Desalination and Water Treatment
www.deswater.com

34 (2011) 367–373
October

doi: 10/5004/dwt.2011.2806

Ceramic membrane behaviour in anionic dye removal by ultrafiltration

Katarzyna Majewska-Nowak*, Joanna Kawiecka-Skowron

Institute of Environment Protection Engineering, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
Email: katarzyna.majewska-nowak@pwr.wroc.pl

Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

The study is aimed at investigating the suitability of ceramic membranes to the decolourization of organic dye solutions. The process involved commercially available ceramic membrane modules Céram*INSIDE*® (Tami Industries) of various cut-off values (15 and 150 kDa). The ultrafiltration (UF) experiments were performed at a transmembrane pressure of 0.2 MPa with the use of cross-flow system J.A.M INOX PRODUKT. Comparable studies including the effect of hydraulic conditions existing in the system on membrane performance were reported. Transport and separation properties of the membranes towards dye solutions were investigated at varied linear velocity in the modules (1.5; 2.9; 4.4; 5.9, and 6.9 m/s). Seven anionic organic dyes (Methyl Orange, Indigo Carmine, Amido Black, Titan Yellow, Direct Blue, Direct Green, and Direct Black) of molecular weight ranging from 327 to 1084 Da were used in the tests. The UF tests were carried out with dye solutions and dye solutions containing mineral salt (NaCl). The results showed that increasing the linear velocity generally improved the membrane permeability, whereas dye selectivity was strongly affected by the molecular weight of the dye tested and the membrane cut-off. Nevertheless, the ceramic membranes yielded an 85–99% retention of the high-molecular-weight dyes (above 600 Da) irrespective of the hydraulic conditions in the module, membrane cut-off and dye solution composition.

Keywords: Water reuse; Dye; Ultrafiltration; Membrane cut-off; Ceramic membrane; Textile industry

1. Introduction

Many industries, such as dyestuff, textile, paper and laundry generate a considerable amount of coloured wastewater. The effluents from dyeing units in a textile plant are often rich in colour due to the residual of applied dyes. They also contain mineral salts and surface active agents, as well as some other chemical additives (lubricants, foam reducing agents, egalisers, etc.) [1]. Because of increasingly stringent restrictions on the organic content of industrial effluents it is necessary to eliminate organic load from wastewater before it is discharged. Taking into account the necessity of sustainable development in industry as well as economic reasons, it is advisable to develop advanced treatment methods to minimize waste fractions (involving zero discharge).

Membrane processes, especially nanofiltration (NF) and reverse osmosis (RO) with polymeric membranes, are being increasingly used in the treatment and reuse of coloured wastewater [2–5]. However, the limitation in polymer membrane operation occurs when the chemical, thermal or mechanical stability of the membrane is exceeded by the solution to be treated. Due to extremely high chemical and physical stability, possibility of regeneration and long life, ceramic membranes may be more favourable economically, than polymeric membranes, in the dye effluent treatment. On the other hand, low-pressure membrane processes (microfiltration, MF and ultrafiltration, UF) seem to be more profitable, than NF or RO, due to low energy consumption

*Corresponding author.

Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

and high hydraulic efficiency. Taking into consideration these arguments it can be anticipated that the ultrafiltration process with the use of ceramic membranes could be an advantageous technique of dye effluent treatment.

It is interesting to note that within last decade only a few papers on the application of microfiltration or ultrafiltration, especially with the use of ceramic membranes, in the treatment of textile dye baths have been available. The recovery of polymeric dyes and low-soluble dyes (indigo) by ultrafiltration was reported as an efficient process in industrial applications [6]. Also Porter et al. [7,8] found that it was possible to retain anionic dyes by ceramic microfilters and polymeric ultrafiltration membranes. Currently, due to decreasing costs and enhanced properties the ceramic membranes are of great interest. Barredo-Damas et al. [9] studied the performance of UF tubular ceramic membranes as a pretreatment for a later NF/RO stage, whereas Calvo et al. [10] characterized the ceramic membranes by giving the pore size distribution and the mean pore size.

