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**Modification of a polyamide reverse osmosis membrane by heat treatment
for enhanced fouling resistance**

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Modification of a polyamide reverse osmosis membrane by heat treatment for enhanced fouling resistance

Abstract

The use of heat treatment to improve solute rejection and fouling resistance of a polyamide reverse osmosis (RO) membrane was investigated in this study. Heat treatment was carried out by immersing the membrane samples in Milli-Q water at 70 degrees celcius for a specific duration. Heat treatment reduced the pure water permeability from 4.1 to 2.8 L/m² bar but improved conductivity rejection from 95.5 to 97.0 percent. As a result, a correlation was observed between changes in the two parameters. Marginal changes in the membrane surface characteristics were observed as a result of heat treatment. Heat treatment significantly improved the fouling resistance property of the RO membrane. When the secondary effluent was filtrated at an elevated permeated flux, the virgin RO membrane exhibited 30 percent flux decline while the heat-treated membrane showed only 12 percent flux decline. This is possibly because heat treatment resulted in a denser cross-linked active skin layer, thus reducing the blockage caused by small organic foulants.

Keywords

membrane, enhanced, osmosis, fouling, resistance, reverse, treatment, polyamide, heat, modification

Disciplines

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Modification of a polyamide reverse osmosis membrane by heat treatment for an enhanced fouling resistance

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Abstract

The use of heat treatment to improve solute rejection and fouling resistance of a polyamide reverse osmosis (RO) membrane was investigated in this study. Heat treatment was carried out by immersing the membrane samples in Milli-Q water at 70 °C for a specific duration. Heat treatment (24 hours) reduced the pure water permeability from 4.1 to 2.8 L/m²hbar but improved conductivity rejection from 95.5 to 97.0%. As a result, a correlation was observed between changes in the two parameters. Marginal changes in the membrane surface characteristics (i.e. zeta potential, hydrophobicity, chemistry and roughness) were observed as a result of heat treatment. Heat treatment significantly improved the fouling resistance property of the RO membrane. When the secondary effluent was filtrated at an elevated permeated flux, the virgin RO membrane exhibited 30% flux decline while the heat-treated membrane showed only 12% flux decline. This is possibly because heat treatment resulted in a denser cross-linked active skin layer, thus reducing the blockage caused by small organic foulants.

Keywords: Membrane fouling; modification; reverse osmosis (RO); water reuse.

Introduction

Fresh water resources for drinking water have been increasingly insecure in many parts of the world due to prolonged droughts and increased water consumption. Accordingly, water authorities in these regions are considering water reuse and seawater desalination as attractive and viable options to supplement their drinking water supply (Elimelech 2006). In these applications, reverse osmosis (RO) membrane is often employed for removing pathogenic agents, colour, salt and trace organic chemicals (Bellona *et al.* 2008; Traves *et al.* 2008; Wintgens *et al.* 2008). However, impurities that are present in wastewater can cause membrane fouling after a sustained period of operation (Fritzmann *et al.* 2007; Matin *et al.* 2011). The development of fouling layer on the membrane surface results in an increase in energy consumption to maintain a constant water production and consequently it leads to frequent chemical cleaning for restoring membrane permeability.

Commercially available RO membranes consist of a thin active polyamide skin layer on top of a porous supporting layer. The permeability, separation performance and fouling susceptibility of RO membranes are exclusively governed by the characteristics of their active skin layer. Thus, numerous previous studies have investigated the development and modification of the active skin layer for better membrane performance (Kang & Cao 2012). These investigations include the development of polymerisation monomers materials, interfacial polymerisation processes (Lee *et al.* 2011) and hybrid active skin layers containing inorganic particles (Li & Wang 2010). Other approaches have also focused on the active skin layer modification using commercial RO membranes. Among them, physical modification approaches include adsorption and coating, while chemical modification approaches are mainly based on hydrophilisation, radical grafting, chemical coupling and plasma polymerisation (Kang & Cao 2012). In fact, when the active skin layer has higher hydrophilicity and lower negative charge, less membrane fouling occurs due to reduced adsorption of organic matters on membrane surface (Gerard *et al.* 1998; Bartels *et al.* 2008). A recent study also reported that the anti-fouling property of RO membranes can be improved by surface hydrophilic modification using plasma polymerisation (Zou *et al.* 2011). However, the execution of these membrane surface modifications requires manufacturing steps, resulting in additional production costs.

