Desalination and Water Treatment
www.deswater.com

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doi: 10.1080/19443994.2012.705089

50 (2012) 440–445
December

Taylor & Francis
Taylor & Francis Group

Advanced treatment of wastewater with BTEX

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Received 1 March 2012; Accepted 15 June 2012

ABSTRACT

Standards for concentrations of pollutants in wastewaters discharged to the environment are especially restrictive for BTEX, the compounds which are recognized to be particularly toxic. There is a need to lower the BTEX concentration in the stream coming out of the bioreactor. For this purpose, a high-pressure membrane process was proposed. A series of salts and benzene/toluene membrane separation processes on Nanomax 95 membrane were carried out. On the basis of these experiments, a pressure in the field 20–25 bar at 20°C was shown as the most efficient and effective for BTEX retention in the biodegradation zone.

Keywords: Nanofiltration; BTEX; Membrane bioreactor; Pressure membrane techniques; Biodegradation

1. Introduction

At a time when the environment protection is a global problem, biological methods that use natural ability of micro-organisms to utilize the carbon contained in noxious compounds are particularly attractive. This is the most natural circulation of matter.

Taking into consideration very harmful effects of volatile organic compounds (VOCs) present in the air and water on living organisms, standards referring to these substances are very stringent. Especially, low limit concentrations are demanded for substances from the so-called BTEX group, i.e. benzene, toluene, ethylbenzene, and xylenes—the compounds which are recognized to be particularly toxic [1,2]. Unfortunately, BTEX are common in the environment. They are used as industrial solvents for organic synthesis (e.g. plastics, synthetic fibers, and pesticides) and are the major aromatic components in the petroleum products.

The process of biodegradation of VOCs (inter alia BTEX) has been described in the literature [3–6]. It was often highlighted that micro-organisms are sensitive to high concentrations of xenobiotics, so the kinetics of growth on these compounds proceeds with substrate inhibition. In the case of using as a substrate compounds from the group of BTEX, it is even more complicated [7–9]:

(1) These compounds are characterized by low or very low water solubility.
(2) Specific growth rate (resulting from the point (1) and/or the substrate inhibition) is very small, the order of $10^{-2}\,h^{-1}$, thus residence times in the reactor are very long.
(3) The concentrations occurring in the reactor during continuous processes and consequently in leaving stream exceed 100–1,000 times the concentrations limits.

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Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

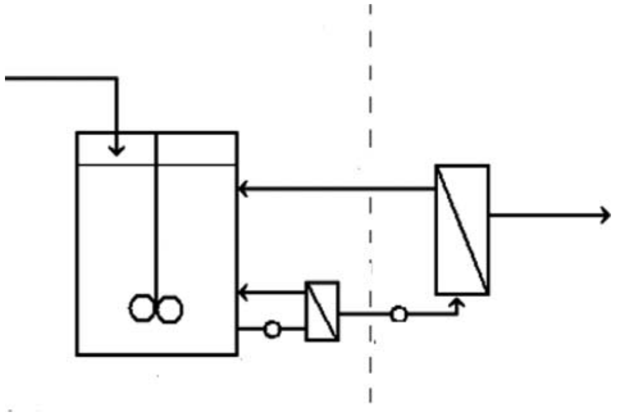

Fig. 1. Scheme of an integrated system: microbial bioreactor with MF and NF/RO module.

To solve the above problem it is proposed to connect the zone of biodegradation with two membrane modules (Fig. 1).

The first module is the microfiltration (MF) module, which increases the concentration of active biomass in the bioreactor. Increasing the biomass several times gives a significant increase in the rate of substrate conversion. This intensification is particularly strong for dilute feed streams [10].

The task of the second module (nanofiltration/reverse osmosis [NF/RO]) is a tertiary treatment of the permeate coming out of the MF module to the level described using standards. The permeate stream from NF/RO module is almost completely free from toxic substances and the retentate stream is recycled to the bioreactor. In this way, the substrate concentration inside the bioreactor can be increased above the concentration in the feed stream, which in a certain range of concentrations resulting from the growth kinetics may intensify the rate of conversion of the substrate [11].

Kinetics of biodegradation of benzene and toluene by *Pseudomonas fluorescens* was described previously [12]. The aim of this work was the selection of conditions for the separation of BTEX and salts present in the broth on the Nanomax 95 Millipore membrane.

