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Research & development

Prevent membrane pollution during separation

Ultrafiltration (UF) membrane pollution is one of the main constraints during the practical application of membrane separation technology. It is important to identify the polluting mechanism in order to prevent membrane pollution.

Scanning electron microscopy (SEM), XSAM-800 type X-ray photoelectron energy spectroscopy (XPS), infrared spectrum (IR) and SDS-PAGE were used to analyze the pollution of UF membrane using clavulanic acid fermentation broth. Results showed that the main pollutants are proteins of about 18 kDa in the fermentation broth. Results also showed that pore blocking and adsorption pollution are the main reasons for membrane fouling during production of clavulanic acid.

Membrane separation technology is one of the new high efficient separation technologies which developed rapidly during recent decades. Membrane separation technology is extensively used in chemical, textile, pharmaceutical, food, electronics and other industrial fields because of the advantages of low energy consumption, high separation efficiency, simple processes and no pollution. As one of the membrane filtration methods, ultrafiltration (UF) has been widely used as a separation method in the industry for the fractionation and concentration of protein substance, according to the advantages of compact design, energy consumption and gentle product treatment. Separation of protein is very important for various agro-food, antibiotics and some other bio-filtration applications and research. However, the pollution of membranes has been one of the major obstacles to large-scale industrial applications of membrane technology.

The fouling of the membrane, caused by the adsorption of protein and cake formation has become a vital bottleneck in UF, decreasing the permeability of the membrane and increasing the hydraulic resistance to the cross-membrane flow. Membrane pollution refers to the phenomenon of membrane pore clogging so that the membrane resistance increases and membrane flux declines because the colloidal particles or solute molecules in the fermentation broth deposit in the surface and pore of the membrane. Especially during the separation of fermentation broth, the composition of fermentation liquid is so complex that the membrane flux always declines significantly because some high molecular mass (including a large number of thalli, proteins, nucleic acids, polysaccharides, and colloids) often blocks and pollutes the membrane.

Some research has been concentrated on the efficiency of the UF membranes. Pretreatments on anionic surfactants or surface fluorination have been studied to reduce fouling during UF of proteins. Blending the UF membrane with a multifunctional comb copolymer has been tried to improve the antifouling and antibacterial properties of polyethersulfone UF membrane. Also different cleaning ways, including enzyme, detergent, stream, biosurfactant rhamnolipid and even other antifouling membrane materials were used to improve the effectiveness of the UF membrane. Many factors can affect the efficiency of the UF membrane. The pollution of the UF membrane is complicated and different with various samples.

There is no ideal and simple method to control different kinds of UF membrane pollution, especially the separation of fermentation broth with different constituents. The UF membrane fouling mechanism is not clear yet and no systematic theoretical guidance exists during the production of clavulanic acid. During the industrial production of clavulanic acid, the UF membrane is always heavily polluted by the fermentation broth of clavulanic acid and the membrane flux declines quickly. UF permeates involve a complicated mixture of organic material (including clavulanate, peptides, glycerine, sugars and amino acids) and inor-

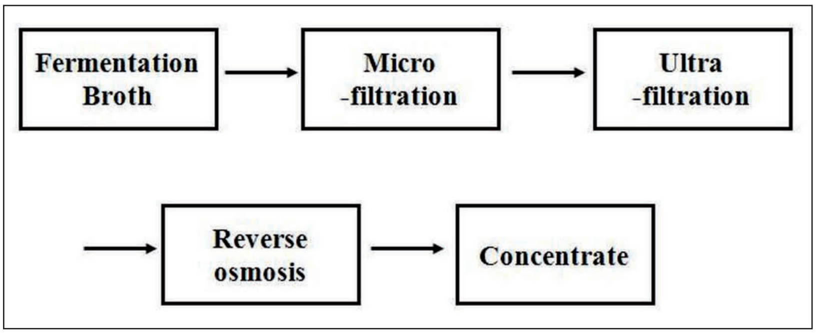

Figure 1. Sketch of membrane separation process of clavulanic acid fermentation broths.

ganic material (including both monovalent and divalent ions). The characterization analysis of membrane pollutants during UF and the polluting mechanism were investigated thoroughly in this research in order to control the pollution of the UF membrane.

Materials and methods

Membrane separation process flow of clavulanic acid fermentation broths

Clavulanic acid is produced by Streptomyces clavuligerus in this instance. Firstly, both mycelium and solid impurities were removed by microfiltration in the fermentation broth. Then some proteins and pigments were removed by UF. And then the fermentation broth was concentrated by reverse osmosis (RO). At last, the final product was collected after extraction and purification. The typical separation process flow is shown in Figure 1. The UF process was pursued by KOCH HpHT HFK -131 serial spiral UF membrane and the version is HpHT 8038-K131-VYV. The molecular weight of being intercepted is 10 kDa.