A recent study by Shintani et al. (2009) applied heat treatment at various air temperatures (40-180 °C) to polyamide RO membranes and revealed that the heat treatment of over 80 °C decreased permeate flux of the RO membranes but increased their salt rejections. During the heat treatment, the polyamide RO membranes were heat-treated for only 30 seconds, which may be more economical than the other surface modification techniques. They suggested that a denser active skin layer can be developed with the heat treatment, resulting in less solute passage and less water permeability. However, Shintani et al. (2009) did not investigate the fouling behaviour of the membrane after heat treatment. In fact, to date, no previous studies have reported the improvement of anti-fouling characteristics of RO membranes using the heat treatment.

The aim of this study is to identify the effects of the heat treatment of RO membranes on membrane fouling. A commercial virgin RO membrane was used for the heat treatment. The impact of the heat treatment on fouling development was investigated using secondary effluent. The changes in membrane characteristics by the heat treatment were also evaluated by examining zeta potential, contact angle, pure water permeability and salt rejection.

Materials and methods

Membranes

The reverse osmosis membrane ESPA2 was supplied by Hydranautics (Oceanside, CA, USA) as flat sheet membrane samples. This is a low pressure reverse osmosis (LPRO) membrane that possesses a thin polyamide active skin layer supported by a porous polysulfone layer. The ESPA2 membrane has been widely used for water reclamation applications (Fujioka *et al.* 2012). The maximum operating temperature of the membrane specified by the manufacturer is 45 °C.

Chemicals

Analytical grade NaCl, CaCl₂ and NaHCO₃ were obtained from Ajax Finechem (Taren Point, NSW, Australia). For background electrolytes during rejection tests, a stock solution of each chemical was prepared in Milli-Q water at 2 M (NaCl) and 0.1 M (CaCl₂ and NaHCO₃).

Membrane filtration system

A laboratory scale cross flow RO filtration system was used in this study (Figure 1). The membrane sample was held in a stainless steel cross flow cell with an effective area of 40 cm² (4 cm × 10 cm) and a channel height of 2 mm. A high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA) transfers the feed solution from a stainless steel reservoir to the membrane cell. The permeate flow rate and cross flow velocity were controlled by a bypass valve and back-pressure valve (Swagelok, Solon, OH, USA). The permeate flow was monitored using a digital flow meter (FlowCal, GJC Instruments Ltd, Cheshire, UK) which was connected to a personal computer. The concentrate flow was monitored by a rotameter. The feed solution temperature was controlled in the feed reservoir using a stainless steel heat exchanging pipe which was connected to a temperature control unit (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA).

[Figure 1]

Experimental protocols

Heat treatment

Prior to the heat treatment, the membrane samples were rinsed with a copious amount of Milli-Q water to remove any preservative chemicals from the membrane surface. They were then immersed in Milli-Q water at 70 °C for a specified period (3, 24 or 72 hours). The temperature of the Milli-Q solution was controlled using a temperature-controlled water bath (SWV20D, Ratek, Victoria, Australia). Following the heat treatment procedure, the membrane samples were stored in Milli-Q water at 4 °C in the dark until they were used for experiments.

Filtration experiments

Prior to each filtration experiment, the membrane sample was compacted at 1,800 kPa using Milli-Q water until the permeate flux has been stabilised. Following the compaction step, the feed solution was conditioned to 20 mM NaCl, 1 mM CaCl₂ and 1 mM NaHCO₃ by adding appropriate volume of stock solution of each chemical. Thereafter, the permeate flux was adjusted to 20 L/m²h. The filtration system was operated for at least 60 min before the

permeate and concentrate were sampled for conductivity analysis. The cross flow velocity and feed temperature in the reservoir were 0.42 m/s and 20.0 ± 0.1 °C, respectively.

