Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article László, Zsuzsanna , Kertész, Szabolcs , Mlinkovics, Edit and Hodúr, Cecilia(2007) 'Dairy Waste Water Treatment by Combining Ozonation and Nanofiltration', Separation Science and Technology, 42: 7, 1627 — 1637
To link to this Article: DOI: 10.1080/01496390701290508
URL: http://dx.doi.org/10.1080/01496390701290508

Separation Science and Technology, 42: 1627–1637, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701290508

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Abstract: The aim of this investigation was to examine the applicability of the membrane technique and the effect of preozonation in dairy waste water treatment technology. The best degree of surfactant removal from model anionic surfactant solution by nanofiltration was achieved at 20°C and 40 bar. Investigations on the effects of ozone treatment of the waste water indicated that preozonation decreased the flux and increased the chemical oxygen demand and surfactant removal efficiency. Ozone treatment enhanced the biodegradability of the retentate from 68.8% to 96.4%.

Keywords: Membrane separation, nanofiltration, surfactant, ozonation, biodegradation, dairy waste water, biological oxygen demand (BOD), chemical oxygen demand (COD)

INTRODUCTION

The dairy industry, one of the largest sources of industrial effluents in Europe (approximately 500 m^3 of waste effluent daily (1), generates waste waters characterized by a high biological oxygen demand (BOD) and a high

Received 11 October 2006, Accepted 15 January 2007
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chemical oxygen demand (COD) because of their high organic content. Most of the waste water volume results from the cleaning of transport lines and equipment between production cycles, the cleaning of tanks, and the washing of milk silos and related equipment. Dairy waste waters contain mainly milk residues, proteins, carbohydrates, fats, and residual cleaning agents (2). Most dairy industrial waste waters are mixed with the municipal waste water, but these effluents can cause serious problems in the urban sewage treatment systems. Dairy waste waters are treated by using physico-chemical and biological methods (3). However, the severe requirements are difficult to meet with biological waste water treatment technologies and there are wide fluctuations in industrial effluent quality. The required cleaning efficiency can be achieved by membrane separation processes, e.g. reverse osmosis or nanofiltration (4, 5). Membrane separation processes offer a number of advantages, such as appreciable energy saving, a clean technology with operational ease, a higher effectivity than that of conventional processes such as filtration, and greater flexibility in system design. Dairy industry effluents have been successfully treated by membrane processes (6). These processes are based on osmotic phenomena: diffusion of the solvent (commonly water) through a semi-permeable film (membrane). The membrane permeability is expressed as the permeate flux through the membrane (J):

$$J = \frac{dV}{d\tau}\frac{1}{A} = K_M(\Delta p - \Delta \pi) \tag{1}$$

where J is the flux [$m^3\ m^{-2}\ s^{-1}$], A is the surface area of the filter [m^2], V is the filtration volume [m^3], τ is time [s], K_M is the permeability coefficient [$m^3\ m^{-2}\ s^{-1}\ Pa^{-1}$], Δp is the pressure difference between the two sides of the membrane [Pa], and $\Delta \pi$ is the osmotic pressure [Pa]. The efficiency of nanofiltration is affected by a number of factors, such as temperature, pressure, the concentration and nature of the rejected solute, and the precipitation of sparingly soluble macromolecular species (gel layer formation) at the membrane surface (7). The proteinaceous materials in dairy waste water have been found to act as severe foulants of existing membrane materials (8), while the surfactants may change the filterability by concentration polarization (9) or micelle formation (10).

Ozonation is considered one of the most promising processes for control of the levels of organic pollutants in water. It can also be used to remove inorganic species, as an aid to the coagulation-flocculation process (11). A preozonation process can improve the TOC (total organic carbon), COD or turbidity removal during the later filtration or coagulation/flocculation (11, 12). In an earlier study (13), the effect of preozonation on the ultrafiltration membrane flux was found to be appreciably dependent on the quality of the raw water: in waters containing considerable quantities of suspended material, preozonation caused the membrane flux to decrease, whereas in "clear" waters the flux increased.

Our primary target was to reduce the surfactant content of waste water to below the legally regulated limit. The aim in the present study was to examine the applicability of the membrane technique and the effects of preozonation in dairy waste water treatment technology by investigating the effects of the surfactant concentration and preozonation on the filterability of dairy waste water. Preliminary studies were carried out on the filterability of an anionic surfactant. During the studies of dairy waste water, the filterabilities of the preozonated and untreated waste water were compared.