2. Materials and methods

2.1. Equipment

Experiments were carried out on the apparatus ProScale Millipore (Rys. 2a) destined to design pressure membrane processes (MF, UF, NF, and RO). Because of high volatility of BTEX, the basic equipment was modified to ensure the integrity of the whole system:

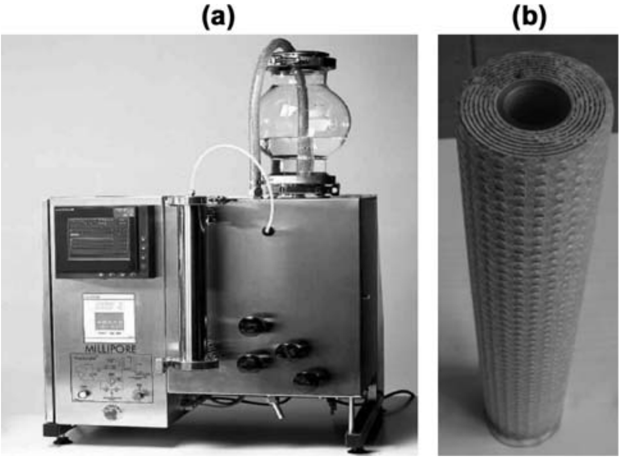

Fig. 2. System ProScale Millipore (a) and Millipore membrane—Nanomax 95 (b).

- Tank cover was made of stainless steel with connectors to enable tight connection with the module and pump.
- Steel tubes resistant to aggressive chemical conditions and to high pressures were used.
- All elements of such couplings, tees, and valves were made of stainless steel.

In NF process, membrane module made of stainless steel included the Millipore membrane Nanomax 95 (Fig. 2(b)) and spiral membrane with effective area of 0.4 m^2. The membrane module could be used under pressure until 42 bar and below 50°C.

2.2. Analytical methods

The concentrations of benzene and toluene were determined by a GC-2014 gas chromatograph (Shimadzu, Japan) with a ZB-WAXplus capillary column (Zebron) of 30 m long and 0.25 mm in diameter, covered with a 0.25 μm layer of polyethylene glycol. Samples were analyzed in isothermal conditions—temperatures of the column 40°C, feeder 180°C, and detector 200°C. These conditions were used to separate peaks of benzene and toluene.

Concentrations of salts were determined by measuring the electrolytic conductivity using a conductivity meter (Crison, Spain). Standard curves were prepared for each tested salt and for their mixture in an appropriate mass ratio.

2.3. Membrane separation under selected conditions

Separation processes were carried out in order to obtain a complete characterization of the impact of the testing parameters (pressure and temperature) and the mutual impact of separated compounds (organic and nonorganic) and their concentrations on the value of permeate stream and retention coefficient (Eq. (1)) [13].

$$R = \frac{C_F - C_P}{C_F} = 1 - \frac{C_P}{C_F} \tag{1}$$

where C_F is the concentration of particular compound in feed and C_P is the concentration of particular compound in permeate.

This study was subjected to solutions of benzene, toluene, and salts, either in a single form or in a mixture form. The salt mixture consisted of NaCl, K_2HPO_3, KH_2PO_3, KNO_3, and $MgSO_4$ in 1:1:1:1:0.2 mass proportions. The composition corresponded to mineral broth for *P. fluorescens*, the strain was used for benzene and toluene biodegradation [12].

The particular process was carried out under conditions of constant temperature and constant pressure with returning both permeate and retentate streams into the tank. The process was stopped several minutes after the system reaches a steady state as shown by no changes (or minor changes) in the concentrations of the analysing components in the permeate and retentate streams.

After each process, the membrane was cleaned using demineralized water at elevated temperature (40°C) and at high turbulence of flow and pressure changing by pulsation. When the salts were separated, 0.5% HCl was added to the cleaning water.

3. Results and discussion

It was observed that usually the system reached a steady state after about 30 min. The permeate drops quickly in the first minute of the process and then, its value began to stabilize. This decrease is probably due to the phenomenon of fouling and/or concentration polarization. It was noted that even under the steady state, the permeate stream does not remain constant and its value still has minimal change. This phenomenon could be described by renewing the surface, which speaks of the instantaneous, local increases in membrane permeability [14].