Membrane fouling was induced using a secondary treated effluent collected from a sewage treatment plant in Wollongong (New South Wales, Australia). The treatment train of the plant prior to the sampling point included screening, grit removal, sedimentation, activated sludge treatment and clarifier. The wastewater contains a large fraction of low molecular weight organics such as building blocks (300-500 Da) and low molecular weight neutrals (<350 Da) (Fujioka *et al.* 2013). Each experiment started with the compaction step as described above. Thereafter, feed solution was replaced with the secondary effluent, and the permeate flux was elevated to 30 L/m²h to induce membrane fouling. The system was then continuously operated for 20 hours maintaining the originally set feed pressure. During the fouling development, the cross flow velocity and feed temperature in the reservoir were also 0.42 m/s and 20.0 ± 0.1 °C, respectively.

Membrane characterisation and analytical techniques

Analytical techniques

Conductivity, pH and temperature of solutions were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo scientific, USA). Total organic carbon (TOC) concentration was determined using a TOC-V CSH analyser (Shimadzu, Japan).

Zeta potential measurement

Zeta potential of the membrane surface was analysed using a SurPASS Electrokinetic Analyser (Anton Paar GmbH, Graz, Austria). The Fairbrother-Martin streaming potential method was used to determine the zeta potential of each sample (Elimelech *et al.* 1994). The background electrolyte solution used in this study was 1 mM KCl. The pH of the background electrolyte was initially adjusted around pH 9 using KOH (1M) solution and it was incrementally decreased to below pH 3 by a titration of HCl (1M) solution. The background solution temperature was 25 ± 1 °C.

Contact angle measurement

Contact angle of RO membrane surface was measured using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ). The sample was rinsed with Milli-Q water and air-

dried for over 24 hours prior to the measurement. The contact angle was measured on ten different locations of each membrane sample to obtain the average value and the standard deviation.

Surface chemistry

Fourier transform infrared spectroscopy (FTIR) spectra were used to analyse functional groups of RO membranes. The FTIR spectrophotometer (IRAffinity-1, Shimadzu, Kyoto, Japan) used in this study is equipped with a diamond crystal plate. The active skin layer of membrane samples was fixed on the diamond crystal plate and the spectrum was obtained in the range of 400-4000 cm^{-1} at 2 cm^{-1} resolution.

Surface topography

Membrane surface roughness of the RO membranes was determined using an MFP-3D atomic force microscope (AFM) (Asylum Research, Santa Barbara, CA, USA). The scanning was performed in air in tapping mode using Nanoworld NCHR silicon cantilevers (spring constant of ~ 40 N/m). The scanning area was 20 μm x 20 μm .

Results and Discussion

Membrane characteristics

After three hours of heat treatment, the membrane permeability decreased from 4.1 to 2.8 $\text{L}/\text{m}^2\text{hbar}$ (Figure 2a). No further discernible decrease in the membrane permeability could be observed as the heat treatment duration increased to 24 and 72 hours. On the other hand, heat treatment led to an increase in conductivity rejection (Figure 2b). **No further statistically significant increase in conductivity rejection was observed after 3 hours of heat treatment.** It is also noteworthy that changes in the membrane permeability and conductivity rejection due to heat treatment appear to be inversely correlated (Figure 3). The effect of the heat treatment reported here is consistent with a previous study by Shintani et al (2009), who investigated the impact of heat treating a polyamide RO membrane at 100 $^{\circ}\text{C}$ on water permeability. They suggested that heat treatment can result in further cross-linking by inducing reaction between the free amine and carboxylic functional groups within the membrane active polyamide skin layer. The increase in cross-linking results in a denser active skin layer, thus leading to a decrease in permeability and an increase in solute rejection as reported in Figure 2.

[Figure 2]

[Figure 3]

Conductivity rejection by RO membranes can also be governed by electrostatic interactions that occur between charged solutes and the charged membrane surface (Bellona *et al.* 2004). However, no significant changes in the zeta potential of the membrane surface were observed (Figure 4). The impact of heat treatment on contact angle, which represents membrane surface hydrophobicity, was also insignificant. The membrane remained hydrophilic with contact angle value ranging from 25 - 40 ° with or without heat treatment. Provided that these analysis (i.e. zeta potential and contact angle) fundamentally represents the membrane properties of the active skin layer surface, these results indicate that heat treatment affected the internal structure and/or internal membrane properties of the polyamide active skin layer but not the membrane surface properties.