The study aimed at evaluation the suitability of ceramic membranes to the decolourization of organic dye solutions. Keeping in mind that fouling is still a major problem in membrane processes, the experiments focused on investigating the transport and separation properties of the ceramic membranes towards anionic dye solutions under variable cross-flow rate in the modules.

2. Materials and methods

2.1. Ceramic modules

Commercially available ceramic membrane modules Céram*INSIDE*® (TAMI Industries) were used in the experiments. The modules were of the tubular single-channel type with a titanium oxide active layer. Technical parameters of the experimental modules applied in the tests are given in Table 1.

Table 1
Characteristics of the experimental ceramic modules

Parameter	J.A.M INOX PRODUKT installation
Configuration	Tubular
Cut-off, kDa	15, 150
Membrane material	titanium oxide/ zirconium oxide
Effective surface area, m^2	0.0042
Number of channels	1
Internal channel diameter, mm	6
External membrane diameter, mm	10
Membrane length, mm	250
Water volume flux at 0.2 MPa, m^3/m^2day	0.35 (15 kDa), 8.45 (150 kDa)

2.2. Ultrafiltration process

The transport and separation properties of the ceramic modules were determined using the set-up presented in Fig. 1. The J.A.M INOX PRODUKT UF installation of the cross-flow system includes the following major parts: ceramic ultrafiltration module, Grundfos pump, feed tank, thermostatic device and permeate sampling beaker. The volume of the feed tank amounted to 10 dm^3. The installation can operate at a constant concentration of the treated solution via permeate recirculation between the feed tank and the membrane module.

The ultrafiltration experiments were performed at 0.2 MPa. The delivery of the pump was changed in the range from 0.042 to 0.194 dm^3/s, and in consequence, the cross-flow velocity within membrane channels was set at 1.5, 2.9, 4.4, 5.9, and 6.9 m/s.

Prior to each cycle, the membrane module was treated with distilled water at 0.2 MPa, until the constant permeate volume flux was established. Permeate volume fluxes and rejection coefficients were determined with respect to the experimental dyes after steady flow conditions were achieved. The permeate flux was measured and the concentration of anionic dye in the permeate and concentrate was analysed. During the ultrafiltration experiments the temperature of circulated solutions was kept constant (at 20°C).

After each experimental run (with a given dye) the ceramic modules were cleaned under dynamic conditions with the use of 0.1 n NaOH solution.

Fig. 1. Laboratory UF installation J.A.M INOX PRODUKT. 1 – ceramic module, 2 – feed tank, 3 – Grundfos pump, 4 – rotameter, 5 – thermostat.

Table 2
Characteristics of the experimental dyes

Dye Parameter	Methyl Orange MO	Indigo Carmine IC	Amido Black AB	Titan Yellow TY	Direct Green DG	Direct Blue HB	Direct Black DB
Molecular weight, Da	327	466	615	696	878	1029	1084
λ_{max},[1] nm	465	610	618	399	370	577	585
pH[2]	5.7	5.5	5.7	5.5	6.1	7.2	7.6

[1]Wavelength corresponding to the maximum absorbance of the dye solution
[2]Determined for the dye solutions of concentration equal to 100 g/m^3

2.3. Experimental solutions

The transport and separation properties of the Céram*INSIDE*® 1-channel modules were determined for distilled water (Table 1), aqueous solutions containing various organic dyes (Merck, Zachem) (Table 2) and aqueous solutions of organic dye and sodium chloride (Ciech S.A.). The applied dyes were of an anionic type and varied in molecular weight.

In the aqueous solutions the dye concentration was equal to 10, 20 and 100 g/m^3, whereas salt content amounted to 1 and 10 kg/m^3. Sodium chloride was added only to solutions containing 100 g of dye/m^3. Model dye solutions were prepared by dissolving dyes (as supplied) in distilled water at room temperature (approximately 20°C).

