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Principles and performance of a submerged internal-circulation membrane coagulation reactor

Dan Liu[a], Zhongguo Zhang[a,*], Yu Qian[a], Peiran He[a], Yue Wu[a], Liming Rong[a], Shuang Liang[a], Jiding Li[b]

[a]*Environmental Protection Research Institute of Light Industry, Beijing Academy of Science and Technology, Beijing 100089, P.R. China, Tel. +86 10 68456047; Fax: +86 10 68456027; emails: liujiatong615@163.com (D. Liu), cn.zhang@163.com (Z. Zhang), seven52125@163.com (Y. Qian), xiaopei1987@hotmail.com (P. He), wuyue_2000@sina.com (Y. Wu), rlm_2010@163.com (L. Rong), liepi_liang@163.com (S. Liang)*

[b]*The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P.R. China, Tel. +86 10 62782432; Fax: +86 10 62770304; email: lijiding@mail.tsinghua.edu.cn*

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ABSTRACT

Coagulation has been the most successful pretreatment for the mitigation of membrane fouling, the improvement of permeate quality, and the extension of membrane service life. Membrane coagulation reactor (MCR), which is a coupled coagulation and membrane filtration process, is a promising technology for surface water purification. In order to decrease footprint, promote flocculation efficiency, and mitigate efficiently membrane fouling, a submerged internal loop MCR with in-line coagulation, sludge thickening, and air sparging was developed. In the MCR, the internal loop flow induced by air lift through a flocculation region can cause a continuous flocculation of raw water and consequently avoid the accumulation of fine flocs prone to blocking membrane pores and forming a compact cake layer. Furthermore, the flocs with a large size and a fast settling velocity can consecutively settle into the sludge thickening region and then are discharged for controlling sludge concentration. The MCR with hollow fiber microfiltration membranes and with polyaluminium chloride (PACl) as coagulant exhibited excellent performance in removing the turbidity, total organic carbon (TOC), and dissolved organic carbon (DOC) of surface water at bench-scale test. The turbidity and TOC of the permeate met the needs of centralized water supply set by "Standards for Drinking Water Quality" (GB 5749–2006) of China, below 1 NTU and 5 mg/L, respectively. The water flux above 55 L/(m^2 h) was achieved at the transmembrane pressure of 0.025 MPa. Air sparging could effectively control membrane fouling of the MCR and continuous air sparging was more favorable than intermittent air sparging. The observations by scanning electron microscope showed that the cake layer on membrane surface was loose and irregular and easily cleaned by air sparging, but $CaCO_3$ was difficult to be removed compared to other precipitates, such as those of Al, Si, and Fe. The experimental results indicated that the MCR has a promising application in treating surface water for drinking.

Keywords: Membranes; Filtration; Coagulation; Polyaluminium chloride (PACl); Drinking water; Air sparging

*Corresponding author.

1. Introduction

The deterioration of water quality and a growing number of trace-persistent toxic organic pollutants and chlorine-resistant micro-organisms exert great pressure on conventional drinking water purification technology. For example, it is very difficult to remove trace organic pollutants and disinfection by-products (DBPs), and also hard to inactivate some harmful micro-organisms. Membrane separation is considered as the twenty-first-century water treatment technology, and has been widely used in water treatment. Ultrafiltration and microfiltration can effectively remove giardia lamblia, cryptosporidium, and other microbe [1] which are difficult to inactivate, and are the most effective technology for removing natural organic matter [2] and the precursors of DBPs by chlorine. The removal of turbidity and bacteria by ultrafiltration or microfiltration is close to 100% [3–6]. Meanwhile, membrane separation technology has a lot of advantages, such as lower capital costs, more simple operation and management, smaller footprints, better permeate quality, and are easier to realize autocontrol [4]. Therefore, membrane separation technology, especially ultrafiltration and microfiltration, is considered as the best alternative to conventional purifying method for drinking water [7–9].