Membrane surface characteristics were further investigated using FTIR and AFM. The bonding structure of the polyamide active skin layer and the polysulfone supporting layer can be found with FTIR spectra of the RO membranes in the range of 1750-750 cm^{-1} . Peaks that are associated with polyamides can be found at 1663, 1609 and 1541 cm^{-1} that represent C-O and C-N stretching and C-C-N deformation vibration (amide I), N-H deformation vibration and C=C ring stretching vibration of aromatic amide, and N-H in-plane bending and N-C stretching vibration of a -CO-NH- group (amide II), respectively (Vrijenhoek *et al.* 2001; Tang *et al.* 2007). No discernible changes in these three peaks were observed with and without heat treatment (Figure 5). Heat treatment resulted in a small increase in the membrane surface roughness from 89.0 nm (virgin membrane) to 119.4 nm (heat treated for 24 hours). Overall, membrane surface characterisation results reported here suggest that heat treatment did not result in any changes in chemical bonding of the membrane surface. However, there were physical changes in the membrane surface evidence by a small increase in surface roughness which can be attributed to the contraction of the polymeric matrix of the cross linked active skin layer, resulting in an increase in salt rejection.

[Figure 4]

[Figure 5]

Resistance to Membrane Fouling

To assess the membrane fouling propensity, filtration of the secondary effluent was conducted at an elevated permeate flux value of 30 L/m²h which is 1.5 times higher than that typically used in a full scale RO installation for water reuse application. The permeate flux of the virgin RO membrane dropped by 20% within the first five hours of filtration and gradually decreased further by about 10% (Figure 6). In contrast, the permeate flux of the heat-treated (24 hours) ESPA2 membrane exhibited only about 5% drop within the first two hours of filtration and a total of approximately 12% decline at the end of the experiment. As a result, fouling caused a considerable reduction of permeability from 4.1 L/m²hbar to 2.9 L/m²hbar for the virgin membrane, while the permeability of the heat-treated membrane revealed a negligible reduction from 2.9 L/m²hbar to 2.6 L/m²hbar. In addition to the effect on fouling resistant, heat treatment (24 hours) also slightly increased the rejection of TOC (from 95 to 96%) and conductivity (from 97.7 to 98.1%). Overall, it appears that heat treatment reduced permeability but this was offset by improved fouling resistance and separation efficiency.

Membrane fouling of RO membranes using the secondary effluent mainly progresses with the adsorption and deposition of organic matter (Xu *et al.* 2010). Nevertheless, a fraction of small organics permeates through RO membranes and these small organics include building blocks, and low molecular weight acids and neutrals (Henderson *et al.* 2010). Some of these small organics may also be trapped within the free-volume hole of the active skin layer, which can lead to a decrease in permeate flux. In general, tighter membranes (e.g. RO membranes) are less susceptible to flux decline than looser membranes (e.g. nanofiltration membranes) (Fujioka *et al.* 2013). Thus, the denser active skin layer of the heat-treated RO membranes may prevent the penetration of low molecular weight organic foulants into the internal structure of the active skin layer, resulting in the slower fouling development. Although it is beyond the scope of this current study, the measurement of free space of the active skin layer may support this hypothesis.

[Figure 6]

Conclusions

Heat treatment of the polyamide RO membrane ESPA2 reduced the pure water permeability but improved the separation efficiency and fouling resistance. On the other hand, the membrane surface characteristics (i.e. zeta potential, hydrophobicity, chemistry and roughness) were not significantly affected by heat treatment. Fouling development on the ESPA2 membrane was retarded significantly by the heat treatment when the secondary effluent was filtrated at an elevated permeate flux. It is hypothesised that the denser active skin layer of the heat-treated RO membranes may prevent the penetration of low molecular weight organic foulants into the internal structure of the active skin layer. Results reported here suggest that heat treatment can be possibly used to refresh used membranes which usually have decreased salt rejection due to aging and chemical damage. Although heat treatment improved fouling resistance, the impact of heat treatment on the long-term performance and life-time of membranes is still unknown. Thus, further research is necessary to clarify the impact of heat treatment on the integrity and aging of RO membranes. In addition, improving the antifouling characteristics and efficiency of the heat treatment by clarifying the mechanism of heat treatment impact will be beneficial for further economical membrane modification.