Dye concentrations in the aqueous solutions were determined spectrophotometrically at the wavelengths given in Table 2, which correspond to the maximum absorbance of the sample. A spectrophotometer UVMINI-1240 (Shimadzu) was used to determine dye solution absorbance. Dye rejection coefficients and permeate volume fluxes were determined in the way described in the previous paper [11].

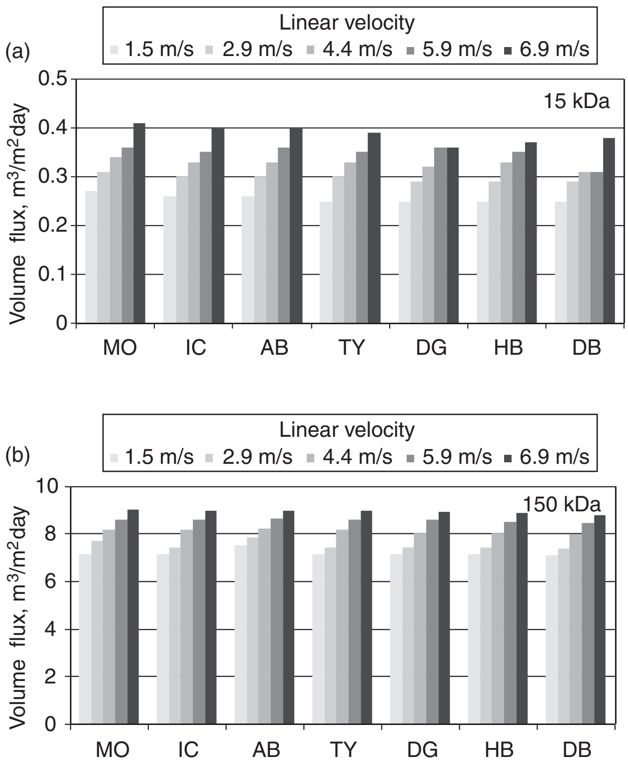

Fig. 2. The effect of linear velocity in the ceramic modules 15 kDa (a) and 150 kDa (b) on volume flux for various dye solutions. Dye concentration: 100 g/m^3 (ΔP = 0.2 MPa).

3. Results and discussion

3.1. Effect of cross-flow rate in the module on membrane properties

The membrane permeability and the dye rejection were related to the hydraulic conditions occurring in the ceramic modules. The effect of linear velocity on the volume flux for membranes of cut-off equal to 15 kDa and 150 kDa is given in Fig. 2. The exemplary relationships were plotted for all experimental dyes and solutions of the highest dye concentration (i.e., 100 g/m^3). In case of low dye concentration (10 and 20 g/m^3) the nature of the observed relations was similar.

As shown by the data in Fig. 2, the increase in linear velocity improved the membrane permeability for both ceramic modules, however the greater rise in volume flux was obtained for the 15 kDa module. According to the diagram in Fig. 2a, the variation of the cross flow rate from 1.5 to 6.9 m/s brought about an almost 50% improvement of the transport properties. For the150 kDa ceramic module, the highest linear velocity caused only 25% increase of permeate flux, compared to permeability obtained at 1.5 m/s. It is evident that the increase in volume flux should be attributed to the tear off of the near-membrane boundary layer of dye particles.

It is interesting to note that the greater the molecular weight of the dye, the intensity of fouling is more distinct, especially in case of the 15 kDa module. The results obtained indicated that the ceramic modules were susceptible to membrane fouling. This contradicts the general view that ceramic membranes exhibit excellent properties, i.e. they are less prone to fouling than polymeric membranes [12]. The experimental results substantiated that increasing the intensity of liquid turbulence at the ceramic membrane surface is an effective method of eliminating the disadvantageous effect of the fouling.