A variety of pretreatment processes for membrane separation have been investigated including coagulation [10–14]. Coagulation is recognized as one of the most successful pretreatment technologies for the reduction of membrane fouling [15–17]. The coupled coagulation–membrane filtration process, or called membrane coagulation reactor (MCR) [18], can improve the quality of treated water by removing the colloidal and soluble compounds smaller than membrane pores [19,20]. In MCR, coagulation is the pretreatment unit of membrane separation, and the sedimentation process in conventional coagulation-settling technology is substituted by membrane separation process [21]. MCR can significantly reduce membrane fouling [22], improve the removal of pollutants [23], prolong the service life of membrane [24], and fits for small- or medium-scale water plants in rural areas or small towns. Various inorganic coagulants were used in previous studies, including $FeCl_3$ [25,26], $FeSO_4$ [27], $AlCl_3$ [27], $Al_2(SO_4)_3$ [28], and polyaluminum chloride (PACl) [29–31], but PACl showed a better performance in membrane fouling control [32], and ferric salt produced a higher filtration resistance than alum [25].

Most of the current MCRs were just designed by simply incorporating coagulation and membrane separation process [33,34], so that some advanced achievements on coagulation, such as micro-eddy flocculation, cyclone flocculation technology, and nonlinear flocculation dynamics, didn't be employed. Therefore, there exist some problems for those MCRs, such as unsatisfactory flocculation performance, flocs broken phenomenon, too large footprint, and accumulation of fine particles inclined to blocking membrane pores [22]. In this paper, a submerged MCR with continuous flocculation of fine particles, highly efficient in-line coagulation, and control technology of sludge concentration, was developed and used for the treatment of surface water.

2. Principles and process of the submerged MCR

2.1. Principles of the submerged MCR

2.1.1. Continuous flocculation of the fine particles in the submerged MCR

Fine particles with a size close to membrane pores are the dominant factors to induce severe membrane fouling due to blocking membrane pores [35–37], and smaller particles are easier to deposit onto the membrane surface [38]. Hence, it is very important to take approaches to remove fine particles or to make them large in ultrafiltration or microfiltration process.

There exist a lot of fine particles in submerged membrane separation reactor, and in some cases, the concentration of fine particles will increase with time. In the submerged MCR, however, an upward internal-circulation flow of wastewater in membrane separation region induced by air lift can cause the mixing and flocculation between the wastewater in MCR and the feed wastewater into MCR, so that the wastewater in MCR can flocculate continuously, which makes fine particles larger and larger.

2.1.2. Control of the sludge concentration in the submerged MCR

Membrane fouling will aggravate following the increase of sludge concentration in a submerged membrane separation reactor, so efficient sludge removal from the reactor is necessary [39,40]. There is a sludge thickening region at the bottom of the submerged MCR for the removal of sludge in order to control the sludge concentration in the membrane separation region, which is beneficial for the membrane fouling control. It should be noted that the settling time of the sludge in the thickening region is just around 30 min, shorter than that of a conventional settling tank where the settling time ranges between 1 and 2 h. Therefore, only the flocs with a large size and a fast settling velocity could settle into the thickening region and then were discharged. It was reported that the supernate from a conventional jar test induced a more serious membrane fouling than the water-containing flocs (without sedimentation) [41], probably because the residual fine particles in the supernate after a long-time sedimentation were inclined to block the membrane pores and to form a dense cake layer. So, a short-time settling was adopted for avoiding the mean size of the particles too small in the MCR and for reducing the MCR footprint.

2.1.3. Highly efficient in-line coagulation

In-line coagulation without sedimentation can reduce the footprint of the whole coagulation–membrane separation facility [42]. Furthermore, in-line coagulation can induce the formation of a thicker cake layer, and consequently, mitigate the blocking of membrane pores, which will induce irreversible fouling, and the total filtration resistance [23,43]. It was also found that in-line coagulation could reduce significantly the consumption of coagulant [43]. Therefore, the in-line coagulation with a tube mixer [44,45] based on secondary flow was employed in the submerged MCR.

Micro-eddy flocculation was also adopted in the MCR in order to improve flocculation efficiency. Micro-eddy flocculation was developed based on the observations by Casson and Lawler who found that micro-eddies of approximately the same size as the particles were relatively more important than the large eddies for flocculation [46]. Micro-eddy flocculation has been proved to be high efficient in many work [47–49].

In addition, flocculation region was directly connected with membrane separation region in the MCR. It can be alleviated that the large flocs break up during the flow of flocculated water from flocculation region to membrane separation region through a pipe, and that the fine particles form due to the breakage of large flocs.