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315 temperature. Error bars show the standard deviation of three replicate experiments.

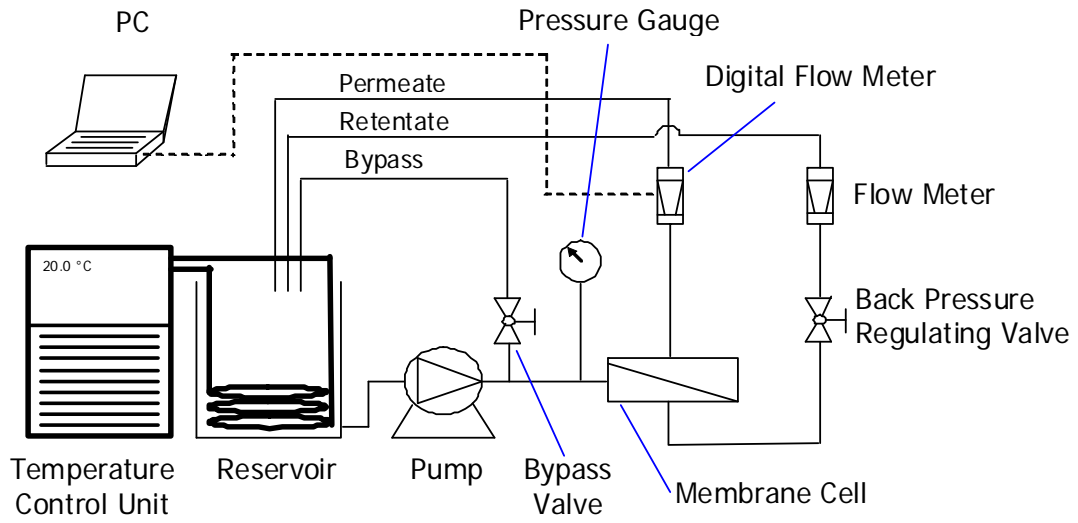