3.1. Separation of single compounds

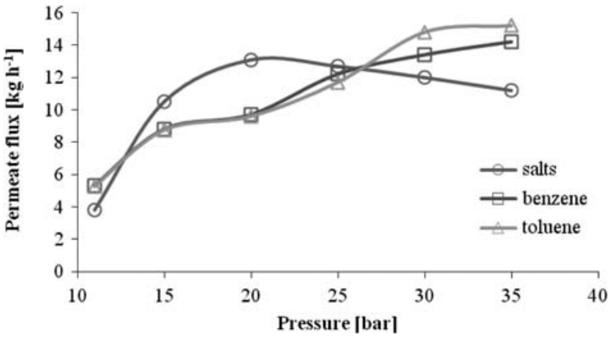

Fig. 3. Permeate flux dependence on pressure (20°C, $C_{\mathrm{salts}} = 4.2\,\mathrm{g\,l^{-1}}$, $C_{\mathrm{Benzene}} = 0.44\,\mathrm{g\,l^{-1}}$, and $C_{\mathrm{Toluene}} = 0.34\,\mathrm{g\,l^{-1}}$).

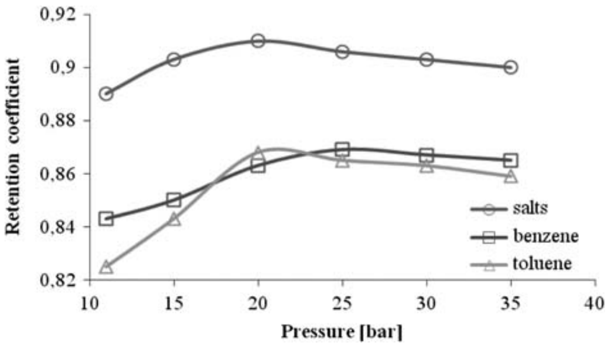

Fig. 4. Retention coefficient dependence on pressure (20°C, $C_{\mathrm{salts}} = 4.2\,\mathrm{g\,l^{-1}}$, $C_{\mathrm{Benzene}} = 0.44\,\mathrm{g\,l^{-1}}$, and $C_{\mathrm{Toluene}} = 0.34\,\mathrm{g\,l^{-1}}$).

The first stage of the study was to determine the effect of pressure on the permeate flux (Fig. 3) and on efficiency of the separation process expressed by retention coefficient. Experiments were carried out separately for solutions of a salts mixture (i.e. nutrient broth for *P. fluorescens* [12]), benzene, and toluene.

The applied membrane meets expectations. For all the compounds tested retention coefficient reaches values over 0.8, while the highest are for salts (Fig. 4).

To study the impact of changes in pressure applied to the separation of single—salt solution showed that the size of the ions has a significant influence on the process, which is consistent with the literature about the NF membranes [13,15]. For the smallest size ions (NaCl) retention was worse than in the case of salts consisting of ions of larger sizes ($MgSO_4$). It was observed that the retention coefficient for the mixture of salts at the same total concentration like for a single salt was always worse than for the single salt (Fig. 5). This phenomenon is caused probably by Donnan effect [13].

It has been observed both during the separation of salt and BTEX (Fig. 3) that an increase of the value of applied pressure caused an increase of permeate flux, but not in whole range. At higher pressures, the permeate flux was maintained at a constant level or slightly decreases. A similar dependence exhibited retention coefficient whose value also increased to a

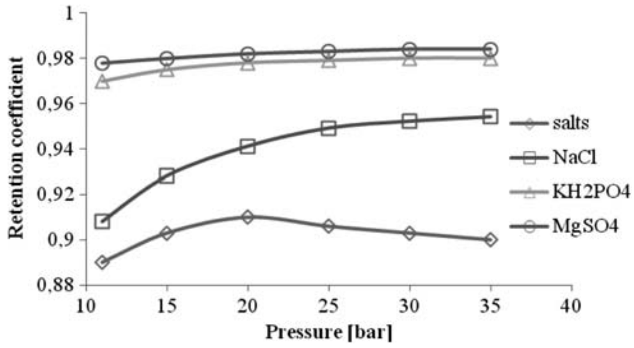

Fig. 5. Salts retention coefficient dependence on pressure (20°C and $C = 4.2\,\mathrm{g\,l^{-1}}$).

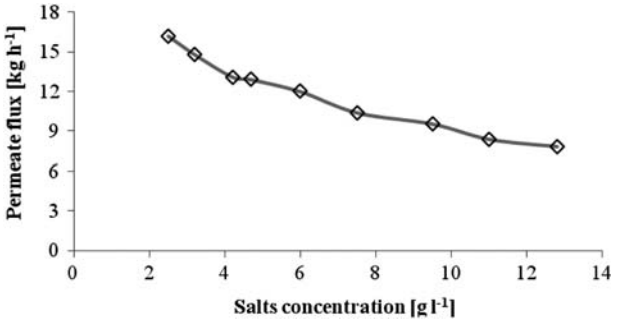

Fig. 6. Influence of salts concentration on permeate flux (20°C and 20 bar).

