficiencies are estimated in column operation for synthetic as well as fermented BDO solutions. This study shows how an environment friendly solvent system comprising of CLAs can be developed to improve the mass transfer and reduce the solvent usage for extraction of bio-based chemicals.

2. Materials and methods

2.1. Chemicals

Synthetic BDO was obtained from Merck Chemicals, Germany, with mass fraction purity of 98%. Solvent *n*-butanol was purchased from the local vendor (Bharat chemicals, Mumbai). The purity of *n*-butanol was 99 (% w/w). Sodium dodecyl sulfate (SDS), sodium lauryl ether sulfate (SLES), benzalkonium chloride (BAC), Tween 80, Triton X-100, polyethylene glycol (PEG), lauryl alkyl ethoxylate (LAE) were procured from Merck chemicals, Germany.

Fermented BDO produced from molasses as feedstock was provided by our in-house fermentation team and this broth was used for extraction runs with fermented solutions. The details of the preparation method of molasses based fermented BDO are reported elsewhere [42,44]. The broth contained BDO as the main product along with minor amounts of other components such as residual sugars, acetoin, and volatile organic acids (<0.3% w/w). Table 1 provides the detailed composition of the fermentation broth used in this study.

2.2. Equilibrium measurements for BDO/n-butanol

Equilibrium curve was generated for the system water + BDO + *n*-butanol as well as for real fermented BDO system. The equilibrium data were was measured in an extraction (250 ml) bottle connected to a water bath maintained at 298 K. The concentration of BDO was varied from 2% to 20% in the equilibrium experiment. Ternary mixtures of different compositions of known components were prepared to obtain the equilibrium measurements. All mixtures were prepared by weighing with a Sartorius scale. Firstly, the different mixtures were stirred for 4 h into the extraction

Table 1
Composition of BDO fermentation broth.

Components	Quantity (% w/w)
Residual sugars	0.11
BDO	3.05
Acetoin	0.24
Acetic acid	0.29
Succinic acid	0.03