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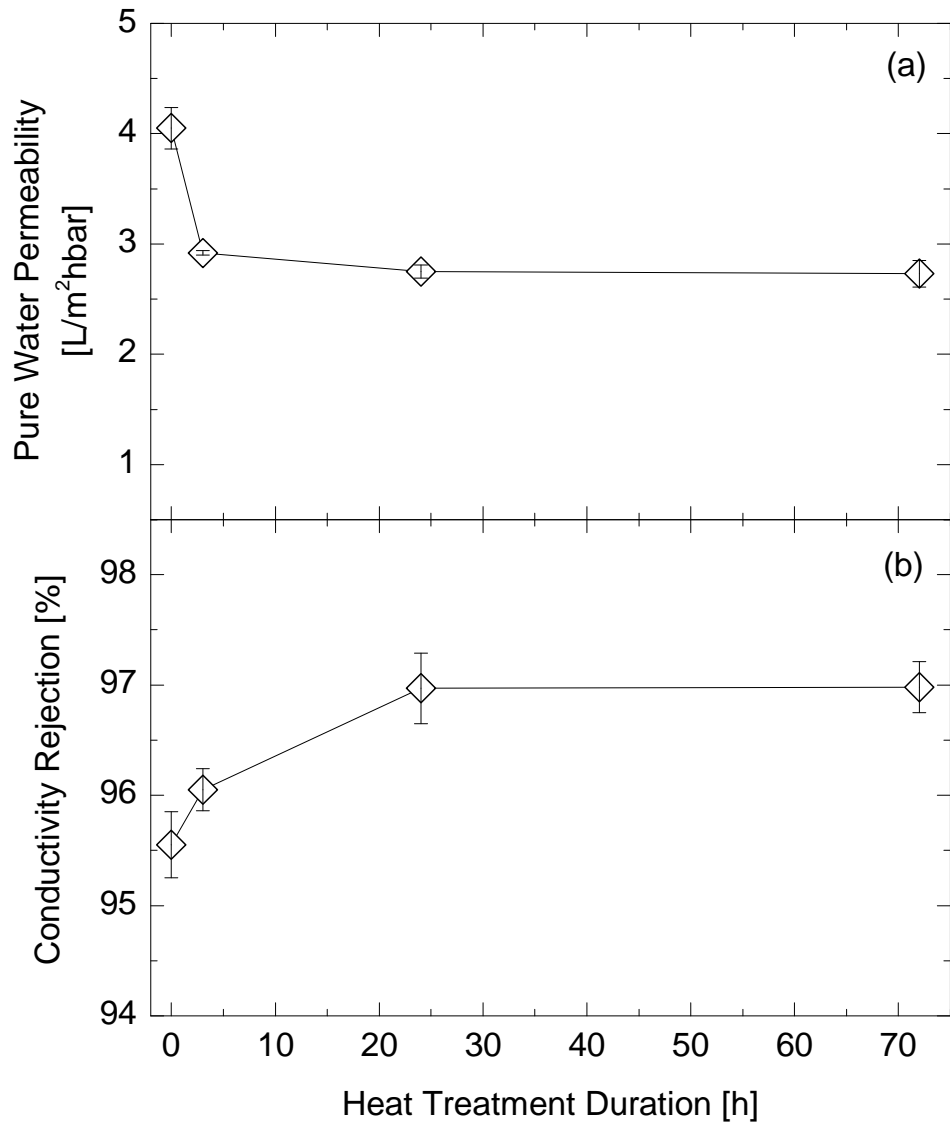
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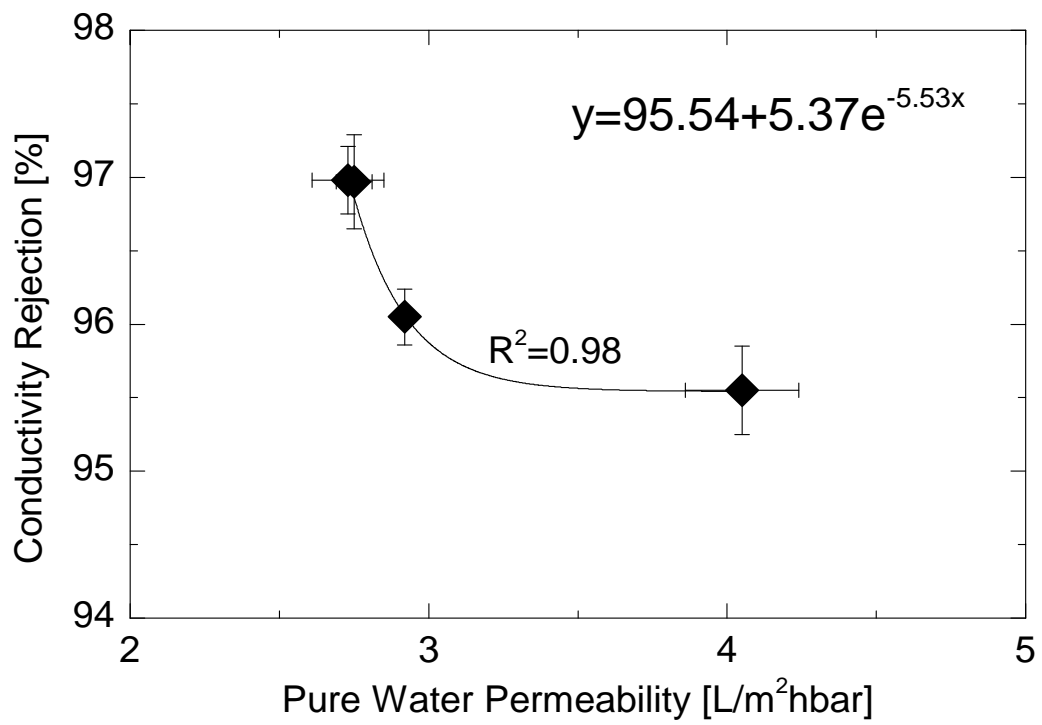