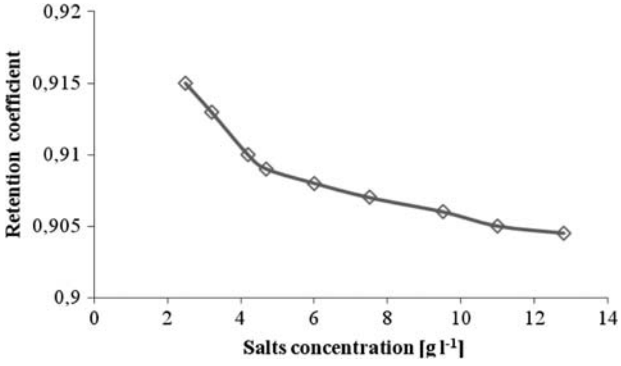

Fig. 7. Influence of salts concentration on their retention coefficient (20°C and 20 bar).

certain point with increasing pressure (Fig. 4). This phenomenon is caused by a stream of water and particular components (salts and benzene/toluene) passing through membrane pores. At low pressure, stream of water is small but transport of ions, benzene, and toluene on convective way is aided by diffusion. Hence, their concentration in the permeate is considerable and the retention coefficient is lower. However, at higher pressures increases significantly the

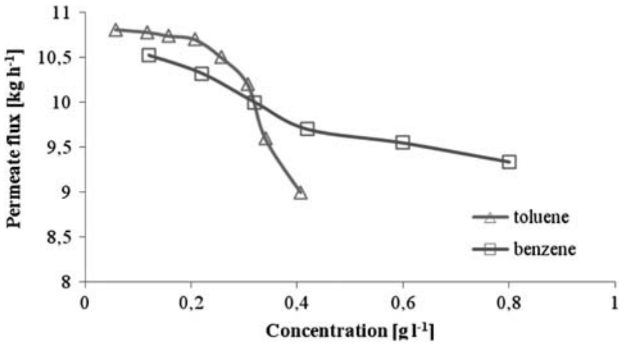

Fig. 8. Influence of concentration of benzene and toluene on permeate flux (20°C and 20 bar).

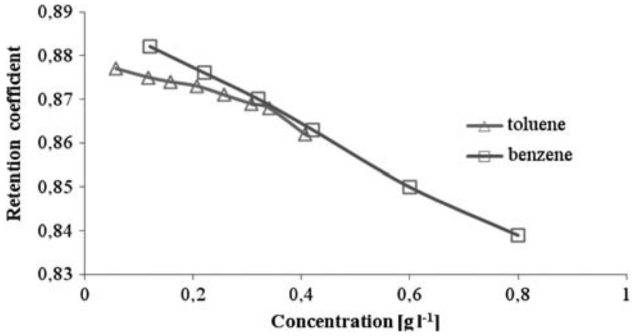

Fig. 9. Influence of concentration of benzene and toluene on their retention coefficient (20°C and 20 bar).

convective transport (mainly water) and process of diffusion in these cases is insignificant.

3.2. Effect of concentration and the presence of other compounds

As a result of salt retention, it is to be expected that their concentration in a continuous process will gradually increase. Effect of salts concentration on the size of the permeation flux and their retention coefficient is shown in Figs. 6 and 7, respectively.

Similar experiments in limited range of concentration caused by low solubility in water were conducted for benzene and toluene. Figs. 8 and 9 present received results of experiments carried out in separate tests for benzene and toluene.

It was remarked that the higher concentrations of salts, benzene, or toluene have slight effect on the value of retention coefficient and cause decrease in the permeate flux. Probably, it is caused by rapid blocking of the membrane pores by separated compounds and/or by polarizing layer at the membrane surface.

Comparing the results of the separation of benzene and toluene you may notice their essential similarity.