2.2. Process of the submerged MCR

The principle diagram of the submerged MCR is shown in Fig. 1. The MCR can be divided into three parts, namely flocculation region, membrane separation region, and sludge thickening region. Raw water is introduced from the top of the reactor and then flows into the flocculation region. The micro-eddy induced by the baffles in the flocculation region will lead to an efficient flocculation. Finally, under the action of air lift, the flocculated water will enter the

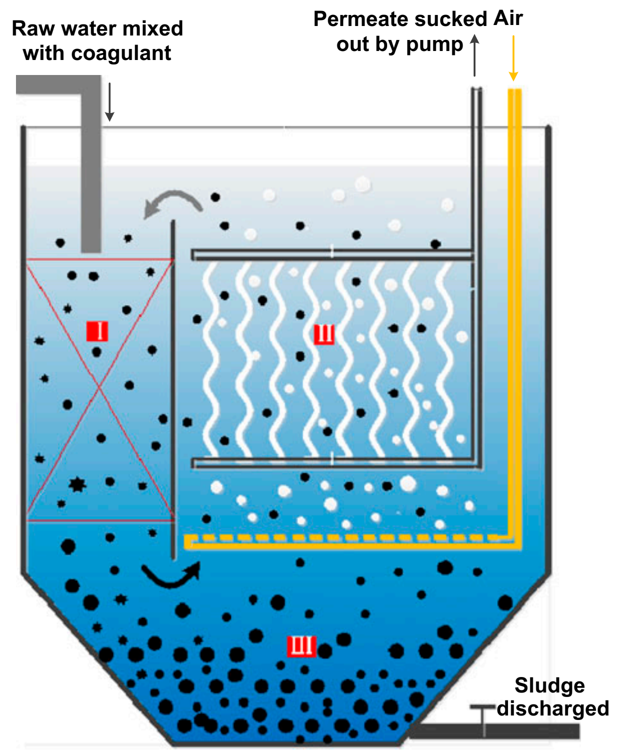

Fig. 1. Principle diagram of the submerged MCR.
Notes: (I) Flocculation region; (II) membrane separation region; (III) sludge thickening region.

membrane separation region from its bottom. Large flocs in the flocculated water will settle into the sludge thickening region, and the suspended fine flocs will flow into the flocculation region from the top of the flocculation region for further flocculation. So, the concentration of flocs, especially fine flocs, in the membrane separation region can remain low, which will alleviate membrane fouling. Air sparging in the reactor not only promotes water circulation, but also controls membrane fouling by affecting the deposition and adsorption of flocs on the membrane surface [50], and even increases retention of micro-pollutants [51].

3. Experiments

3.1. Materials and method

3.1.1. Experimental setup

The process flow of the MCR setup used in this study is shown in Fig. 2, including MCR, influent system, coagulant dosing system, mixing system, permeate system, sludge concentrated system, backwashing system, and air sparging system. An in-line tube mixer for coagulation is employed prior to the MCR.

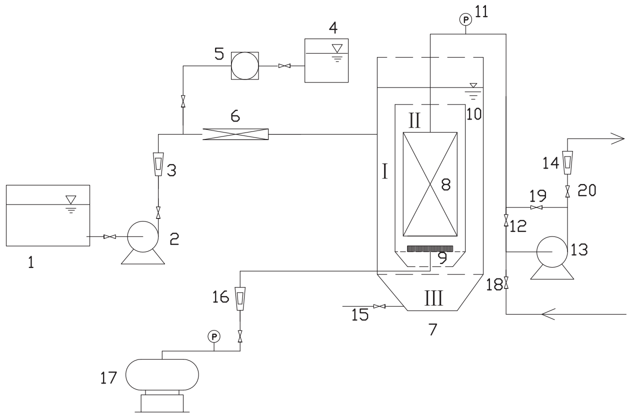

Fig. 2. Process flowchart of the experimental setup.
Notes: (1) Tank; (2) raw water pump; (3 and 14) flow meter; (4) dosing box; (5) coagulant dosing pump; (6) tube mixer; (7) reaction tank; (8) membrane separation unit; (9) air sparging tube; (10) internal circulation cylinder; (11) vacuum meter; (12 and 20) permeate valve; (13) permeate pump; (15) sludge discharge pipe; (16) gas flow meter; (17) air compressor; (18 and 19) backwashing valves. (I) flocculation region; (II) membrane separation region; (III) sludge thickening region.