METHODS

The dairy waste water and the cleaning agent Chemipur CL80 (used to clean dairy equipment) were provided by Sole Hungaria Rt. (Szeged, Hungary). The initial COD of the waste water was 6100 mg dm^{-3}, and BOD_5 (the BOD during 5 days) was 5270 mg dm^{-3}. Chemipur CL80 with 10% anionic surfactant content was examined as an anionic surfactant cleaning agent. Cross-flow membrane filtration measurements were carried out on a Uwatech 3DTA laboratory membrane filter (Uwatech Gmbh., Germany) with use of a flat sheet standard DL composite nanofiltration membrane (theoretical $MgSO_4$ retention 96%) with a filtering surface area of 0.0156 m^2. The pressures used: were 3.0 and 4.0 MPa, the measurements were carried out at 20°C and 40°C, the feed was thermostated, and the temperature was checked before and after the membrane filter. Between each run, the membranes were washed with distilled water until the pure water flux reached the initial value measured after compaction ($\pm 2\%$). Ozone was produced from oxygen (Linde 3.0) with a flow-type ozone generator (Ozomatic Modular 4, Wedeco Ltd., Germany) operating via a silent electric discharge. The ozone-containing gas (flow rate 1.0 dm^3 min^{-1}) was bubbled continuously through 6.0 dm^3 of waste water in a batch reactor during the treatment. The ozone concentration of the bubbling gas was followed at 254 nm with a UV spectrophotometer (WPA Lightwave S2000) before and after the passage through the reactor. The amount of ozone absorbed by the dairy waste water was found to be 150.3 mg dm^{-3} h^{-1}. Because of the high initial COD, a relatively long treatment time (60 min) was necessary to achieve $\sim$0.025 mg O_3/mg COD ozone dose, which is lower than the typical ozone dose for COD removal experiments (0.08–1.5 mg O_3/mg COD) (14, 15), but may be enough to change the colloidal stucture of the solute. The BOD was determined with a respirometric BOD-meter (BOI OxiDirect, Lovibond, Germany) at 20°C. To ensure the consistency of the results, commercial BOD microbe capsules (Cole-Parmer, USA) were used for measurements. The COD was determined in COD tests with an ET 108 digester Lovibond PC CheckIt photometer. The surfactant concentration was measured spectrophotometrically with a methylene blue method) (16).

The selectivity of a membrane for a given solute was expressed by the average retention (R):

$$R = \left(1 - \frac{c}{c_0}\right)100[\%] \tag{2}$$

where c is the average concentration of the solute in the permeate phase ([%] or mg (COD) dm^{-3}, or mg (BOD) dm^{-3}), and c_0 is the concentration of the solute in the bulk solution ([%] or mg (COD) dm^{-3}, or mg (BOD) dm^{-3}).

RESULTS AND DISCUSSION

Nanofiltration of Anionic Surfactant

In preliminary studies, the nanofiltration of aqueous solutions of the anionic surfactant (0.1, 0.5, 1, and 5%) was examined at different temperatures (20°C, 30°C, and 40°C) and pressures (20 bar, 30 bar, and 40 bar). The values of the permeate flux were determined via Eq. (1). It was observed that the flux decreased with increasing surfactant concentration (Fig. 1) at 20°C and 40 bar, while it increased with increasing pressure (Fig. 1) at 20°C.

At 40°C, the permeate flux was higher for the 1% solution than for the 0.5% solution (Fig. 2). This phenomenon can be explained by critical micelle formation concentration (10). Increasing surfactant concentration decreases the surface tension, which may cause a decreased membrane resistance, and thus an increased flux. Further increase of the surfactant concentration causes micelle formation, which increases the surface tension and decreases the flux. It was also observed that at longer filtration times the permeate fluxes tended to the same value. This phenomenon is most marked at 40°C and 40 bar (Fig. 2), but it could also be observed at 20°C (Fig. 1).

This can be explained by the effect of concentration polarization (17): the rejected surfactant builds up a liquid film (gel layer) at the surface of the membrane. The thickness of the boundary layer is determined by the system hydrodynamics. Once the layer is formed, the gel concentration at the membrane surface (where the concentration is about 100 times higher than in the bulk solution) is fixed, and the only mode of transport within this layer is diffusion. Thus, the flux is determined virtually only by the structure of the layer it is only weakly dependent on the pressure or bulk concentration.

