MASS TRANSFER AND PROCESS CONTROL (ADVANCES IN BIOCHEMICAL ENGINEERING SERIES, VOL 13) pdf

1: Roland Ulber (of Advances in Biochemical Engineering/Biotechnology, Volume 97)

Abstract Several new methods besides the usual organic solvent extraction have been developed over the last few years for the extraction of primary and secondary metabolites. Extraction and re-extraction processes are integrated into a single step by emulsion liquid membrane and solid supported liquid membrane extractions. These extraction processes are discussed and compared in this review, along with extraction with reversed micelles, and reactive extraction with the formation of a third phase at the organic-aqueous interface. It is usually applied in biotechnology as the first step in the recovery of primary and secondary metabolites. Extraction competes with many other separation methods, including adsorption, precipitation, chromatography, distillation, membrane separation, crystallisation, ion exchange, and electrodialysis. Adsorption has the disadvantage of low loading capacity, so it is applied if other techniques are less effective such as in case of cephalosporin C. In spite of its low selectivity, precipitation is used as the first step of recovery for many compounds, for instance citric acid. Chromatography and crystallisation are used for purification, not for the first step of product recovery. Distillation is employed for temperature stable metabolites like acetic acid. Ion exchange and electrodialysis are utilised for the separation of low molecular primary metabolites such as lactic acid. Membranes are often used to separate cells, and as the first stage of product recovery, but they are not very selective and are impaired by fouling from proteins, which are ingredients of the cultivation medium. Membranes are often combined with other separation methods, which have higher selectivity. The main problem with the recovery of primary and secondary metabolites by extraction is the complexity of industrial cultivation media, meaning that several by-products are extracted as well as the desired main product. Various alternative extraction techniques, like reactive extraction and aqueous twophase extraction, have been investigated in order to improve the selectivity 4 K. A decrease in production costs can be obtained by integrating downstream processing stages by performing extraction and reextraction in a single stage, for example by using emulsion liquid membrane or solid supporting liquid membrane techniques. If product inhibition prevails, an increase in productivity can be obtained using in situ recovery of the products. In the case of in situ extraction, the toxic effect of the solvent on the cells can be reduced by using membranes to avoid direct contact between cells and solvent. In some cases, the phase separation is not possible or it is a slow process. This problem can be overcome by separating the phases with a membrane. This review is a status report on solvent extraction and its various alternatives. The equilibrium distribution coefficient KD of the product in solvent is decisive for the recovery of primary and secondary metabolites by solvent extraction. To determine KD, basic investigations are performed with model systems using only a single solute in a chemically well defined aqueous feed F by applying a chemically well defined solvent S. The distribution equilibrium and sometimes the kinetics of the extraction process are determined by measuring the concentrations of the solute in the extract E and sometimes in the raffinate R. For in situ product recovery, the biocompatibility of the solvent is important. For these investigations the growth rate, viability of the microorganisms, and the product formation are determined in the presence of solvents. This review is divided into two main sections, two phase systems and three phase systems, and these are subdivided according to the various types of extraction techniques. Different solutes are discussed in these subsections. No third phase is formed. The microorganisms are separated from the cultivation medium at the end of the production process. The product is extracted from the cell free medium by an organic solvent. The main problem is how to extract a hydrophilic compound from the aqueous phase into an organic phase with high efficiency. Several organic solvents have been tested, and the distribution equilibrium of the solutes between Extraction of Primary and Secondary Metabolites 5 water and solvent were determined. In the following, the recoveries of different metabolites by solvent extraction are discussed. Edible ethanol must be produced by

