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Effectiveness of advanced oxidation processes for the removal of manganese and organic compounds in membrane concentrate

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ABSTRACT

The effectiveness of batch UV, ozone, and UV/ozone induced oxidation processes in treatment of manganese and organics in reverse osmosis concentrate stream is evaluated. The most effective advanced oxidation techniques are identified and the optimum operating conditions are determined. Application of UV alone (wavelength of 254 nm, light intensity of 4400 $\mu W/cm^2$, and lighted length of 2.13 in.) was found to be ineffective for removal of organic compounds while it led to a gradual decrease in manganese concentration. Although UV-ozonation could remove manganese completely at initial ozone concentration of 15.2 ppm, oxidation with ozone alone at initial concentration of 6.2 ppm is found to be the most suitable condition for manganese removal. At low initial ozone concentration of 6.2 ppm, the removal for manganese reached 97.2%. The only limitation of ozonation is that over-oxidation occurs when the initial ozone concentration exceeds 6.2 ppm, and therefore the efficiency of the treatment decreases due to the production of soluble permanganate. It was also found that the highest oxidation efficiency for the organic carbon is 89% which occurs in UV-ozonation treatment at the initial ozone concentration of 15.2 ppm.

1. Introduction

Membrane technology is one of the most effective water treatment technologies, and its utilization is rapidly expanding [1]. Membrane processes often include ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), and their combined processes. Generally in membrane water treatment systems, the concentration of the minerals in the permeate water is ultra-low, the permeate water tends to be aggressive toward distribution system facilities. In addition to the issues of quality of water for drinking, the incompatibility of the permeate water with the existing water distribution infrastructure is of concern. Therefore, post-treatment of the permeate water prior to its release to the distribution system as finished water is important [2,3]. Another concern with the membrane processes is the production of concentrates and their proper disposal [4]. The organic materials in membrane concentrates include organic matter in the carrier drinking water, refractory chemicals (e.g. pesticides, pharmaceutical products, endocrine disruptors), and residuals from water treatment processes (e.g. soluble microbial products, partially biodegraded organics, anti-scaling chemicals) [5]. In addition, biological materials (e.g. bacteria, viruses and cell fragments), representing a potential environmental hazard, are present in the membrane concentrates [5,6].

Hence, the challenge is not only to post-treat the permeate stream for reuse but also to further process the concentrate streams. Although feed water has been commonly mixed with permeate water in industry to increase the total dissolved solids (TDS) content and to improve the stability of the permeate water, this paper presents the novel process concept of blending of the permeate water with treated RO concentrate. The treated RO concentrate refers to the water after advanced oxidation processes, which is almost free of organic pollutants and unwanted metals such as manganese. Compared to the RO feed, the idea of the application of treated RO concentrate for blending with the permeate water to meet hardness and corrosion protection concerns has the following advantages:

1. No disposal of the RO concentrate will be required, and therefore there would be no environmental concerns regarding the produced RO concentrate after RO processes. In fact, the RO concentrate is processed further and is re-used in the water system. Therefore, this new technology is much more environmentally friendly.

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2. Compared to RO feed, the RO waste stream contains high concentration of minerals. A very small volume of the treated concentrate water is sufficient to adjust hardness (Ca/Mg) and alkalinity (HCO_3) of the permeate stream. Thus smaller equipment will be needed for the post-treatment of the permeate water. Therefore, this novel technology is more cost effective.

The treatments of concentrate stream primarily using coagulation/flocculation and activated carbon adsorption, powdered activated carbon adsorption combined with nanofiltration and bank filtration have been studied in the literature [1]. Among these methods, adsorption with 5 g/L granular activated carbon showed the highest dissolved organic carbon removals of 91.3% [1].

Alternatively, advanced oxidation processes (AOPs) have proved to be very efficient in the oxidation of a wide range of recalcitrant chemicals and micro-pollutants such as residual pharmaceuticals and pesticides in water [7–9]. The highly reactive hydroxyl radicals formed in the AOPs oxidize organics rapidly and produce oxygenated by-products. Continued oxidation ultimately can lead to mineralization of pollutants, in which carbon dioxide or other semi-volatile carbon products are produced [10,11].

Among various AOPs adopted for the water treatment, catalyst, ultraviolet (UV)-based, ozone (O_3)-based, and hydrogen peroxide (H_2O_2)-based oxidation processes are increasingly being considered as effective methods for degradation of the organic substances in water and waste water [5,6,8,12,13]. For instance, the results of UV/H_2O_2 treatment on natural organic matter (NOM) in raw water indicated that recalcitrant NOM were oxidized into more readily biodegradable compounds with considerable increase in formaldehyde and acetaldehyde concentrations [13]. Catalytic ozonation was also introduced as a promising method to enhance the mineralization of organics in water in short reaction time [9,14,15].

