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Cleaning effects of oxalic acid under ultrasound to the used reverse osmosis membranes with an online cleaning and monitoring system

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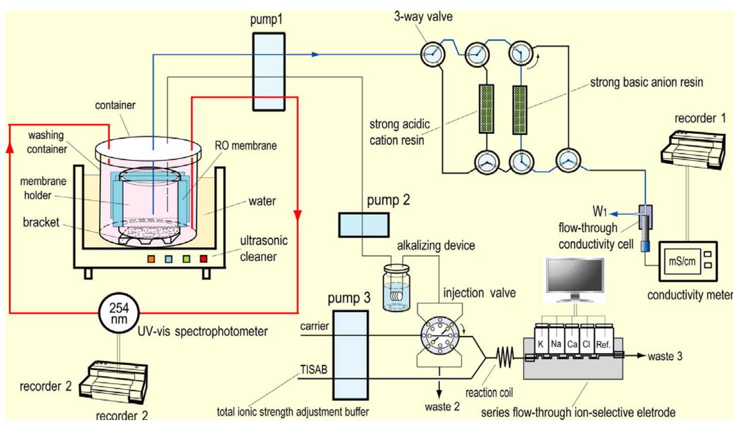
HIGHLIGHTS

- A system was developed for researching the used reverse osmosis membrane cleaning.
- Oxalic acid was first used for cleaning reverse osmosis membrane.
- Obtained dynamic info cleaning organic and inorganic foulings on RO membrane.
- Defouling rate of the used RO membrane was more than 91% in optimum conditions.
- Oxalic acid plus ultrasonic cleaning the used RO membrane has remarkable effect.

GRAPHICAL ABSTRACT



Sketch of a new ultrasonic-chemical cleaning system for researching cleaning effects of the waste reverse osmosis membranes with acids or alkali under ultrasound.

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ABSTRACT

A new system was developed for the research on the cleanings of ultrasonic acid and alkali to the used reverse osmosis membrane (UROM). By continuously detecting the absorbance, conductivity and K^+/Na^+/Cl^-/Ca^{2+} contents in the cleaning solutions with this system, the cleaning information of organic and inorganic fouling on the UROM can be obtained and their cleaning effects can be judged directly. In the research, after comparing the cleaning effects of five kinds of acid solutions to the used polyamide ROMs, it was found that the ultrasonic cleaning effect of oxalic acid is the best. Therefore the concentration and pH of the oxalic acid, the sequence of acid and alkali cleanings were investigated, the results showed that, when the pH of 0.2% oxalic acid was regulated to 2.5 by the ammonia water, the defouling rate of the UROM can be reached 91%, and if employing the acid and alkali solutions to simultaneously clean, the best cleaning effect will be obtained, in which the cleaning order should be the first acid then alkali plus the ultrasound. The results and parameters obtained in this study can be used as a reference basis for designing large-scale chemical and ultrasonic cleaning system of UROM.

1. Introduction

At present, the water treatment system based on the reverse osmosis membrane (ROM) is one of the most effective in the desalination technologies [1]. For a ROM yielding water system, if contents of organics, microbial or colloid in the treated water exceeded the set

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index, this will lead to the RO pollution, the water quality depravation, the water yield declining, the increasing of energy consumption and pressure difference of the system. If the ROM's desalination performance cannot be recovered in time, its service life should be shortened [2].

Therefore, in order to recover the ROM's desalination performance and prolong the service life, the common practice is that ROM contaminated is cleaned with physical or chemical means [3]. Physical cleaning is with the help of the mechanical force, sound wave, heat or light to remove the fouling and to achieve the purpose of recovering the separation performance of ROM. Chemical cleaning is by the aid of the chemical reaction, dissolution, emulsification, dispersion and adsorption to achieve the purpose of removal the ROM contamination [4–5]. The chemical cleaning agents in common use are acid [6], alkali [7], metal-chelator, surfactants, etc. [8]. Hydrochloric acid and citric acid are frequently-used. Hydrochloric acid can clean off the outermost calcium carbonate contaminants on the ROM surface [9], but its cleaning effect is poor for the relatively dense intermediate layer contaminants, such as the deposed sulfate, hydroxides and oxides of iron and other metals, as well as the inner pollutants. Citric acid can be used for cleaning carbonate and metal oxides, and it is safe, non-toxic but its cost is higher. Oxalic acid is an organic acid, its corrosivity to equipments is <1 of inorganic acid, and its complexing ability with the metal ion is stronger, and its cost is lower than that of citric acid. So, we chose the oxalic acid as the cleaning agent of ROM in the research.

In addition, the literatures showed that ultrasonic can effectively remove nano-filtration membranes' contaminant, improve the cleaning efficiency, reduce the cleaning frequency, shorten the cleaning time and prolong the cleaning period [10], and also can reduce the adsorption rate of surface fouling in the operation of the ROM yielding water [11]. However, the ultrasonic for chemically cleaning contamination on the ROM surface has not been reported.