The influence of the cross-flow rate on dye rejection by ceramic membranes of cut-off equal to 15 and 150 kDa is shown in Fig. 3. The relationships were plotted

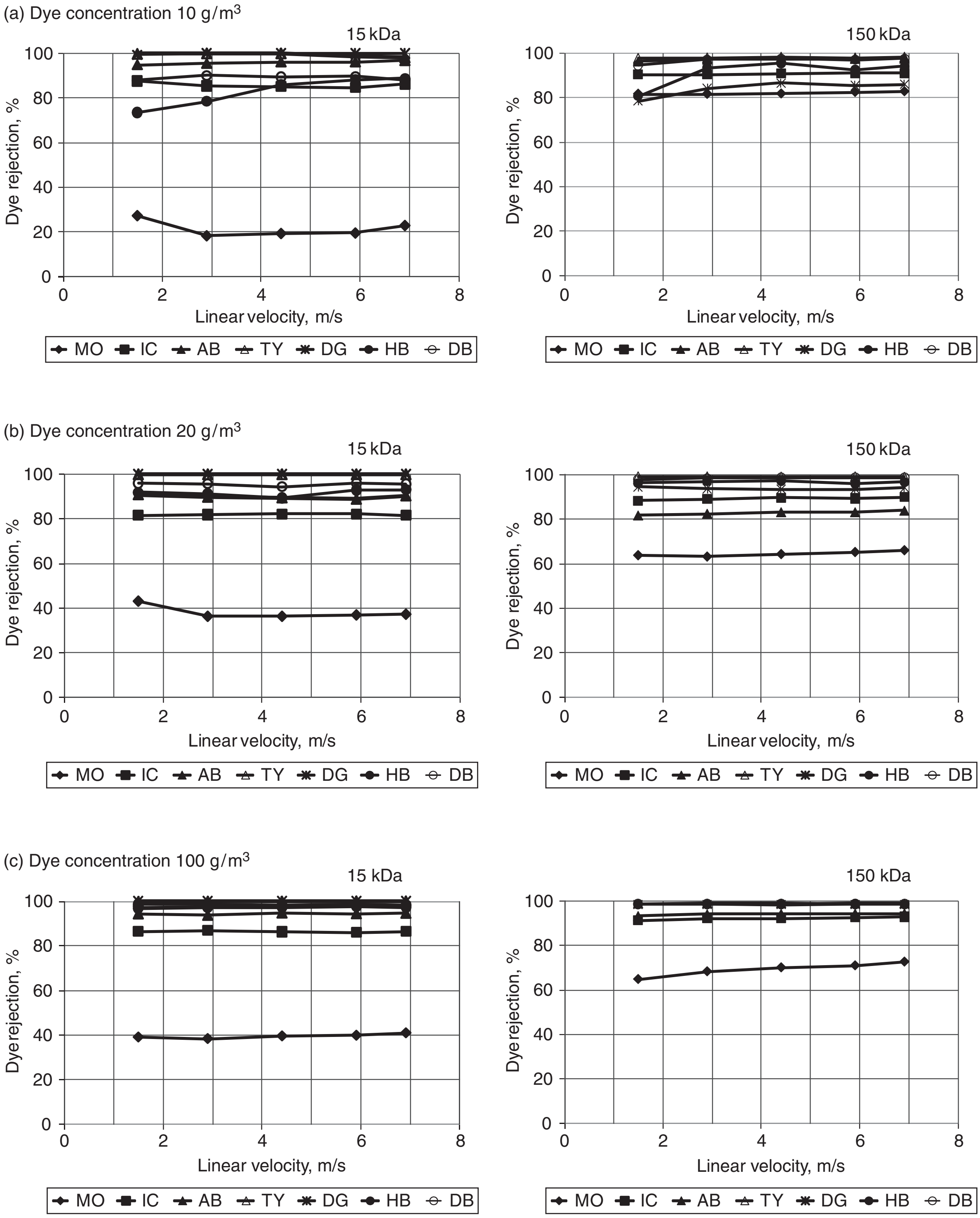

Fig. 3. The effect of liquid velocity in the ceramic modules 15 kDa and 150 kDa on dye rejection for various dye solutions. Dye concentration: 10 g/m³ (a), 20 g/m³ (b), 100 g/m³ (c) (ΔP = 0.2 MPa).

