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Stability of an ultrafiltration system for drinking water treatment, using chlorine for fouling control

Hang Xu [a,b], Wei Chen [a,b,*], Hongyao Xiao [b], Xinghua Hu [b]

[a] Ministry of Education Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Hohai University, Nanjing 210098, PR China
[b] College of Environment, Hohai University, Nanjing 210098, PR China

HIGHLIGHTS

- Chlorine as a preoxidant for UFsystem pretreatment.
- We examine the mechanism of membrane fouling with preoxidation by chlorine.
- The chlorine oxidation changed the characteristics of organic pollutants.
- The chlorine pretreatment indicated some potential for mitigating transmembrane pressures.
- The chlorine combined with UF system can affect the qualities of the membrane materials.

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ABSTRACT

An ultrafiltration (UF) system for the purification of raw water from the Yangtze River was used as an advanced treatment, following a conventional purification process. We investigated the performance of membrane fouling control, using chlorine for the pre-oxidation of the raw water. The former process was implemented via direct continuous dosing of chlorine prior to coagulation, during which the supernatant was used as an influent into a UF system. Investigations into this option indicated that the optimal dose of chlorine is 1.5 mg/L. These conclusions were reinforced by results from an investigation into molecular weight distribution and hydrophilic and hydrophobic fractions in the water treated with and without chlorine in the UF system. Scanning electron microscopy indicated that loose fragments were formed on the filtration cake during the chlorine/UF process, which was easy to remove by hydraulic washing. The analysis of tensile strength shows that the tensile ability of material is weakened during the chlorine pretreatment of the raw water in the UF system. Meanwhile, the contact angle and the field emission scanning electron microscopy experiment also indicated that the membrane material could be affected by the chlorine, which oxidizes the raw water in the UF system.

1. Introduction

A large number of preventable deaths in developing countries are due to microbial infections resulting from the consumption of polluted drinking water [1]. Compared with other methods such as nanofiltration and reverse osmosis, ultrafiltration (UF) is a relatively low-cost method to remove contaminants from the drinking water [2]. Due to intense regulatory activity and the scarcity of high-quality source water, UF is a suitable method for the treatment of drinking water, because of its compactness, easy automation, efficient removal of turbidity and organic matter (such as humic substances) and pathogens such as *Giardia* and certain viruses [3–7]. The widespread use of UF membranes for drinking water treatment is, however, limited because of membrane fouling, which is regarded as a major disadvantage associated with this method [8,9]. Pollutants tend to from a cake layer on ultrafiltration membranes due to deposition or adsorption on the membrane surface, pore blockage, and biofilm formation [10]. This fouling results in a reduction in membrane permeability and membrane permeate flux, and an increase in the applied pressure required, which leads to higher operating costs. Over time, fouling causes a deterioration of membrane materials, resulting in compromised effluent water quality and a shorter membrane lifetime.

Several studies have demonstrated that natural organic matter (NOM) is a major foulant of UF membranes when treating lake and river waters [11–13]. Furthermore, NOM is a complex matrix of organic chemicals derived from a number of sources such as soil, living organisms and plant detritus. These affect the odor, color and taste of the treated water, form complexes with heavy metals and pesticides, and react with chlorine to form chlorinated disinfection by-products (DBPs) [14]. Pretreatment of raw water has been used as an important

* Corresponding author at: College of Environment, Hohai University, Nanjing 210098, PR China. Tel.: +86 13913899869; fax: +86 02583787618.
E-mail address: cw5826@hhu.edu.cn (W. Chen).

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means to reduce membrane fouling. The efficiency of pretreatment, in terms of mitigating membrane fouling, is strongly associated with the type of agent (coagulant, adsorbent, or oxidant), dosage, dosing mode (continuous or intermittent), dosing point, mixing method, temperature, NOM properties (hydrophobicity, charge density, molecular weight (MW) and molecular size), solution environment (pH and ion strength), and membrane characteristics (membrane charge, hydrophobicity and surface morphology) [15].

Pre-oxidation is frequently adopted as a pretreatment process to prevent UF membrane fouling, and feasible preoxidants have been widely investigated [16,17]. Oxidation normally involves the use of chlorine, potassium permanganate or ozone as oxidizing agents, the purpose being to control NOM, metals and microbial growth during water treatment processes, since these compounds have a negative effect on coagulation efficiency [18,19]. Previous reports have demonstrated that the pre-oxidation of the UF influent significantly mitigates organic fouling, which had been primarily attributed to changes in the molecular characteristics of NOM [20,21]. The NOM macromolecules are oxidized into lower-molecular-weight compounds, which may involve the mineralization or transformation of some humic/hydrophobic NOM fractions to form less absorbable organic acids.

Chlorine is widely used in water treatment processes, during which the pre-oxidation of chlorine facilitates the removal of NOM, ions and algae [22]. Compared to other oxidation processes–such as those involving potassium permanganate and ozone–chlorine pre-oxidation has a number of advantages: it is a low cost method and does not affect the water color, as is the case when using potassium permanganate as an oxidant. A number of previous studies have dealt with the control of membrane fouling by means of chlorine, but there have been no detailed studies on the mechanisms involved or on effects of these reactions on NOM materials. Furthermore, the stability of the chlorine/UF process must be considered when applied to particular drinking water treatment plants.