The submerged MCR was a cylinder (called "outer cylinder") with a cone at the bottom. The effective volume of the outer cylinder with an inner diameter of 50 cm was 70 L. An internal circulating cylinder was located in the upper center of the outer cylinder. Flocculation region and membrane separation region were located in the outside and inside of the internal circulating cylinder, respectively. Raw water was tangentially introduced along the inter wall of the outer cylinder from the top of the reactor and then flowed rotationally downward into the flocculation region (the gap between the internal circulating and outer cylinders).

Four curtain hollow fiber membrane modules were used in the MCR with a total membrane area of 1.26 m^2. Modified polyvinylidene fluoride (PVDF) MF membranes (Tianjin MOTIMO Membrane Technology Co., Ltd, China) with a nominal pore size of 0.1 μm were used in the membrane modules. The PVDF membrane was hydrophilic.

The permeate was sucked out from hollow fiber membranes by a spiral pump running for 7 min and then stopping for 3 min. Throughout the experiments, transmembrane pressure (TMP) was kept constant at 0.025 MPa and the air flux was 1.0 m^3/h at 20℃.

In order to control the concentration of the sludge in the MCR, the MCR was stopped for 30 min, one time each day for the purpose of facilitating the sludge sedimentation, and then the concentrated sludge at the bottom of the MCR was discharged.

3.1.2. Coagulant

The coagulant used in this work was commercially available from PACl in powdered form with a basicity (OH/Al) of 1.44 and an Al_2O_3 content of 30%. The stock solution was obtained by dissolving PACl into deionized water to an Al concentration of 2 mol/L. The fresh PACl solution for the tests had an Al concentration of 0.1 mol/L obtained by diluting the stock solution one day before each batch of tests to avoid ageing and to maximize repeatability [52]. The PACl dosage used in the work was 90 mg/L, with a corresponding zeta potential of around 0 mV. It was reported that an excess coagulant dosage was prone to produce low-porosity cake layer and aggravated membrane fouling [15,53–55].

3.1.3. Raw water

All experiments were performed using the surface water taken from Chang River in Beijing. During the study period, the raw water was taken once a day and stored in the tank as shown in Fig. 2 for the experiments of a whole day. The quality of raw water was measured one time each day because the fluctuation of water quality was negligible. The characteristics of raw water are shown in Table 1.

3.1.4. Analytical method

Turbidity measurements were conducted using a turbidimeter (2100AN, Hach, USA).

A pH meter (310P, Thermo Fisher Scientific, USA) was used for pH measurements.

Zeta potential was analyzed by a zeta potential analyzer (NanoZ, Malvern, UK).

The images of membrane surface were taken by a Scanning Electron Microscope (SEM) (S-4800, Hitachi, Japan). The elements in the cake layer were determined by energy dispersive X-ray spectroscopy system on the SEM.

TOC and DOC were determined using a TOC analyzer (Liqui TOC II, Elementar, Germany), and

Table 1
Characteristic of raw water

Parameters	Unit	Value
pH	–	7.70–8.56
Turbidity	NTU	11.3–81.0
TOC	mg/L	4.26–6.57
DOC	mg/L	3.73–4.56
UV_{254}	1/cm	0.028–0.067

platinum catalysis was used in the combustion process. Oxygen was used as the carrier gas for analysis with a flow rate of 200 mL/min.

3.2. Results and discussion

3.2.1. Effects of air sparging on membrane flux

Air sparging can produce significant shear stress on the membrane surface, and so is an efficient approach to reduce concentration polarization and fouling of membrane surface [56,57]. The effects of air sparging mode, namely continuous air sparging and intermittent air sparging, on membrane fouling was evaluated with relative flux (J/J_0), which is the ratio of the flux (J) at any time during the test to the initial flux (J_0). In intermittent air sparging process, air sparging was run for 7 min just in the period of sucking permeate, and then stopped for 3 min. The test was carried out using relatively stable raw water with the turbidity of 18.2–19.5 NTU and was finished within one working day. The results are shown in Fig. 3. Under the condition of continuous air sparging at the TMP of 0.025 MPa, J/J_0 was dropped by 2.86% per hour on average within the running time of 6.4 h. However, under the condition of intermittent air sparging, the membrane flux dropped by 6.57% per hour on average within 2.3 h. This indicates that continuous air sparging was more efficient to alleviate membrane fouling than intermittent air sparging.