for three various dye concentrations in model solutions (10, 20, and 100 g/m^3). Generally, the results obtained were rather surprising. The expected improvement in membrane separation properties with the increasing turbulence in membrane channel occurred in a slight extent. The highest increase of the dye rejection was achieved for the high-molecular-weight dyes at low concentration (10 g/m^3) and for the 150 kDa ceramic module (Fig. 3a). The rejection coefficient of Direct Green, Helion Blue and Direct Black increased from 78%, 80%, and 94% (at linear velocity of 1.5 m/s) to 86%, 94%, and 98% (at linear velocity of 6.9 m/s), respectively. It seems that cake layer formation is faster in case of the 150 kDa, thus at higher linear velocity better final performance can be observed. For the 15 kDa ceramic membrane the improvement effect of increasing cross-flow rate on dye separation was rather insignificant. Even a slight worsening of Methyl Orange rejection with the increase of the linear velocity from 1.5 to 2.9 m/s was observed.

Moreover, it was found that the 150 kDa ceramic membrane exhibited better separation properties, especially towards low-molecular-weight dyes, than the 15 kDa membrane, although its permeability was much higher. Barredo-Damas et al. [9] investigated the performance of ceramic membranes in the textile effluent treatment and found that the removal efficiencies for COD, turbidity and colour were quite similar irrespective of the membrane cut-off. This unexpected fact could be attributed to the membrane structure. According to Calvo et al. [10] the Céram*INSIDE*® membranes of cut-off varied from 15 to 150 kDa are characterized by similar mean pore radius (5.5-8.0 ±1.4 nm), whereas the membrane porosity differs considerably (8.6% and 45% for 15 kDa and 150 kDa membrane, respectively). In view of this data, the results reported in this paper became more evident, indicating that membrane porosity is a crucial parameter influencing the performance of filtration process with the use of Céram*INSIDE*® membranes.

3.2. Effect of mineral salt on cross-flow ultrafiltration performance

The influence of salt content (NaCl) in the treated solutions and the linear velocity in the ceramic module on the dye rejection is presented in Fig. 4. The relationships were plotted for both tested membranes and three exemplary dyes (Methyl Orange, Amido Black and Direct Black). Similarly to the results presented in Fig. 3, the effect of cross-flow rate on the dye selectivity was almost negligible in case of the 15 kDa module, whereas a slight improvement in Methyl Orange and Amido Black rejection was observed for the 150 kDa module. The linear velocity rise from 1.5 m/s to 6.9 m/s caused the increase of MO rejection from 55% to 58.4% (salt content 1 kg/m^3) and the AB rejection from 55.1% to 61.7% (salt content 10 kg/m^3).

It was also found that the presence of mineral salt in the separated solution generally deteriorated the dye selectivity. This observation was more pronounced for low-molecular-weight dyes (Methyl Orange and Amido Black) and the 150 kDa membrane module. Mineral salts may unfavourably affect the efficiency of membrane filtration due to the interactions with the membrane and dye particles. This phenomenon is well known when polymeric membranes are used in the process [11]. The results reported in this paper suggest that electrostatic interactions are also important in ceramic membrane applications. Considering the value of isoelectric point for ceramic membranes consisting of TiO_2/ZrO_2 layer (pH equal to 6–6.9) [13] and the pH values of treated solutions (Table 2) it can be anticipated that in most cases the ceramic membranes will be positively charged, which can facilitate the adsorptive fouling caused by anionic dyes. In the ultrafiltration of dye solutions containing Direct Blue and Direct Black, ceramic membranes can be slightly negatively charged. The presence of Na^+ cations or Cl^- anions in treated solution can cause shielding of membrane charge by the counter ions, thus facilitating passing of low-molecular-weight-dyes through the membrane or reducing the electrostatic repulsive interactions between membrane surface and high-molecular-weight dyes.

The applied salt concentrations (1 and 10 kg/m^3 in dye solutions) did not influence the ceramic module permeability at all. It was according to expectations, because mineral salts can freely pass the ceramic membranes and the increase in osmotic pressure of feed solution does not play a role in UF membrane transport. Yu et al. [14] and Kopeckŷ et al. [15] arrived at similar findings, indicating however that electrostatic and electrodynamic interactions could be of significant importance in the final membrane transport.