fermentation. During the s, research into microbial alcohol production from renewable sources was intensified because of the energy crisis. During this time several investigations were carried out on ethanol and butanol production and recovery from cultivation media. The recovery of ethanol from the cell free cultivation media was performed by distillation. In situ removal of ethanol and butanol during the cultivation is necessary for high productivity, because cell growth and product formation are inhibited at high alcohol concentrations. Solvent extraction was considered to be one possible solution for maintaining the alcohol concentration in the cultivation medium at a low level. The main problem was that common organic solvents with high distribution coefficients for alcohols were toxic to the cells, and solvents which were biocompatible had low distribution coefficients. Therefore, large numbers of different compounds were tested for their suitability as solvents in terms of their distribution coefficients and biocompatibility. Daugulis et al investigated compounds [1â€”6] for their suitabilities as extractants. Other research groups for example [7, 8] also tested a large number of solvents. The main interest was in improving the productivity of the process by reducing the product inhibition. This was performed by in situ extraction of the alcohols during the cultivation. The microorganisms were retained in the bioreactor by the membrane. The product was extracted in situ from the cell free cultivation medium, and the medium was recycled into the reactor or the cells in direct contact with the solvent. In Table 1 some solvents are listed that are relatively useful for the in situ extraction of ethanol and butanol. The aqueous and organic solvent phases are sometimes separated by a membrane in order to avoid the direct contact of the cells with the solvent. Some of these investigations are described in Table 2. Ethanol was formed by the cultivation of Saccharomyces cerevisiae or Zymomonas mobilis. The ethanol productivity was improved using in situ extraction by a factor of 2. Butanol is produced by Clostridium acetobutylicum, which forms acetone, ethanol, acetate, butyrate and a small amount of acetoin. The equilibrium distribution coefficients of acetone in these solvents are lower than those of butanol Table 3. At particular cultivation conditions the KD values in n-decanol are: Because acetone, ethanol and butyrate are co-extracted, a separation step by fractionated distillation is necessary after their recovery.

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Mass Transfer and Process Control Advances in Biochemical Engineering: Volume 13 Edited by T. K. Ghose, A. Fiechter and N. Blakebrough Springer-Verlag; Berlin, Heidelberg, New York, pages.

This is an open access article distributed under the Creative Commons Attribution License , which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. Abstract Increasing interest in biomining process and the demand for better performance of the process has led to a new insight toward the mining technologies. From an engineering point of view, the complex network of biochemical reactions encompassed in biomining would best be performed in reactors which allow a good control of the significant variables, resulting in a better performance. The subprocesses are in equilibrium when the rate of particular metal ion; for example, iron turnover between the mineral and the bacteria, is balanced. The primary focus is directed towards improved bioprocess kinetics of the first two subprocesses of chemical reaction of the metal ion with the mineral and later bacterial oxidation. These subprocesses are linked by the redox potential and controlled by maintenance of an adequate solids suspension, dilution rate, and uniform mixing which are optimised in bioreactors during mining operations. This paper reviews the basis of process design for biomining process with emphasis on engineering parameters. It is concluded that the better understanding of these engineering parameters will make biomining processes more robust and further help in establishing it as a promising and economically feasible option over other hydrometallurgical processes worldwide. Introduction Biomining is gaining importance as a unit process which involves biological organisms in mineral extraction industries worldwide. With the decreasing high grade ore reserves and increased concern regarding the effect of mining on the environment, biomining technology, which was nevertheless age old deserted technique, is now being developed as a main process in the mining industry to meet the demand [1]. Another important aspect is the feasibility of biomining technologies to treat ores deposits with complex mineralogy, which could be difficult to treat by conventional methods [2]. Besides, the most attractive feature of biomining is economic feasibility compared to other competitive techniques [2]. Their analysis indicated that most biohydrometallurgical innovations have been commercially implemented during leaner times [3]. Economic factors such as eliminations of net Smelter Royalties associated with smelting and refining and possibility of the use bioleaching for on-site acid production to eliminate or reduce acid purchases are the reasons behind this observation. This has made us look toward the biomining with a broader insight into performance and profit oriented research to meet the commercial requirements. For this purpose, the process stoichiometry, kinetics, and the key parameters involved in the process have been studied [4 â€” 7] and the promising concepts like design and control of reactors for mining operations are yet to be practised [8]. Biomining in general is used to describe the exploitation of chemolithotrophic microorganisms to assist the extraction of metals from sulphide or iron-containing ores or concentrates [9 , 10]. It is a combination of two major operations bioleaching and biooxidation. The metal-solubilisation process is a blend of microbiology and chemistry. Conventional biomining is usually performed in heaps of ground ore or in the dumps of waste or spent material. Though this process offers several advantages such as simple equipment and operation, low investment, operational costs, and acceptable yields, it is beset with severe operational limitations, such as high heterogeneity of piled material and practically no close process control. Moreover, the low oxygen and carbon dioxide transfer rate and extended periods of operation to achieve sufficient conversions are very challenging [8]. From the process engineering point of view, bioreactors are the best choice for regulating the complex network of biochemical reactions comprehended in biomining as they allow for a close control of the variables involved, rendering significantly better performances. The reactors are usually arranged in series, with a continuous flow of material into the first, which overflows to the next, and so on for reduction of reaction volume required [13]. Therefore, process designing approach along with the defined application and monitoring of the abundance and activity of the metal sulfide oxidizing