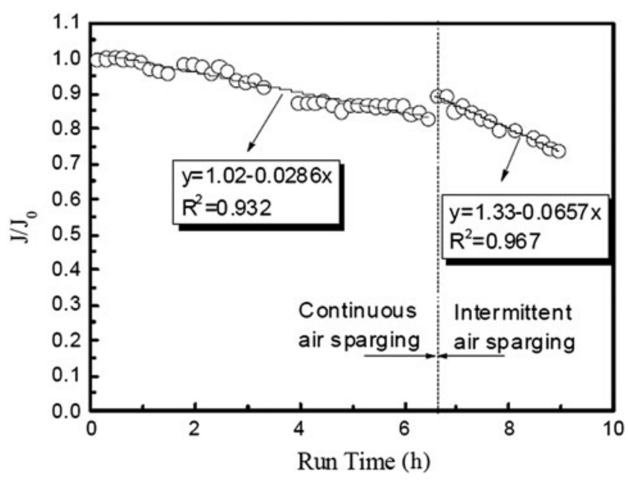

Fig. 3. Effect of air sparging condition on membrane flux. The TMP was 0.025 MPa. The air flow was 1.0 m^3/h at 20˚C. The intermittent air sparging was to aerate for 7 min and then stop for 3 min. The spiral pump sucking permeate out from membranes ran for 7 min and then stopped for 3 min. The PACl dosage was 90 mg/L, with a corresponding zeta potential of around 0 mV.

Under continuous air sparging mode, the rising air bubbles were always scrubbing the membrane surface during filtration process, thus mitigated the formation of concentration polarization and fouling layer on the membrane surface. On the contrary, the concentration polarization and cake layer would be easily formed on the membrane surface during the idle time under intermittent air sparging mode [58]. Based on the result, a continuous air sparging with the air flow of 1.0 m^3/h (20˚C) was adopted in the following experiments.

It was also reported that intermittent air sparging was better for controlling membrane fouling than continual air sparging in submerged membrane system [55,59]. It is probably due to the difference in the duration of peak shear stress which was 3–5 s for the intermittent air sparging in previous study [55,60]. In fact, a lot of factors affect the performance of intermittent air sparging in membrane fouling control, such as air sparging frequency, hollow fiber membrane packing density, bubble size, and membrane module configurations (i.e. loosely vs. tightly held) [56,60].

3.2.2. Membrane flux at a constant TMP

When running at a constant TMP, membrane flux would decrease with time due to membrane fouling even though in the case of dosing coagulants [61–63]. After running for a period of time, an online cleaning, namely increasing the air flux from 1.0 to 1.5 m^3/h and keeping it for 2 min, was employed to recover membrane flux. During the running period of 45 h, membrane flux dropped by 22.2%, but was still above 55 $L/(m^2\ h)$, as shown in Fig. 4. The membrane flux decreased very rapidly in the initial running period, and then slowly and slowly after each online cleaning. In general, the decrease of flux was not obvious in a long running period, just by 0.49% per hour on average within 45 h under the condition of online cleaning. This indicated the significant importance of coagulation and air sparging in membrane fouling control.

3.2.3. Removal of pollutants

3.2.3.1. Removal of turbidity. The turbidity of surface water is positively linearly related to total suspended solids, and even the concentrations of some hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons have correlative relationships with turbidity [64]. So the removal of turbidity is extremely important to obtain safe drinking water.

The removal of turbidity by the MCR is shown in Fig. 5. The turbidity of raw water was 44.3

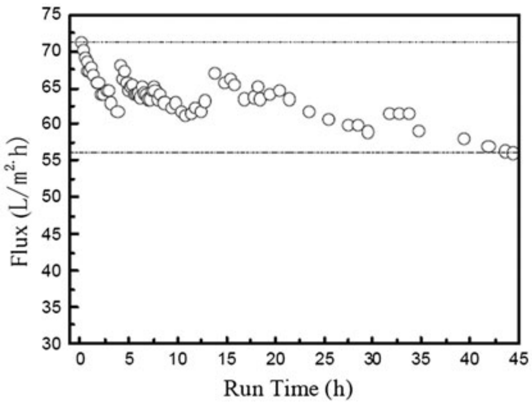

Fig. 4. Membrane flux at a constant TMP of 0.025 MPa with a continual air sparging process. The air flow was 1.0 m^3/h at 20℃. The spiral pump sucking permeate out from membranes ran for 7 min and then stopped for 3 min. The PACl dosage was 90 mg/L, with a corresponding zeta potential of around 0 mV.