The effect of the critical micelle concentration was confirmed by the changes in the retention (Fig. 3a). In the 1% solution, a higher flux was associated with the lower retention values caused by the lower membrane resistance. In the 5% solution, the formation of large micelle particles increased the retention. The tendency observed at 40°C implies the temperature sensitivity of the behavior of the surfactant.

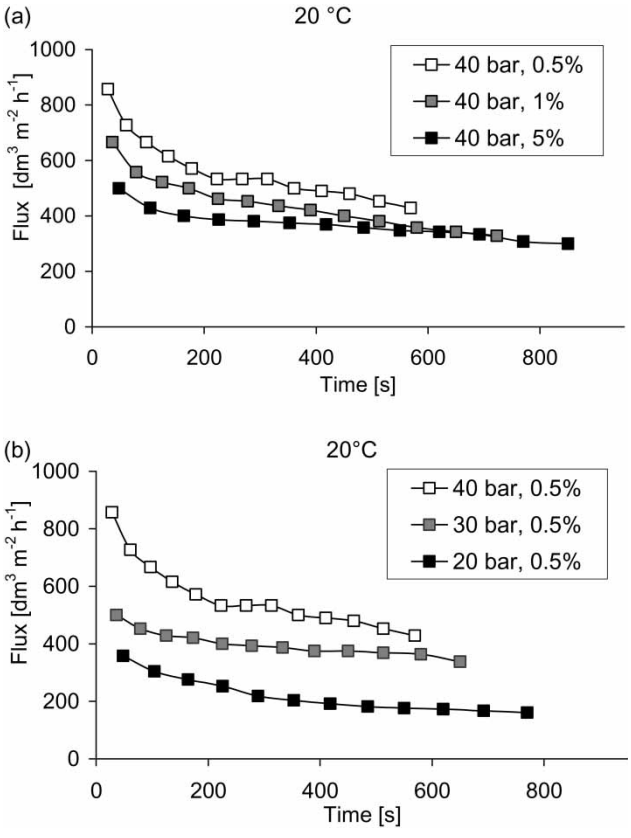

Figure 1. Effects of surfactant concentration (a) and pressure (b) on permeate flux at 20°C.

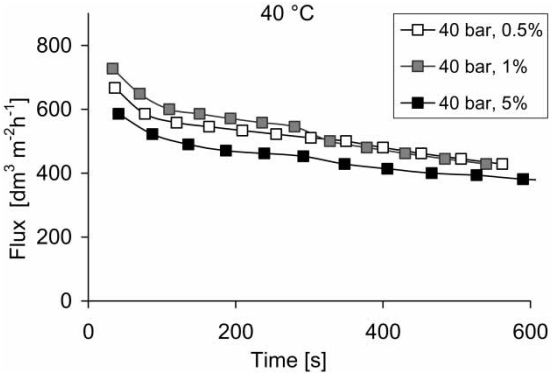

Figure 2. Effect of surfactant concentration on permeate flux at 40°C.

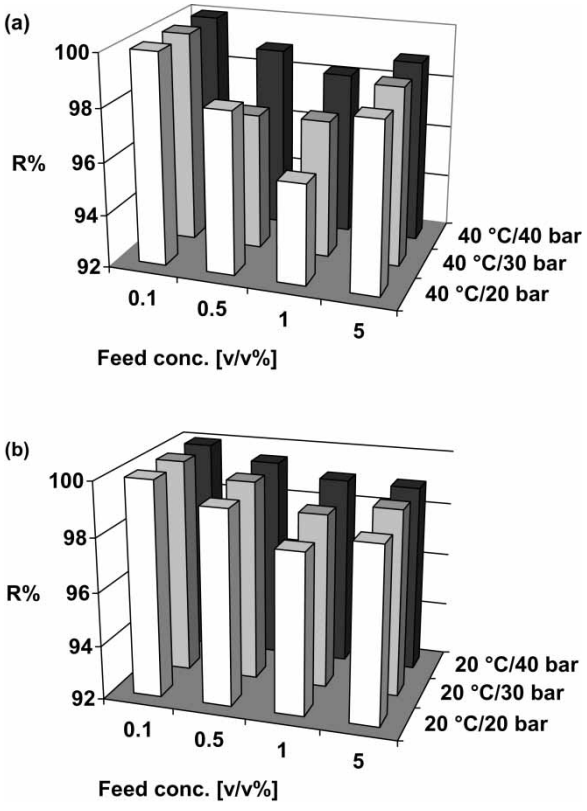

Figure 3. Retention values at 40°C (a) and 20°C (b).

