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Influence of organic matter from waste water on the permeability of membranes

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Abstract

The progress in the development of membranes for the treatment of aqueous solutions in the last years has attracted much interest in this technology. In order to find out the application limits, for example by ultrafiltration and reverse osmosis for waste water, research was carried out into the influence of organic matter, expressed as chemical oxygen demand (COD), on the permeability of the membrane on a pilot-scale. Different waste waters (pig and cattle slurry, milkhouse waste water and vegetable wash water) with different concentrations of organic matter were treated by ultrafiltration, and the permeates were treated partly by reverse osmosis. These tests as well as experiments for ultrafiltration with anaerobically treated mixtures of pig slurry and potato wash water showed that the permeability of membranes is determined by the concentration of organic matter of waste water and is independent of the kind of waste water. By ultrafiltration of different waste waters with an anorganic silicon-carbide membrane with a nominal pore diameter of 0.05 μm for example, the permeability decreased from 158 l/m² * h to 26 l/m² * h when the COD-concentration increased from 0.63 g/l to 42.8 g/l, respectively.

Keywords: Ultrafiltration; Reverse osmosis; Concentration polarization; Permeability; Waste water treatment

1. Introduction

Membrane separating processes are widely used in biotechnology and waste water treatment. For application of membrane separating processes the following factors are important among others:

- flow conditions
- selectivity of the membrane for the rejection of defined components of the treated medium
- permeability of the membrane.

The last point determines the necessary membrane area and thus the costs of the equipment. The permeability of membranes is decisively affected by fouling and scaling [1]. Scaling can prevented if the saturation concentrations (s.c.) of solved anorganic components in water are not exceeded (e.g., $CaCO_3$, $CaSO_4$) or by changing the s.c. by adding acid, respectively. But it is impossible to

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change the solved organic components in such a way that membranes are protected against fouling.

In the early 1980s Potts et al. [2] and Matthiason and Sivik [3] published reviews about membrane fouling, including its relationship to concentration polarization. The fouling factor is the major unknown in most system designs [4]. At the surface of the membrane there is a balance between the rejection of material and the back-diffusion into the bulk. This phenomenon is known as "concentration polarization". The greater the concentration polarization, the higher the concentration at the interface, and the worse the rejection. The increasing concentration within a system has an impact on the performance. Barger and Carnahan [5] have also announced that concentration polarization can be an important cause of membrane fouling. Negative effects of the higher wall concentration include decreasing the pure water permeation rate, and increasing the salt concentration that passes through the membrane in the product stream.

It has been demonstrated by tests with various agricultural waste waters such as pig and cattle slurry, milkhouse waste water, as well as vegetable wash water (wash water from carrots, celery, kohlrabi, potatoes, leek and black waste water from sand washing bay), that the organic components of the waste water influence the permeability of membranes for ultrafiltration (UF) and reverse osmosis (RO). The tested waste waters showed in each case different concentrations of organic components, expressed by chemical oxygen demand (COD), and these were also influenced also by anaerobic treatment of pig slurry and wash water of potatoes.

2. Material and methods

UF and RO trials were carried out on a pilot scale. For UF a tube module with an anorganic silicon-carbide membrane with a nominal pore diameter of 0.05 μm and a channel diameter of 16 mm was used. The membrane had an area of 0.05 m^2. The transmembrane pressure was adjusted at 2 bar. Fig. 1 shows the test equipment. The investigated medium was cooled in a double casing storage tank. During the tests, the temperature, the pressures before and after the membrane, as well as the permeate flux were recorded regularly. The overflow velocity of waste water over the membrane resulted from the adjusted pressure and amounts to 6.3 m/s. The permeate flowed back in the storage tank. Therefore, the concentration of organic matter in the waste water at the feed side of membrane was constant over the test time. From different components samples were taken regularly, and the COD-concentration was determined.