SEM analysis of the components of membrane pollutants during production of the clavulanic acid

The exterior glass fiber reinforcing plastic package of the polluted UF membrane was removed. Membranes were cut into small sections of 5 mm × 5 mm using a knife. The small membranes were immersed in hexane overnight to eliminate the conditional oil. Then the membranes were dried for 15 min and broken 90° to the surface of the membrane so as that the cross-section was exposed. Each sample was coated by platinum at 1.1 kV for 180 s and then inserted into the SEM. DXS-10A type scanning electron microscope (SEM, purchased from Shanghai Photoelectric Research Institute) was used to observe the changes of microstructure in the exterior and cross section of the UF membrane. All the images were focused on the layer surface and cross-section of the UF membrane.

Elemental analysis of the UF membrane pollutants

XSAM-800 type XPS (Kratos, produced in England) was used to analyze the elemental composition of pollutants in, on and near the UF membrane. Samples to be tested were arranged in the beam by maximizing photoelectron counts according to the primary C 1 s peak in C - C bonds at a binding energy of 284.8 eV. Also a neutralizer beam was used during the XPS analysis to compensate for peak shifting that exists according to charging of samples during X-ray exposure.

Infrared absorption characteristics of UF membrane pollutants during production of clavulanic acid

IFS660 Type Fourier Transform Infrared Spectrometer (Bruker, produced in Germany) was used to collect the infrared adsorption spectrum. The spectra were collected as the average of 128 scans with a resolution of 4 cm^{-1}, and were recorded from 4000 to 400 cm^{-1} in absorption mode.

SDS analysis on proteins in the pollutants during purification of clavulanic acid

The molecular weight of protein in the pollutants during production of clavulanic acid was detected by SDS-PAGE. 2 mm × 2 mm of the polluted membrane elements were immersed in 0.6 mL mixture of PBS buffer and SDS-PAGE loading buffer (5:1). The solution was

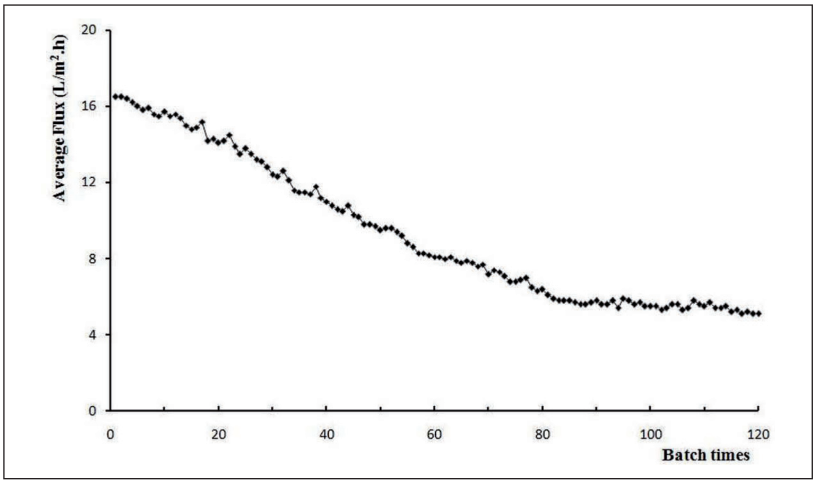

Figure 2. The average flux tendency of UF membrane during the industrial production of clavulanic acid.

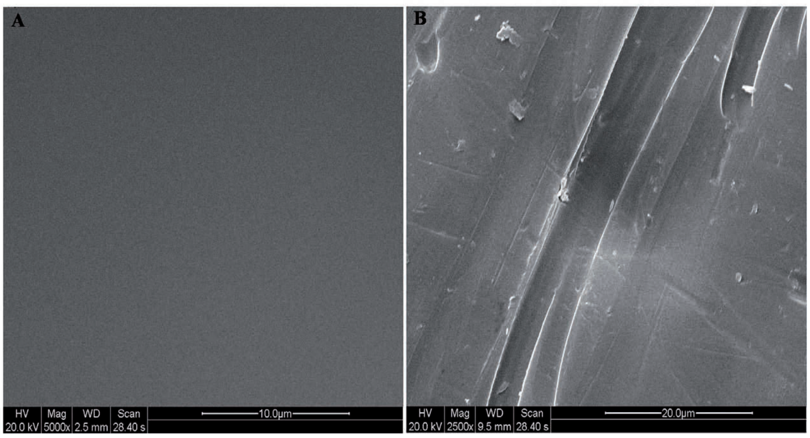

Figure 3. SEM photograph of UF membrane. A: Surface of new membrane; HV: 20.0 kV; WD: 2.5 mm; Scan: 28.40 s; B: Surface of polluted membrane; HV: 20.0 kV; WD: 9.5 mm; Scan: 28.40 s.