4. Conclusions

1. Ultrafiltration ceramic membranes showed good rejection coefficients (>85%) towards anionic dyes of molecular weight above 600 Da, irrespective of the hydraulic conditions in the module, membrane cut-off and dye solution composition.
2. The increase of the cross-flow rate brought about significant improvement of ceramic membrane permeability, whereas variations in the dye rejection were less distinct.
3. The presence of mineral salt in the dye solutions had an adverse effect on membrane selectivity, whereas membrane permeability remained unchanged.

The financial support of the Ministry of Science and Higher Education Grant # N N523 424637 is greatly appreciated.

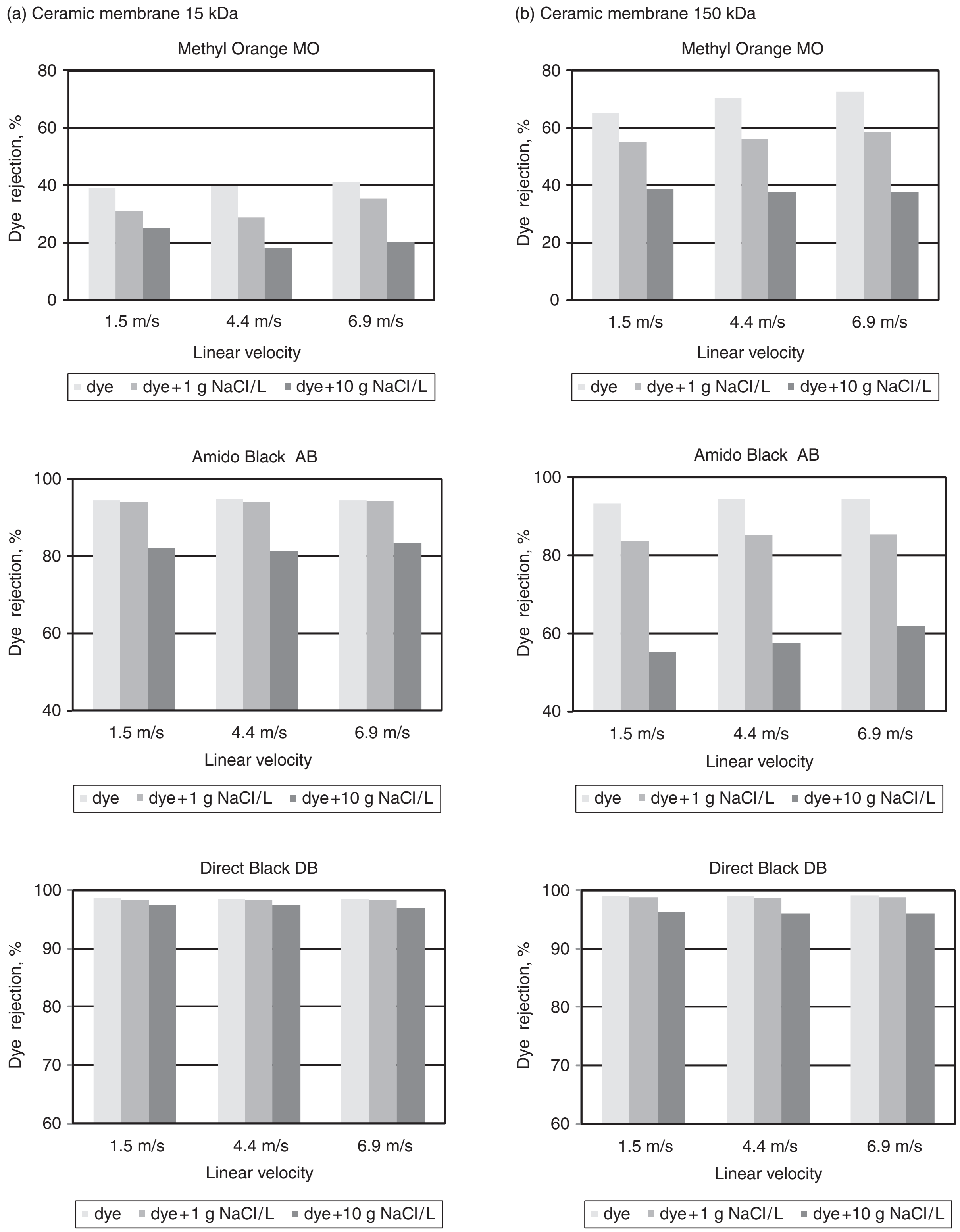

Fig. 4. The effect of NaCl concentration and linear velocity on dye rejection for ceramic membrane 15 kDa (a) and 150 kDa (b). Dye concentration: 100 g/m^3 (ΔP = 0.2 MPa).

References

[1] B. Van der Bruggen, E. Curcio and E. Drioli, Process intensification in the textile industry: the role of membrane technology, J. Environ. Manage., 73 (2004) 267–274.
[2] I. Koyuncu, D. Topacik and E. Yuksel, Reuse of reactive dyehouse wastewater by nanofiltration: process water quality and economical implications, Sep. Purif. Technol., 36 (2004) 77–85.
[3] G. Capar, L. Yilmaz and U. Yetis, Reclamation of acid dye bath wastewater: Effect of pH on nanofiltration performance, J. Membr. Sci., 281 (2006) 560–569.
[4] L. De Florio, A. Giordano and D. Mattioli, Nanofiltration of textile effluents for on-site treatment and reuse, Desalination, 181 (2005) 283–292.
[5] N. Uzal, L. Yilmaz and U. Yetis, Nanofiltration and reverse osmosis for reuse of indigo dye rinsing waters, Sep. Sci. Technol., 3 (2010) 331–338.