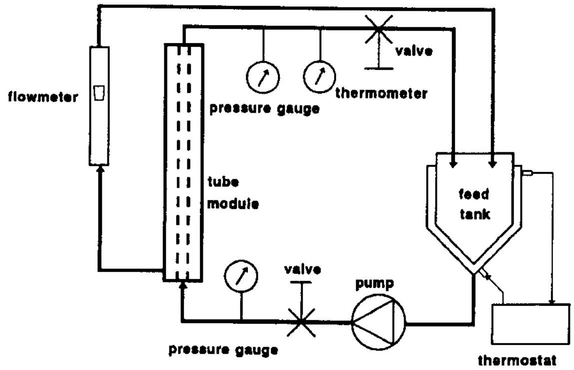

Fig. 1. Test equipment for ultrafiltration.

The RO tests were carried out with the permeate of the UF process. For these tests the RO equipment, RO-120-TW with FILMTEC TW 30 composite membrane, was used in the form of a spiral-wound element. The membrane had an area of 4.56 m^2. Fig. 2 shows the test equipment. The operation mode of RO was the same as the UF. Conductivity as an additional parameter was measured.

For the tests with pig slurry and a mixture of pig slurry and wash water of potatoes, these media were treated anaerobically in stirred tank reactors in batch mode before UF (reactor volume: 120 l; digesting temperature: 33°C). Organic substances from waste water were degraded by microorganisms. As a result of the anaerobic digestion process, methane (CH_4) and

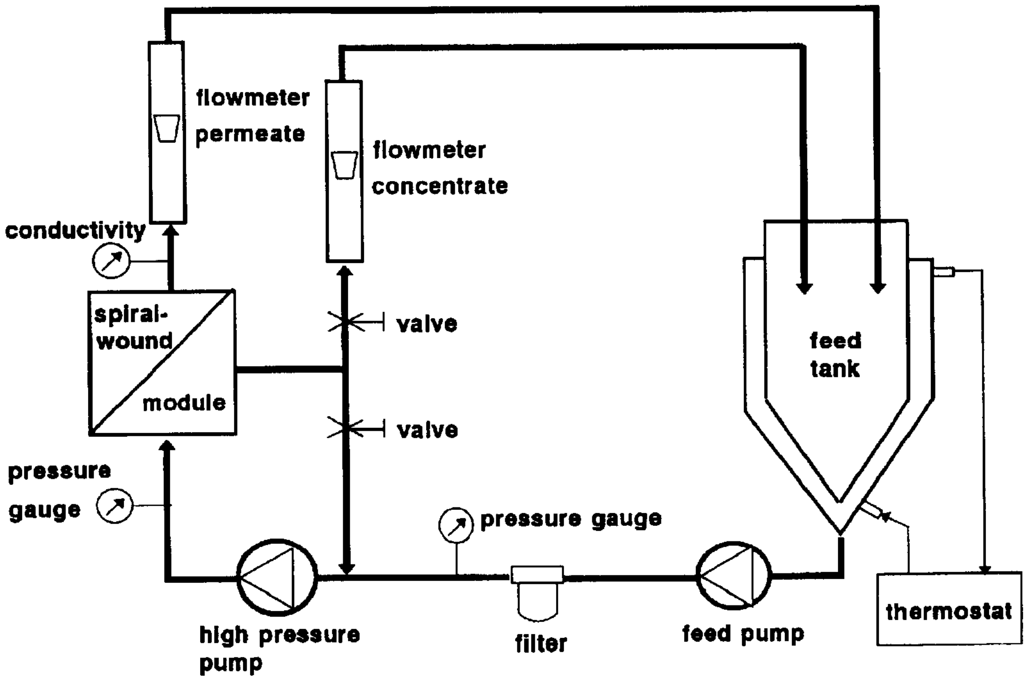

Fig. 2. Test equipment for reverse osmosis.

CO_2 were generated. Biogas production resulted in different COD concentrations in the waste water used for UF. The biogas production was measured in course of time, and samples were taken from waste water at different times. During the UF of the waste water, the permeate flux was measured. The concentration of COD in the digested substrate and the corresponding biogas production are reliable parameters for degradation of organic matter and are set in relation to the permeate flux in the UF.