± 21.0 NTU. The permeate turbidity was lower than 1.0 NTU, with a corresponding turbidity removal of higher than 96% (98.0 ± 1.0%). The result was similar with other studies [65]. It should be noted that the turbidity fluctuation of raw water had little effect on the permeate turbidity [66].

3.2.3.2. Removal of TOC. The TOC removal by the MCR is shown in Fig. 6. The TOC of permeate remained stable at the concentration of about 3 mg/L, which is lower than the TOC limit (5 mg/L) prescribed by "Standards for Drinking Water Quality" (GB 5749-2006) of China. The minimum removal of TOC was higher than 30%, the maximum removal was close to 55%, and the mean removal was 41.5% with the standard deviation of 7.0%. This indicates that the MCR could efficiently remove organic pollutants. The TOC removal was close to that in the treatment of nature water by a coupled coagulation and microfiltration process with chitosan as a coagulant [67], where a TOC removal of 47% was obtained at the water flux of 45 L/(m^2 h).

Coagulation can play an important role for removing the organic matter in surface water, especially hydrophobic fraction and high molar mass compounds [68]. Increasing coagulant dosage is favorable for the removal of organic compounds to some extent, but will probably aggravate membrane fouling.

3.2.3.3. Removal of DOC. TOC represents the concentration of total carbon-containing organic matters, including dissolved organic matter (DOC) and the organic matter suspended or adsorbed on suspended solids. For further understanding the removal of organic matter, the DOC of raw water and permeate were measured, as shown in Fig. 7. In the experiment, the DOC of permeate declined slightly by time, with a corresponding gradually increased removal from initial 25% to final 50%. The reason may be that the ability of the cake layer in absorbing or retaining low molecular mass organic matters was improved due to the thickening of the cake layer by time. The removal of DOC is 38.4 ± 9.2%, lower than that of TOC (41.5

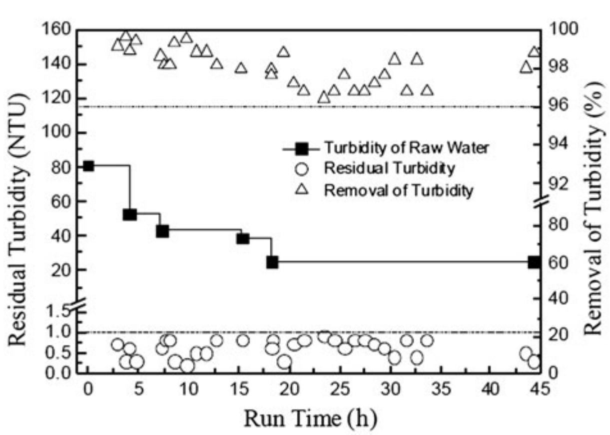

Fig. 5. Removal of turbidity by the MCR with a continuous air sparging process. The TMP was 0.025 MPa. The air flow was 1.0 m^3/h at 20℃. The spiral pump sucking permeate out from membranes ran for 7 min and then stopped for 3 min. The PACl dosage was 90 mg/L, with a corresponding zeta potential of around 0 mV.

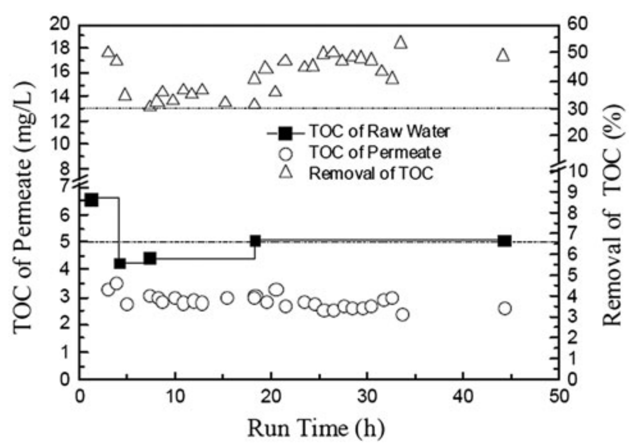

Fig. 6. Removal of TOC by the MCR with a continuous air sparging process. The TMP was 0.025 MPa. The air flow was 1.0 m^3/h at 20℃. The spiral pump sucking permeate out from membranes ran for 7 min and then stopped for 3 min. The PACl dosage was 90 mg/L, with a corresponding zeta potential of around 0 mV.