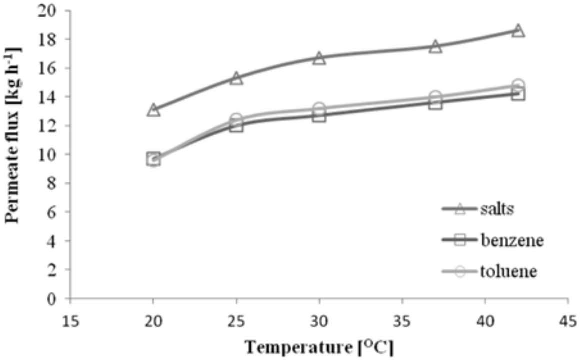

Fig. 10. Influence of temperature on permeate flux (20 bar, $C_{\text{salts}} = 4.2\,\text{g l}^{-1}$, $C_{\text{Benzene}} = 0.44\,\text{g l}^{-1}$, and $C_{\text{Toluene}} = 0.34\,\text{g l}^{-1}$).

The presence of a methyl group at the benzyl ring has no influence on retention coefficient of toluene and under the same operating parameters the retention coefficients for toluene and benzene are similar.

Experiments carried out for multicompounds solutions containing salts, benzene, and toluene allowed us to formulate the following conclusions: (1) benzene and toluene are separated on the membrane as effectively as for single-component solutions; (2) presence of salts in the solution does not affect in any way the separation of BTEX; (3) presence of toluene and/or benzene slightly (<10%) improves the separation of salts; and (4) permeate flux is a function of the concentration of all components in the system, decreases with increasing concentration.

3.3. *Effect of temperature*

The effect of temperature was tested in 20–42°C (Figs. 10 and 11). The range was chosen with respect to the membrane properties (<50°C) and temperature maintained in bioreactor. The optimum of temperature for strains of *P. fluorescens* is 30°C; usually, in biodegradation processes temperature is in the range 20–37°C.

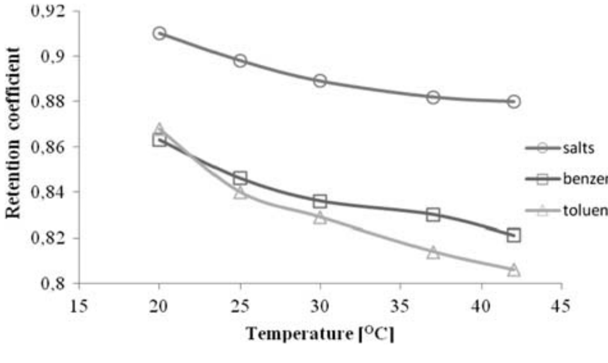

Fig. 11. Influence of temperature on retention coefficient (20 bar, $C_{\text{salts}} = 4.2\,\text{g l}^{-1}$, $C_{\text{Benzene}} = 0.44\,\text{g l}^{-1}$, and $C_{\text{Toluene}} = 0.34\,\text{g l}^{-1}$).

Higher temperature causes an increase of membrane permeability to both water and salts and BTEX. Rising temperatures caused an increase in process efficiency (increase of permeate flux), while decrease of retention coefficient both for salts and BTEX.

4. Conclusion

Membrane Nanomax 95 is suggested by the manufactures to the separation of ions, indicating its usefulness in desalination systems. The manufacturer also mentions its usefulness at the separation of organic compounds.

The study confirms these features of Nanomax 95. The membrane meets two basic requirements for separation of BTEX; the retention coefficients are high and the membrane is not sensitive to these compounds.

Retention coefficient of ions at 0.9 and higher and high retention of VOCs ($R > 0.8$) are evidence for the hypothesis of integration of high-pressure membrane processes with microbial wastewater treatment.

The received data indicated that the change of operating parameters of the process has a greater impact on the separation of salts rather than BTEX. Additionally, separation of BTEX is the same in both situations when the feed solution is a single-component solution (only with benzene or toluene) as well as in situations when both compounds were introduced into the feed solution at the same time, as well as salts. This feature simplifies design of the integrated process connecting biodegradation zone and membrane separation unit.

Separation of toxic, hazardous to the environment compounds should be characterized by the greatest possible efficiency. Thus, the highest value of retention coefficient for benzene and toluene is the key determinant of the membrane separation conditions. Anyway, the economy of the process (e.g. an increase of pressure or temperature) also should not be missed.

As mentioned above, by analyzing the results obtained it was found that the process of separation of BTEX and salts on the membrane Nanomax 95 best conducted at pressure in the field 20–25 bar at 20°C.

Elaboration of mathematical model and designing the integrated process using presented data, kinetic data for *P. fluorescens,* and data of the MF process of active biomass [12] will be the next milestone in the framework of the realized project.

Acknowledgment

The Polish Ministry of Science and Higher Education supported this work in the framework of grant N N209 414739.

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