3. Results and discussion

3.1. Ultrafiltration of different waste waters

In Fig. 3 the test results of the UF with various agricultural waste waters (pig and cattle slurry, milkhouse waste water and vegetables wash water such as wash water of potatoes, carrots, kohlrabi, celery and leek as well as black waste water from sand washing bay) have been plotted. Permeate flux decreases with increasing concentration of

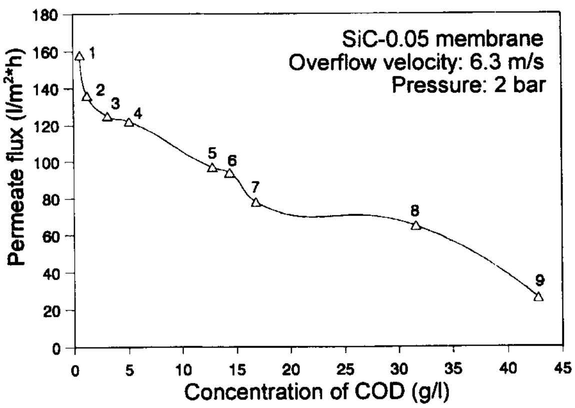

Fig. 3. Evolution of permeate flux vs. concentration of COD for ultrafiltration of different agricultural waste waters (1: black wash water of leek; 2,3: milkhouse wash water; 4: wash water of celery; 5: wash water of kohlrabi; 6: wash water of potatoes; 7: cattle slurry; 8: pig slurry; 9: wash water of carrots).

COD in waste waters at constant process conditions. Independently of the kind of waste water used, the permeate flux is affected by fouling of organic components on the feed side of membrane.

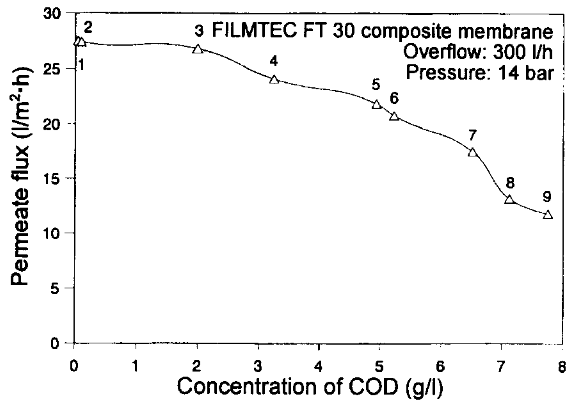

Fig. 4. Evolution of permeate flux vs. concentration of COD for reverse osmosis of agricultural waste waters after ultrafiltration (1: black wash water of leek; 2: black wash water; 3: milkhouse wash water; 4: wash water of celery; 5: wash water of kohlrabi; 6: cattle slurry; 7: wash water of potatoes; 8: pig slurry; 9: wash water of carrots).

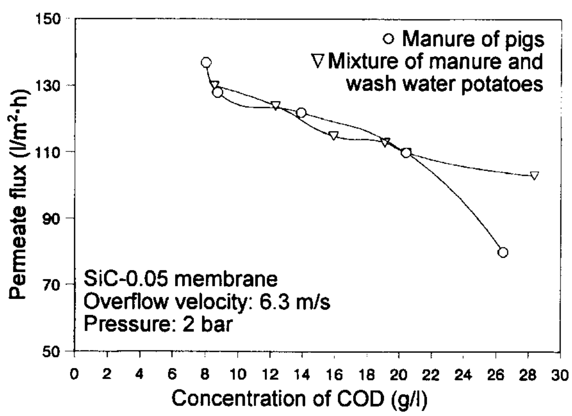

Fig. 6. Evolution of permeate flux vs. concentration of COD at the ultrafiltration of anaerobically treated pig slurry and a mixture of pig slurry and wash water of potatoes.