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327 **Figure 1**

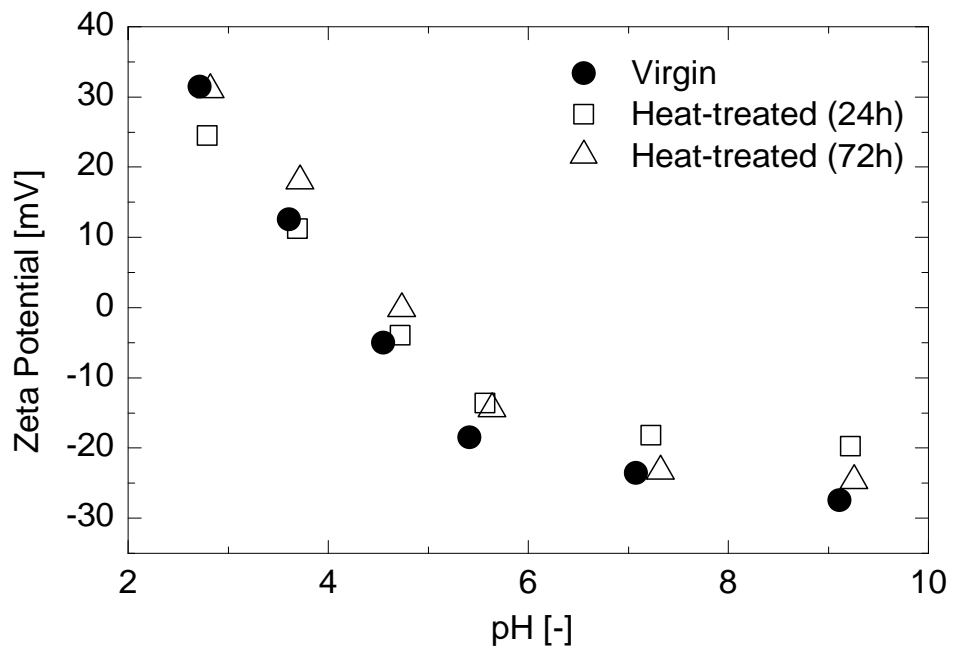
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330 **Figure 2**