We investigated the characteristics and mechanisms of controlling membrane fouling in a combined coagulation/UF system, with and without chlorination. The effects of membrane material on pre-chlorination were also investigated. A bench-scale UF system was used as an advanced treatment process, following coagulation, to purify raw water from the Yangtze River. The objective of this research was to perform pre-oxidation before membrane filtration, to investigate membrane pressure variation and the quality of filtrates associated with the UF process, and to evaluate the stability of the UF system by chlorine pretreatment in the point of the membrane material.

2. Materials and methods

2.1. Raw water

Water samples were obtained from the Beihe Kou Water Treatment Plant, which receives raw water from the Yangtze River, the major water source of the city of Nanjing. The Yangtze River, an important source for raw water supply to many cities of China, is characterized by a low NOM concentration (mostly less than 3 mg/L). After collection, the water samples were taken to the laboratory and the key water quality characteristics were determined (Table 1).

2.2. UF experiments

Hollow fiber UF membranes of modified polyvinylchloride (PVC), provided by Litree Purifying Technology Co., Ltd., were used for experiments. A UF membrane filtration area of 0.1 m^2 was used in the bench-scale tests. Bench-scale UF experiments were performed with an outside-in type. Detailed characteristics of the membrane are summarized in Table 2. All the membranes were initially rinsed, using pure water, following the manufacturer's instructions. The bench-scale chlorine/UF system is shown schematically in Fig. 1.

Table 1
Water quality of raw water.

Category	Characteristics	Values
Toxicological indexes	Chloroform (μg/L)	1.9–5.3
	Phenoxin (μg/L)	0.6–1.3
	Turbidity (NTU)	100–15
	Color (Pt–Co)	<20
	pH	6.82–7.64
Sensory traits and physical indicators	Manganese (mg/L)	0.018–0.047
	Iron (mg/L)	<0.06
	Aluminum (mg/L)	0.009–0.021
	Calcium (mg/L)	21.3–41.6
	Hardness (as$CaCO_3$mg/L)	95–117
	COD_{Mn} (mg/L)	1.89–4.16
	Temperature (°C)	7.1–25.3
	Conductivity (us/cm)	229.52–291.61
Other Values	UV_{254} (cm^{-1})	0.051–0.079
	TOC (mg/L)	2.04–3.68
	SUVA ($L/mg^{-1}.m^{-1}$)	1.38–3.87
	DO (mg/L)	4.79–8.16

Our principal aim was to investigate chlorine pre-oxidation as a means of controlling membrane fouling of a UF system. To assess the feasible control effect, we carried out an initial investigation into the influence of chlorine dosage on membrane fouling. Different dosing levels of chlorine were investigated to ensure the optimal dosage of chlorine pretreatment in the UF membrane system by assessing the change in transmembrane pressure (TMP). It was necessary to dose with chlorine before coagulation. To facilitate coagulation we made use of a six-unit stirrer apparatus. The following operating parameters were employed: a stirring regime of 200 rmp/min for 1 min, followed by 60 rmp/min for 6 min, then 30 rmp/min for 6 min, after which the solution was left without any stirring for 20 min. The supernatant represented the effluent from the feed water tank. The coagulant of polyaluminum chloride (PACl), at a dosage, of 20 mg/L, was provided by the Beihe Kou water plant in Nanjing of china. The supernatant into the collecting tank was maintained at a constant flux of 5 L/h by a feed pump and an overflow tube was installed on the collecting tank in order to maintain a constant water level. The water in the collecting tank flowed into the UF membrane pool by gravity. The flux of the UF membrane module in the membrane pool was 3.0/h (30 L/m^2 h), using a production pump.

The UF experiments were designed as a submerged membrane reactor in which the permeate flux was maintained at a constant flux of 30 L/m^2 h. The UF membrane system had a filtration cycle of 45 min. The following processes were performed at the end of each filtration cycle: first wash: 6 m^3/h, 15 s; backwash: 8 m^3/h, 30 s; and wash again: 6 m^3/h, 15 s. The backwash water of the experiment was produced by the system and, subsequent to use, was discharged directly into the sewer. The effluent pump was controlled by a timer with a time sequence of 45 min on and 60 s off. The aeration was used to provide suitable hydraulic conditions for the filtration process. Aeration was operated when the feed water was being filtered by the UF membrane and was stopped during the backwash cycle. Air was intermittently supplied, via the bottom of the membrane tank, through a diffuser at a flow rate of 20 m^3/h.

Prior to the commencement of continuous UF, the pure permeate TMP (P_0) was measured by filtrating deionized water. The TMP of the sample (P_1) was compared with the pure permeate TMP (P_0) to provide a comparison between the different pretreatment conditions. TMP may

Table 2
Characteristics of the UF membrane.

Average molecular weight cut-off/Da	50,000
Internal diameter/mm	0.85
External diameter/mm	1.45
Fiber length/m	0.500
Effective surface area/m^2	0.1
Type	Outside-in