3.2. Reverse osmosis of different waste waters

In Fig. 4 the test results of RO with different waste waters (permeate after UF) were plotted. Like UF, the permeate flux is dependent on the concentration of organic components (COD) at the feed side of the RO membrane. Independently of the kind of waste water used, the permeate flux decreases with increasing concentration of COD at the feed at constant process conditions.

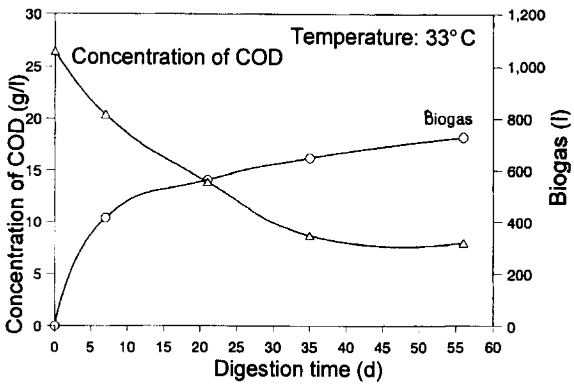

Fig. 5. Evolution of amount of biogas and concentration of COD vs. digestion time at anaerobic treatment of pig slurry.

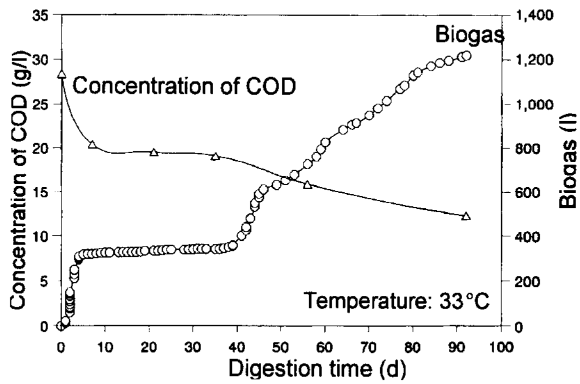

Fig. 7. Evolution of amount of biogas and concentration of COD vs. digestion time at anaerobic treatment of a mixture of pig slurry and wash water of potatoes.

3.3. Ultrafiltration of anaerobically treated slurry and a mixture of slurry and wash water of potatoes

The biodegradable organic components of pig slurry and a mixture of slurry and wash water of potatoes were transformed to biogas (CH_4 and CO_2) in anaerobic batch digesters. In Fig. 5 the decrease of COD and the production of biogas from pig slurry has been plotted vs. digestion time. As the concentration of organic acids from the start accounted for 6.42 g/l and methane-forming bacteria were in surplus by adding inoculum, the production of biogas started without a lag-phase. Therefore, organic matter was degraded. The high reduction of concentration of COD after 35 d points to the fact that the production of biogas was finished at this moment.

In Fig. 6 the test results have been plotted from the UF of waste waters after different digestion times. The permeate flux decreases with increasing concentration of COD not only for pig slurry but also for a mixture of slurry and wash water of potatoes. The concentration of organic acids in the mixture of pig slurry and wash water of potatoes at the beginning of batch trials accounted for 3.47 g/l and these were degraded directly in biogas by microorganisms. In batch trials the concentration of COD decreases with an increase in biogas production. After 5 d the volatile fatty acids increased, and biogas production was inhibited. This resulted in stagnation of COD removal (Fig. 7), and the permeate flux decreased compared to the trials with inhibited biogas production (Fig. 6).

4. Conclusions

The test results show that the permeate flux of membranes for UF and RO is considerably affected by the concentration of organic matter of waste water, expressed as COD. This is caused by concentration polarization at the membrane as a boundary layer effect. Membrane permeability decreases with increasing concentration of organic matter in waste water, and that is independent of the kind of waste water.

Tests by Harada et al. [6] with a synthetic waste water with a total strength of 5,000 mg/l COD consisting of soluble and particulate COD (cellulose) in the ratio of 1:1 confirm the decrease of permeate flux with increasing COD-concentration. Also the results by Bilstad et al. [7] for treatment of raw and anaerobically digested pig slurry by RO have shown that the permeate flux is not proportional to solid concentration and therefore of COD-concentration.

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