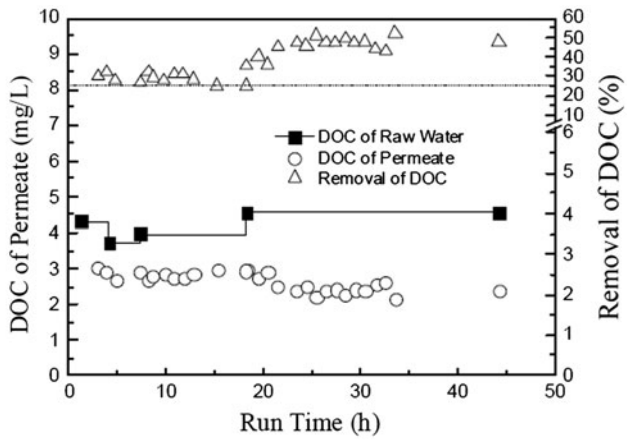

Fig. 7. Removal of DOC by the MCR with a continuous air sparging process. The TMP was 0.025 MPa. The air flow was 1.0 m^3/h at 20˚C. The spiral pump sucking permeate out from membranes ran for 7 min and then stopped for 3 min. The PACl dosage was 90 mg/L, with a corresponding zeta potential of around 0 mV.

± 7.0%) as shown in Fig. 6. This is attributed to the higher removal of the organic matter suspended or adsorbed on suspended solids. Based on Figs. 6 and 7, it can be calculated that the mean removal of the organic matter suspended or adsorbed on suspended solids is 56.6%, significantly higher than those of TOC (41.5%) and DOC (38.4%), but far lower than that of turbidity (98.0%). It seems to indicate that the suspended organic matter and the suspended solids adsorbing organic matter are smaller in size than the other suspended solids, or that the organic matter is inclined to adsorb on smaller suspended solids.

3.2.4. Membrane fouling and cleaning

Membrane fouling is an inevitable phenomenon during membrane separation process. Fig. 8 shows the membrane surface of the MCR after running for 110 h. There existed an obvious cake layer on the membrane surface, but the cake layer did not

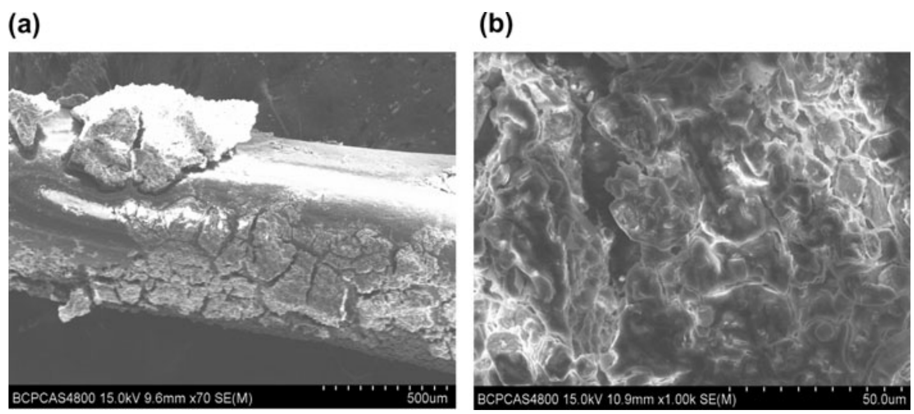

Fig. 8. Fouled membrane surface images obtained by a SEM after 45 h of running for the MCR. The TMP was 0.025 MPa. The air sparging process was continuous at the air flow of 1.0 m^3/h (20˚C). The spiral pump sucking permeate out from membranes ran for 7 min and then stopped for 3 min. The PACl dosage was 90 mg/L, with a corresponding zeta potential of around 0 mV. (a) 70 times magnification of membrane surface and (b) 1000 times magnification of cake layer.