Application of AOPs for removal of organic carbons from RO concentrate has been investigated. For instance, ozonation of RO concentrate showed that the moderate ozone doses (5–10 mg/L) were sufficient to remove beta blockers efficiently although ozone had a lower stability in RO brine samples with elevated dissolved organic carbon concentration [7]. Compared to coagulation and adsorption, the AOP of UV/H_2O_2 was found to be more effective in complete decolorization with 50–55% removal efficiency for organics [16]. Furthermore, more than 80% of the dissolved organic carbons in RO concentrate (pH 4–8.5 and conductivity up to 11.16 mS/cm) was removed after 2 h of UVC/3 mM H_2O_2 treatment followed by biological treatment [17]. The results on the feasibility of four AOPs (photocatalytic oxidation, sonolysis, ozonation, and H_2O_2 oxidation) on the treatment of organics in RO concentrate from a municipal wastewater reclamation plant showed that photocatalysis (UV/TiO_2) with pretreatment of $FeCl_3$ coagulation could finally lead to 95% removal of the organics from the RO concentrate within 6 h [8]. In addition, it was demonstrated that the combination of UV/TiO_2 and biodegradation is a feasible technique for the oxidation of organic pollutants discharged to the environment from RO wastewater reuse facilities [6]. This technique reduced the concentration of the dissolved organic carbon to 9% of its initial value [6]. It was recently reported that photocatalytic reaction is useful for removal of color and degradation of conjugated compounds in municipal RO concentrate [5].

In addition to organic materials, membrane concentrates usually contain relatively high amounts of metals such as manganese, iron, boron, copper, chromium, lead, and selenium [18,19]. Different processes have been used to remove the metals from RO concentrate stream due to their significant environmental risks [18,19]. However, the application of AOPs in the oxidation of the target metal species in RO concentrate water has been rarely studied. In this paper, the feasibility of oxidizing manganese and dissolved organics in RO concentrate stream using ozone-based, UV-based, and combined O_3/UV-based oxidation processes are investigated and compared. The main objective of this study was to determine the most effective AOP technique and its optimum operating condition to minimize the amounts of organic compounds and manganese in the reject water stream from membrane treatment process.

2. Materials and methodology

2.1. Materials

The RO concentrate water sample was taken from the water treatment plant in the town of Carlyle in Saskatchewan, Canada. Table 1 presents the most important results of inductively coupled plasma (ICP) analysis for the raw, concentrate, and permeate water, respectively, for the reverse osmosis water treatment plant. In most of the RO concentrate water streams produced from the RO process of the local wells in Saskatchewan and Manitoba in Canada, only the concentrations of manganese, iron, and dissolved organic compounds are above their allowable thresholds. Thus only manganese, iron, and dissolved organic compounds of RO concentrate are considered as hazards in this work. The concentration of the rest of metals listed in Table 1 fall below the standard critical toxicity level, and therefore they are not considered as toxic at the reported concentrations.

Since this new process concept (application of AOPs for the treatment of RO concentrate water) is in its infancy stage, the studied compounds in this paper were initially limited to the compounds of concern in Saskatchewan (i.e. manganese, iron, and dissolved organics). The data for the oxidation of iron were not reported in the paper because the experimental data show that iron tends to get oxidized promptly. The collected data on the oxidation of iron with ozone show that iron becomes fully oxidized in the first 1 min of the reaction. Therefore, compounds of interest in the paper include manganese and organic pollutants, and their removals by AOPs were the main objective of this study.

Table 1
The results of ICP analysis for the raw, concentrate, and permeate water.

Analyte	Units	Raw water	Concentrate water	Permeate water
Aluminum	mg/L	<0.0005	<0.0005	<0.0005
Antimony	mg/L	<0.0002	<0.0002	<0.0002
Arsenic	μg/L	17	35	12
Barium	mg/L	0.0054	0.021	<0.0005
Beryllium	mg/L	<0.0001	<0.0001	<0.0001
Boron	mg/L	0.88	0.91	0.84
Cadmium	mg/L	0.00001	0.00002	<0.00001
Chromium	mg/L	<0.0005	<0.0005	<0.0005
Cobalt	mg/L	0.0008	0.0028	<0.0001
Copper	mg/L	<0.0002	<0.0002	<0.0002
Iron	mg/L	1.28	4.39	0.0060
Lead	mg/L	<0.0001	<0.0001	<0.0001
Manganese	mg/L	0.55	2.04	0.0022
Molybdenum	mg/L	0.0023	0.0084	<0.0001
Nickel	mg/L	0.0016	0.0056	<0.0001
Selenium	mg/L	<0.0001	0.0003	<0.0001
Silver	mg/L	<0.00005	<0.00005	<0.00005
Strontium	mg/L	1.56	6.1	0.0069
Thallium	mg/L	<0.0002	<0.0002	<0.0002
Tin	mg/L	<0.0001	<0.0001	<0.0001
Titanium	mg/L	<0.0002	0.0003	<0.0002
Uranium	μg/L	5.0	19	<0.1
Vanadium	mg/L	<0.0001	<0.0001	<0.0001
Zinc	mg/L	0.0029	0.016	<0.0005

A Pen-Ray® UV Lamp (UVP, LLC Upland, CA, USA) with wavelength of 254 nm, light intensity of $4400\,\mu W/cm^2$, and lighted length of 2.13 in. (Cole-Parmer in Canada) was used for UV radiation. The UV lamp is a low-pressure mercury UV lamp which