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Cleaning results of new and fouled nanofiltration membrane characterized by contact angle, updated DSPM, flux and salts rejection

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Abstract

In membrane process industries, membrane cleaning is one of the most important concerns from both economical and scientific points of view. Though cleaning is important to recover membrane performance, an inappropriate selection of cleaning agents may result into unsatisfactory cleaning or irreparable membrane.

In this study the cleaning performance has been studied with measurements of membrane contact angle, Updated Donnan steric partitioning pore model (UDSPM) and salt rejection as well as flux measurement. Thin film nanofiltration (NF) membranes such as DK, HL and DL provided by GE Osmonics are used in this study. Tests were carried out with virgin DK, HL and DL as well as fouled DK membranes. Several cleaning agents were investigated; some of them were analytical grade such as HCl, NaOH and others such as SDS, mix agents were commercial grade agents that are already in use in commercial plants. Contact angle, DSPM and salt rejection as well as flux of virgin and fouled membranes before and after chemical cleaning were measured and compared. The contact angle measurements with and without chemical cleaning of different virgin and fouled membranes revealed very interesting results which may be used to characterise the membrane surface cleanliness. The contact angle results revealed that the cleaning agents are found to modify membrane surface properties (hydrophobicity/hydrophilicity) of the treated and untreated virgin and fouled membranes. The details of these results were also investigated and are reported in the paper. However, UDSPM method did not give any valuable information about pore size of the untreated and treated NF membranes. The salt rejection level of monovalent and divalent ions before and after cleaning by high and low pH cleaning agents is also investigated and is reported in the paper.

Keywords: Cleaning; Contact angle; Fouling; Nanofiltration membranes; Cleaning agents

1. Introduction

The separation characteristics of nanofiltration stand between ultrafiltration (UF) and reverse osmosis (RO) and the membrane selectivity has often been attributed to the interchange of both molecular sieving properties of ultrafiltration and diffusion properties of RO. It is generally recognized that membrane hydrophobicity/hydrophilicity, pore size (and its distribution) and surface charge can be important factors in the separation performance and fouling tendency of nanofiltration membranes [1,2]. The interaction of organic and inorganic colloidal substances with membrane surfaces in aqueous media is also an important factor which is dependent not only on the membrane surface charge but also on the hydrophobicity/hydrophilicity of the surface and pore size and pore size distribution. Therefore, study of membrane surface characteristics and environment are critical to understand and controlling membrane fouling and cleaning processes.

A large number of chemical cleaning agents are commercially available; five categories of cleaning agent commonly used are: alkalis, acids, metal chelating agents, surfactants and enzymes [3,4]. Commercial cleaning products are usually a mixture of these chemicals but the actual composition is often unknown. The choice of the optimal cleaning agent or mix composition depends on the feed characteristics. For example, acid cleaning is suitable for the removal of precipitated salts,

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such as $CaCO_3$, while alkaline cleaning is used to remove adsorbed organics [5].

Flux measurement is a direct assessment of fouling and cleaning process. It is usually accepted that flux decline in aqueous solutions containing organic and inorganic molecules is mainly caused by adsorption or crystallization, possibly enhanced by pore blocking and/or cake formation [6,7]. Effective chemical cleaning would therefore be necessary to detach different classes of foulants from the membrane and restore its permeate flux characteristics [8]. Furthermore, the selection of appropriate chemical cleaning agents might be critical because incompatible combinations of cleaning agent and membrane material could lead to irreversible flux loss, unnecessary costs through excessive chemical use and reduction in membrane life [3,8].

A contact angle measurement provides information on the hydrophobicity and hydrophilicity of the membrane surface. The hydrophobicity/hydrophilicity characteristics of the membrane surface are expected to govern the surface wettability by liquids, especially water, and subsequently govern the membrane performance in various applications. A number of researchers have tried to find a way to express hydrophobicity in a quantitative way using contact angle measurement. The effect of surface characteristics has generally been evident in efforts to select optimal pretreatment schemes and operating conditions for various membrane separation processes. However, the characterization of NF membrane surface by contact angle measurement after cleaning is seldom available in literature.

In order to predict the membrane separation performance, it is often necessary to know the mean pore size and pore size distribution at the membrane surface. Bowen et al. [9,10], developed a method called Donnan steric partitioning pore model (DSPM), which is based on the extended Nernst–Planck equation, modified to include steric effects, and a modified Donnan equation accounting for the sieving effect as well. Theoretical background description of the DSPM has been given in detail elsewhere [9,10]. The DSPM has been successfully used to describe retention of neutral solutes and ions on NF and Ultrafiltration (UF) membranes and on titania membrane with nanofiltration membrane properties use [11,12]. In this work, an updated version of the DSPM model has been used [13,14] using this model has the benefit that the membrane thickness is removed from the rejection equation because the nanofiltration driving force is redefined in term of an effective pressure as opposed to the volumetric flux. As a direct result the rejection equation for uncharged solute is now only dependent on the pore radius. Therefore, fitting experimental rejection at various applied effective pressures for a solute of known size will directly characterize the membrane pore radius.

It is well established that these chemical cleaning agents such as SDS, EDTA, NaOH and HCl are widely used in the applied industrial plants. The major message of this work and previous works is to open the discussion of cleaning strategies to those who have applied these cleaning agents in their plant in order to restore the production. The cleaning processes do regenerate the quantity but simultaneously deteriorate the quality. Therefore, the efficiency of cleaning agents, which have been used widely in the industrial plants, has to be investigated thoroughly in the laboratory scale before being applied in industrial plants. This study is intended only to evaluate the validity of these techniques, whether it is possible to obtain useful information about the membrane surface after cleaning or not, and also to find out whether a correlation exists between the flux and/or salt rejection and the data obtained from these techniques. If it does, then subsequently the variation of cleaning concentration and the cleaning process will be worthy of study in order to find out what is the optimum cleaning system with the aim of restoring the plant performance without deteriorating the water quality. Thereby the cost of the membrane replacement can be saved and membrane life can be extended.

Kim and Fane [15] studied cleaned and fouled UF membranes using flux methods combined with microscopical methods. The results were also analyzed by determining the pore size distributions before and after cleaning. Warczok et al. [16] recently reported that it is possible to find out whether the cleaning procedure was correctly designed or not by analysis of AFM (Atomic Force Microscope) images.

In order to evaluate the cleaning results it is important to compare the characterisation of the fouled membranes to those of the virgin and cleaned membranes. Fouled membranes have been investigated in many different ways using various characterisation methods. In most cases, the virgin membranes were cleaned before use and the characteristics of the membrane after precleaning could have changed considerably from that of the virgin membranes.

In this study, different kinds of analytical grade and commercial grade cleaning agents have been used to clean both virgin and fouled NF membranes. Both virgin and fouled membranes have been characterized before and after cleaning by contact angle, use of the UDSPM, flux measurements and rejection of monovalent and divalent ions.

The overall goal of this study was to investigate the following:

(a) To investigate different techniques (using contact angle measurements, UDSPM, rejection and flux) to find out the most suitable option for restoring the membrane flux without harming the quality of the product water.
(b) To compare between untreated and treated NF membranes on the basis of the contact angle measurements, UDSPM, rejection and flux.

2. Experimental

2.1. Materials

2.1.1. Membrane

Three types of commercial NF membranes, GE Osmonics-DK, DL and HL flat sheet membrane were used in this study. DK, DL and HL thin-film membranes (TFM) are negatively charged having a proprietary active nanopolymer layer based