[6] M. Cheryan, Ultrafiltration and Microfiltration Handbook, Technomic, Lancaster, USA (1998), 388–391.
[7] J. Porter and A.C. Gomes, The rejection of anionic dyes and salt from water solution using a polypropylene microfilter, Desalination, 128 (2000) 81–90.
[8] J. Porter and S. Zhuang, Microfiltration of sodium nitrate and Direct Red dye using asymmetric titanium dioxide membranes on porous ceramic tubes, J. Membr. Sci., 110 (1996) 119–132.
[9] S. Barredo-Damas, M.I. Alcaina-Miranda, A. Bes-Piá, M.I. Iborra-Clar, A. Iborra-Clar and J.A. Mendoza-Roca, Ceramic membrane behavior in textile wastewater ultrafiltration, Desalination, 250 (2010) 623–28.
[10] J.I. Calvo, A. Bottino, G. Capannelli and A. Hernández, Pore size distribution of ceramic UF membranes by liquid-liquid displacement porosimetry, J. Membr. Sci., 310 (2008) 531–538.
[11] K. Majewska-Nowak, M. Kabsch-Korbutowicz and T. Winnicki, Concentration of organic contaminants by ultrafiltration, Desalination, 221 (2008) 358–369.
[12] R. Weber, H. Chmiel and V. Mavrov, Characteristics and application of new ceramic nanofiltration membranes, Desalination, 157 (2003) 113–115.
[13] M. Kabsch-Korbutowicz and A. Urbanowska, Applicability of ceramic membranes to the removal of natural organic matter from water, Ochrona Środowiska, 31 (2009) 15–19 (in Polish).
[14] S. Yu, M. Liu, M. Ma, M. Qi, Z. Lü and C. Gao, Impacts of membrane properties on reactive dye removal from dye/salt mixtures by asymmetric cellulose acetate and composite polyamide nanofiltration membranes, J. Membr. Sci., 350 (2010) 83–91.
[15] V. Kopecký and P. Mikulášek, Desalination of reactive yellow 85 by nanofiltration, Environ. Prot. Eng., 31 (2005) 187–198.