The results showed that the efficiency of removal of the surfactant from the solutions was always >94%, but at lower temperature a removal efficiency of even >97.5% was achieved. Surfactant residues were not detected in the permeate from the 0.1% model surfactant solution: the surfactant was successfully removed. It was also observed that at lower temperature a higher retention was attained. The best surfactant removal was achieved at 20°C and 40 bar (Fig. 3b). Accordingly, the subsequent experiments were carried out with these parameters.

Nanofiltration of Ozonated and Untreated Dairy Waste Water

To examine the effects of the surfactants on the filterability of real dairy waste water, in the next series of experiments the following series of solutions were prepared: raw dairy waste water, 0.1% surfactant-containing waste water, 0.01% surfactant-containing waste water, ozone-treated raw dairy waste

water, ozone-treated 0.1% surfactant-containing waste water, and ozone-treated 0.01% surfactant-containing waste water. The examined concentrations were adjusted to the concentration range that actually occurs in the waste waters of the dairy factory. The nanofiltration parameters applied were 40 bar and 20°C. It was observed that the flux decreased greatly in the surfactant-containing solutions. This can be explained by micelle formation: the surfactant aggregates with the large molecules in the waste water to form micelles, enhancing the membrane fouling, and decreasing the flux. The ozonation alone also decreased the flux, in accordance with the results of others (13). In the case of the ozonated waste waters, the presence of the surfactant did not exert a significant effect on the flux. The mechanism responsible for the microflocculation effect of preozonation of organic matter the in presence of a complexing metal ion (e.g. calcium) in water is known (11). The microflocculation effect of ozone has not been investigated in detail in the case of dairy waste eaters, but a possible explanation could be that microflocculation occurs during the preozonation of dairy waste water: the components of dairy wastes, the ozonation by-products and metal ions e.g. calcium (present in considerable amount in dairy wastewaters) preclude the formation of aggregates, the decline of the average flux during nanofiltration. The surfactant content did not change the size of the particles formed during preozonation, and the flux in the presence of the surfactant is therefore not significantly different (Figure 4).

As one of our primary targets was to reduce the surfactant content of the waste water to below the regulated limit, the retention of the surfactant, BOD, and COD were calculated. Our results indicated that the COD and BOD of the dairy waste water were not changed significantly by ozonation, whereas significant changes in filterability were observed.

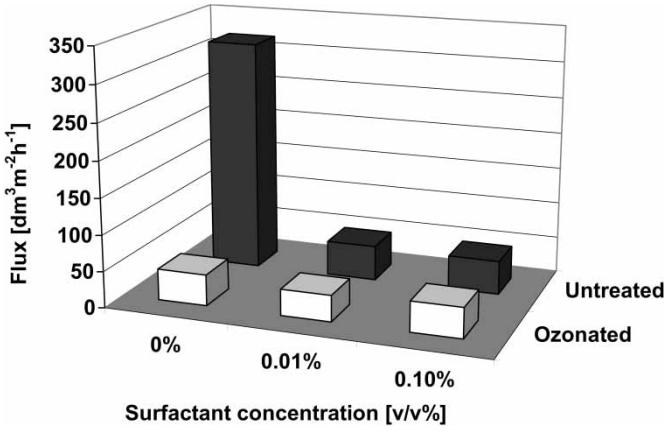

Figure 4. Average permeate fluxes of treated and untreated waste water at different surfactant concentrations.

As concerns the COD, it was found that during nanofiltration a higher retention could be achieved with ozonated waters (Fig. 5), in consequence of the microflocculation effect of preozonation. The cleaning efficiency of this waste water should be $>83\%$ to ensure its admissibility into the sewer system. For the untreated samples, the 80% retention attained did not ensure a sufficient degree of cleaning efficiency. Although the addition of the surfactant did increase the retention, this effect was not sufficiently marked. Ozone treatment enhanced the retention significantly, but the presence of the surfactant decreased the cleaning efficiency. The COD could be considered sufficient for all ozonated samples. The elimination of the biologically degradable waste correlated well with the COD. The retention from the ozonated waste water was in all cases sufficient, although the presence of the surfactant then exerted a more profound effect on the cleaning efficiency.