Therefore, in order to install the ultrasonic-assisted equipment in a chemical cleaning system for ROM [6] and obtain some information on the ultrasonic cleaning, first a small dynamically cleaning and monitoring system was designed. Subsequently, by using the system, first under ultrasonic the cleaning effects of alkaline solutions to pollutants of the ROM surface were examined [7]. Of course, this system can be also used for the screening of the ultrasound-chemical cleaning solutions of seawater desalination or wastewater treatment membranes. In this paper, it mainly focused on under ultrasonic the results of the oxalic acid cleaning the used ROM from wastewater treatments.

2. Experimental and methods

2.1. Apparatus and reagents

The main equipments used in this research are SG7200HB-I type supersonic cleaner (Shanghai, Guante), UV-1800PC type UV–vis spectrophotometer with a flow-through cell (Shanghai, Meipuda), L1600300 type Fourier infrared spectrometer (US, Perkin Elmer), JSM-7500 type SEM (Japan, JEOL), X-MAX50 type *x*-ray energy spectrometer (English, OXFORD), DJS-1 type conductivity electrode and CM-230 type conductivity meter ($k = 0.933$, Hebei, Keruida), JC202 type electrothermal constant-temperature dryer (Shanghai, Chengshun), CP224S type electronic balance (Sartotius, Germany), KL-UP-IV-10 type ultrapure water system (Chengdu, Kangning), FWT-1044S type recorder (Shanghai, Hongdao), KH206 type paperless recorder (Xiamen, Kehao); H-type strong cation resin column (i.d. 3.0 mm, length 100 cm) was homemade [12,13].

Related reagents used in this research are oxalic acid, citric acid, phosphoric acid, acetic acid, sodium hydroxide, hydrochloric acid and potassium hydrogen phthalate (AR, Chengdu, Kelon).

Experimental specimens were some used polyamide ROMs (TM720-370 and BW30-400 type), which have been heavily contaminated, offered by some Pharmaceutical Co. Ltd. Fig. 1 is the EDX curve and the element content percentage obtained by detecting the used ROM surface with an energy dispersive *x*-ray detector. It can be seen that components of the used ROM surface were mainly composed of hydroxide, calcium carbonate, silicate, metal oxides of iron, aluminum and manganese, and organic compounds.

2.2. Preparation of specimens and calculation of fouling removal rate

The used ROM specimens used in the experiment were cut into rectangles by using a fillet slicing machine. Four corners of the rectangle were cut into semicircle. The specimen area (S_m) was 46.36 cm^2 (5.4 cm × 8.6 cm). An undefiled ROM specimen mass (W_m) is 0.4532 g and its surface density (d_m) is 9.776 mg/cm^2, and it is used as the reference in the research. Through mathematical derivation, the formula for calculating the defouling rate of the ROM surface was obtained as follows:

$$d_m = \frac{W_m}{S_m} \quad (1)$$

$$d_{m+p} = \frac{W_{m+p}}{S_m} \quad (2)$$

$$d'_{m+p} = d_{m+p} - d_m \quad (3)$$

$$R_p = \frac{d'_{m+p} - d_m}{d'_{m+p}} \times 100\% \quad (4)$$

where, d_{m+p} is the total surface density of ROM carrying the fouling (mg/cm^2); W_{m+p} is the total mass of ROM carrying the fouling (mg); d'_{m+p} is the surface density after cleaning ROM (mg/cm^2); R_p is the defouling rate of ROM (%). In addition, W'_{m+p} was used to indicate the mass of ROM after cleaning.

2.3. Testing system and experimental procedure

Combining physical and chemical cleaning methods, the system was designed as Fig. 2, which can be used for the research of the used ROM specimen cleaning. It consists of an ultrasonic cleaner, peristaltic pumps, strong-anion and -cation resins columns, three-way switch valves, a conductivity meter, an $K^+/Na^+/Cl^-/Ca^{2+}$ detector and a flow-through type UV spectrophotometer, a filter and two recorders. Its operation process is as follows.

Under suction of the first pump (pump1), ultra-purified water (hereafter referred to as "water") of a cleaning container in the ultrasonic cleaner (50 kHz, 0.636 W/cm^2) are flowing successively into a_1/b_1, a_2/b_2 and a_3/c_3 of three-way switch valves, strong-cation resin column, b_5/c_5 and a_6/c_6 of three-way switch valves, flow-through conductivity detector to the waste1. At the same time, the conductivity electrode gives water's blank signal, which will be recorded by the recorder 1. In another flow way, water in the container are flowing into the UV-spectrophotometer, and returning to the container to circulate; in the meantime, the UV-spectrophotometer gives the blank absorbance of the water, which will be recorded by the recorder 2.

When two blanks tend to stable, the pump1 stops, some ROM specimens are placed in the container, then the pump1 starts to run, the process of the water circulation cleaning (C_w) begins to carry out; the conductivity change value (ΔS_c) of the water will reflect the washed amount of inorganic contaminants on the ROM specimen surface, and the absorbance change value (ΔA) of the water will reflect the washed amount of organic pollutants on the ROM specimen surface.

When the conductivity and absorbance values in the C_w are no longer changed, the supersonic cleaner is powered on to conduct next process of the ultrasonic water cleaning (U_w), in which the changes in the conductivity and absorbance values are recording in accordance with a certain period.