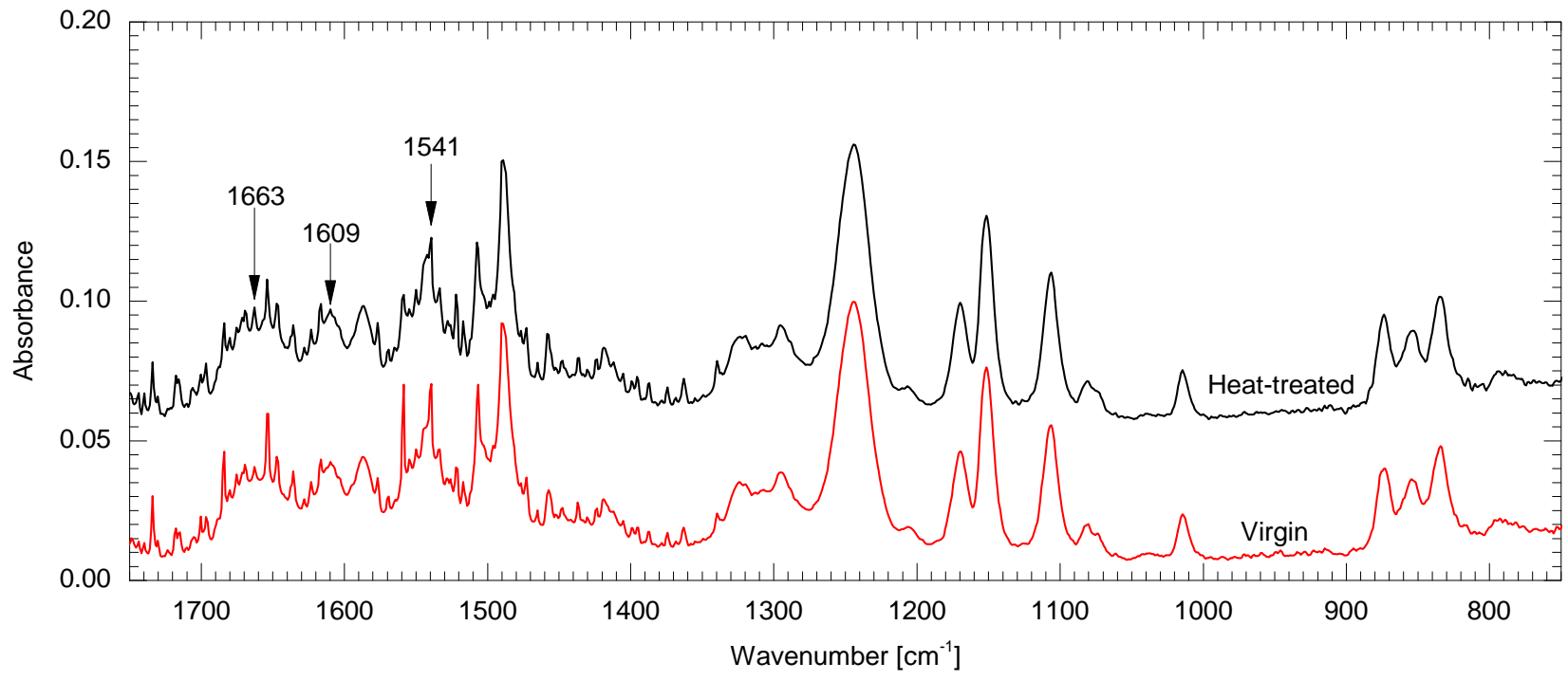


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332 **Figure 3**

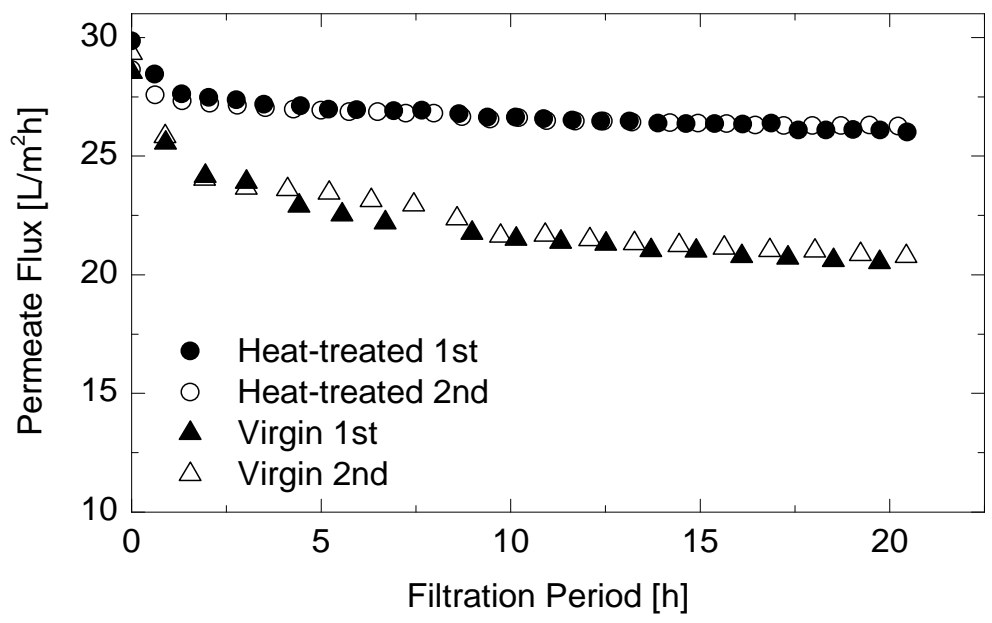


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334 **Figure 4**



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336 **Figure 5**



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338 **Figure 6**