microorganisms will make the biomining process more industrially popular and as a portfolio of flexible techniques to provide a way of recovering metal Figure 1. Factors involved in application of bioreactors in biomining. In this paper we discuss many of the theoretical considerations regarding the development of process for application of continuous-flow stirred-tank reactors in biomining with focus on different engineering parameters which should be taken into consideration for better control and design of biomining processes. Mining Mechanisms and Stoichiometry The most important mineral degrading microorganisms in biomining applications are the iron and sulphide oxidizing chemolithotrophs which grow autotrophically by fixation of atmospheric CO2. However, the mineral dissolution mechanism is not the same for all metal sulphides. Schippers and Sand [14] reported that the oxidation of different metal sulphides proceeds via different intermediates: Scheme of the two metal sulphide oxidation pathways mechanisms via thiosulphate or via polysulphides and sulphur based on the properties of metal sulphides MS. In the thiosulphate mechanism, solubilisation is through ferric iron attack on the acid-insoluble metal sulphides, with thiosulphate being the main intermediate and sulphates the main end-product. Schippers and Sand [14] proposed the reactions using pyrite as an example: In the polysulphide mechanism, solubilisation of the acid-soluble metal sulphide is through a combined attack by ferric iron and protons, with elemental sulphur as the main intermediate. This elemental sulphur is relatively stable but can be oxidized to sulphate by sulphur-oxidizing microbes [14] 3 â€” 5: This explains why strictly sulphur-oxidizing bacteria, such as A. The ferrous iron produced during metal dissolution and biomining might also be reoxidised by iron-oxidizing organisms to ferric iron: The role of the microorganisms in the solubilisation of metal sulphides is, therefore, to provide sulphuric acid 5 for a proton attack and to keep the iron in the oxidized ferric state 6 for an oxidative attack on the mineral. In another methodology proposed by Byrne and Luo [15], it was experimentally shown that the ferric iron precipitation process in the basal medium could be described by the following stoichiometry: This stoichiometry provides the numeric relation between moles of precipitated iron and moles of released protons to be used in the calculations. For the formulation of microbial metabolic reaction occurring during this course, the three half reactions for cell synthesis , electron donor should be combined. So the overall metabolic reaction is the sum of the half reactions [15] given as The negative sign of an electron donor reaction means that this reaction should be reversed before adding it to the others. Process Kinetics Kinetics of biomining process depends mainly on the overall sum of the kinetics of the two subprocesses of bioleaching and biooxidation in the mineral matrix. The ferric leach kinetics can be described by and the kinetics of the bacterial oxidation of ferrous iron is given by According to the shrinking core model by Lizama et al. If the particle shrinks at a uniform rate, the leaching rate is proportional to the surface area of the mineral particle. Assuming that the ferrous oxidation kinetics follows a Monod dependence on ferrous iron and includes a term related to ferric inhibition, the rate of ferrous iron oxidation can be given [17] as where is being the yield for ferrous iron oxidation. Using this expression, value of can be obtained from the values of at particular pH in a system operated under broad pH range. The kinetics of the chemical reaction in the biomining can also be related to the chemiosmotic mechanism [17 , 18] which can be given as where the diffusional process can be related to diffusion of protons across the ferric iron precipitates layer formed on the bacteria in the leaching sample. Thus, can be expressed as represents the thickness of the precipitates layer and is a constant directly proportional to the ratio between the diffusional and the kinetics constant. In broad terms the overall microbial growth during biomining is modelled via Michaelis-Menten kinetics described as.

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Abstract. Biochemical reactors are treated as heterogeneous catalytic reactors in which physical mass transfer completely or significantly controls the overall rate of the process being promoted in the reactor.

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