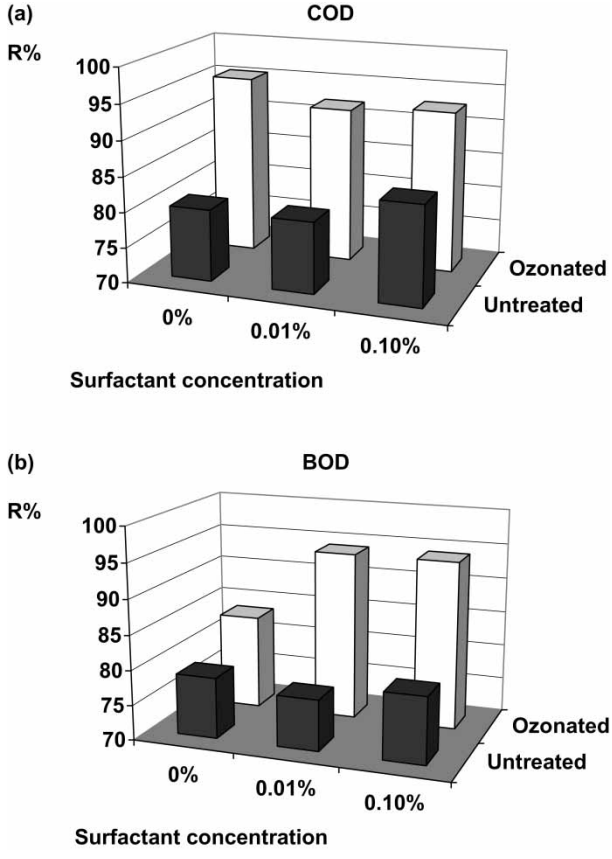

Figure 5. Retention of chemical (a) and biological oxygen demand (b) during nanofiltration of ozonated and untreated solutions.

For elimination of the surfactant content from waste water the required level of retention at a surfactant concentration of 0.01% is >50%, while at a surfactant concentration of 0.1%, it is 95%. The results revealed that the ozonation increased the retention of the waste materials considerably. In 0.01% solutions, the efficiency of nanofiltration was sufficient to ensure the limit for sewer admission for both the untreated (59.8%) and the ozonated (90.5%) solutions. At 0.1% surfactant concentration, however, the filtration was close to sufficient (94%) only for the preozonated sample, while for the untreated sample it was only 49.5%.

Biodegradability of Retentate

Although nanofiltration is appropriate for cleaning waste water and the quality of the permeate is acceptable for admission into the natural waters, the fate of the concentrated waste in the retentate is questionable. The efficiency of ozone for the degradation of concentrated waste water, and the biodegradabilities of the retentates obtained from ozone-treated and untreated waste water were also investigated. The biodegradability of the concentrated waste water was estimated as follows:

$$BD_5\% = \frac{BOD_5}{COD} \times 100\% \tag{3}$$

A comparison of the biodegradabilities of concentrates of untreated and ozone-treated waste waters demonstrated that the residual waste from the ozonated solution is more biodegradable ($BD_5\% = 96.4\%$) than that from the untreated solution ($BD_5\% = 68.8\%$). This means that preozonation probably enhances the efficiency of biological treatment of the retentate.

CONCLUSIONS

The effectivity of a combination of a membrane separation technique and ozone treatment for the removal of surfactant from dairy waste water was investigated. The preliminary studies with "clean" surfactant solutions indicated that 40 bar and 20°C were the most appropriate filtration parameters. The results revealed that the dairy waste water matrix significantly changed the retention of the surfactant: in this case, less surfactant was eliminated from the waste water. The results of filtration experiments demonstrated that preozonation increased the retention of both the COD and BOD and surfactants from the waste water during nanofiltration, which can be explained by the microflocculation effect. For dairy waste water, nanofiltration alone was not sufficient to eliminate the waste materials, whereas the desired cleaning efficiency could be achieved through preozonation. The residual wastes from the ozonated solutuions were found to be more biodegradable than the

residues from the untreated solutions. This means that preozonation may enhance the efficiency of biological treatment of the retentate. These results indicate that preozonation may enhance the treatability of dairy waste waters with nanofiltration, but further experiments are required to optimalize the ozone dosage and the ozonation time.

ACKNOWLEDGEMENTS

The authors are grateful to the National Research and Technology Institute (NKTH) and the Research and Development Competition and Research Utilization Agency (KPI) (RET-07/2005).

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