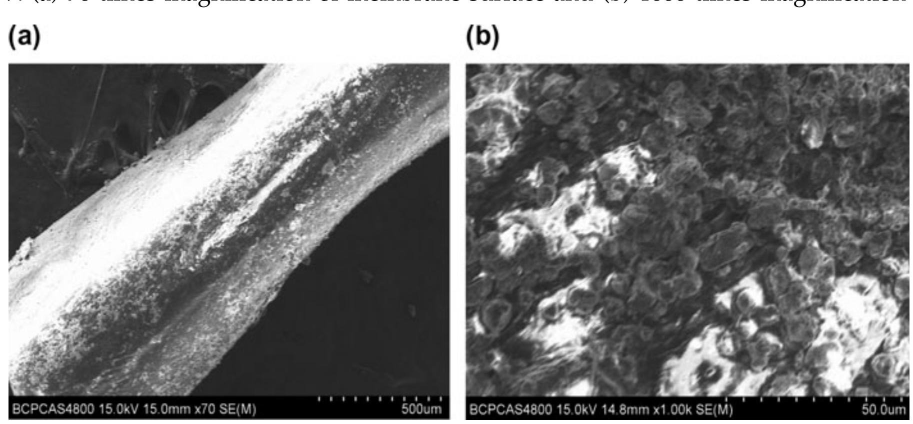

Fig. 9. SEM images of membrane surface after online cleaning by air sparging. TMP = 0.02 MPa. (a) 70 times magnification of membrane surface and (b) 1000 times magnification of cake layer.

Table 2
Characteristic of the cake layer on the membrane surface

Element	Weight percentage (%)	Atom percentage (%)
O	68.99	81.33
Al	12.56	8.78
Si	7.16	4.81
Ca	9.56	4.50
Fe	1.73	0.58
Total	100.00	100.00

completely cover the whole membrane surface as shown in Fig. 8(a). It can be seen that the cake layer was loose and irregular in Fig. 8(b). According to the results of spectrum analysis shown in Table 2, the component elements of cake layer included O, Al, Ca, and a small amount of Si and Fe. Carbon element was not detected because little organic matter was present in the cake layer.

In order to recover membrane flux, the fouled membrane was cleaned by online air sparging. No obvious cake layer was seen on the membrane surface after online cleaning as shown in Fig. 9(a), and the membrane flux could recover more than 90% after each cleaning as shown in Fig. 4. It is because coagulation changes the structure of cake layer and makes it easier to be removed by air sparging [69]. But there existed still a small quantity of residual contaminants, as shown in Fig. 9(b). An energy spectrum analysis showed that the residual contaminants contained the elements of C, O, F, Cl, and Ca (Table 3). Among these elements, C, O, and F are the components of membrane materials, and only Ca is the component of cake layer. It indicates that on the membrane surface most contaminants were removed by air sparging, except $CaCO_3$ scaling. Lee and Kim [70] also found that $CaCO_3$ scaling resulted in significant fouling on membrane surface and that air sparging didn't play a major role in removing it. However, chemical cleaning using citric acid solution could efficiently remove $CaCO_3$ scale from the membrane surface [70]. It indicates that $CaCO_3$ has stronger affinity to the surface of PVDF membrane than other precipitates, such as those of Al, Si, and Fe.

Table 3
Element characteristic of membrane surface after cleaning

Element	Weight percentage (%)	Atom percentage (%)
C	34.79	44.28
O	24.49	23.40
F	39.62	31.88
Cl	0.45	0.19
Ca	0.65	0.25
Total	100.00	100.00

The observations corresponded to the previous research results that flocculated particles formed a porous, low-density cake layer on the surface that can be easily removed by scouring or backwashing [71–73].

4. Conclusions

Aimed at promoting flocculation efficiency, mitigating efficiently membrane fouling, and decreasing footprint, a submerged internal loop MCR with in-line coagulation, sludge thickening, and air sparging was developed.

Compared to intermittent air sparging, continuous air sparging could more significantly mitigate the membrane fouling of the MCR, and slow down the decline in water flux.

The turbidity and TOC of the permeate from the MCR with modified PVDF hollow fiber MF membrane and PACl met the needs of centralized water supply set by "Standards for Drinking Water Quality" (GB 5749-2006) of China. The removal of turbidity was above 96%, and the maximum removal of TOC and DOC was close to 55 and 50%, respectively. The permeate quality was not affected by the concentration fluctuation of pollutants to a certain extent.

The cake layer on the membrane surface was loose and irregular, mainly consisted of inorganic matters, and was easily removed by air sparging. However, $CaCO_3$ was difficult to be removed compared to other precipitates, such as those of Al, Si, and Fe.

The experimental results indicated that the submerged MCR has a promising application in producing drinking water of excellent quality from surface water with a slight membrane fouling.

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