Performance of the submerged membrane electro-bioreactor (SMEBR) with iron electrodes for wastewater treatment and fouling reduction

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A B S T R A C T

This paper presents the results of the performance of a novel technology called submerged membrane electro-bioreactor (SMEBR). The SMEBR treats wastewater by combining membrane filtration, electrokinetic phenomena, and biological processes in one reactor, and improves treatment performance while helping to control membrane fouling. The newly designed SMEBR system was based on applying an intermittent direct current (DC) field between immersed circular perforated electrodes around a membrane filtration module. The SMEBR system significantly reduced the fouling rate when iron worked as electrodes and an intermittent DC with an operational mode of 15 min ON–45 min OFF was applied. In terms of effluent quality, the SMEBR system enhanced the removal of COD and PO<P sub>4 sub>P up to 96% and 98%, respectively.

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1. Introduction

Conventional wastewater treatment technologies are no longer responding to new standards, and there is an increasing desire for the development of innovative, more effective and inexpensive techniques for wastewater treatment [1]. Recently, a new technology was developed at Concordia University, Montreal, Canada, called submerged membrane electro-bioreactor or SMEBR [2–4]. The principal objectives of designing the SMEBR were to generate a high-quality effluent, while minimizing membrane fouling, which has been considered a major challenge to the widespread application of membrane bioreactor (MBR) technology [5,6].

The design of SMEBR technology was based on applying an intermittent direct current (DC) field between immersed circular perforated electrodes around an immersed membrane filtration module (Fig. 1). The treatment of wastewater with the SMEBR system involves the simultaneous application of biodegradation, electro-coagulation and filtration through a membrane module. The design of the SMEBR system consists of two zones being in contact (Fig. 1): Zone I (electro-bioreactor) extends from the internal wall of the bioreactor to the cathode, and Zone II is located between the cathode and the membrane module. Generally, Zone I is dominated by the processes of biodegradation and electro-coagulation, while Zone II is responsible for further biodegradation and membrane filtration.

The treatment performance with SMEBR is affected by electrode design and material, and the applied direct current field between the electrodes [3]. Designing the electrodes in SMEBR should allow effective distribution of aeration and should not hinder mixed liquor circulation [3].

The SMEBR design is the first attempt to combine electrophoretic principles, using electro-coagulation (EC) processes and submerged membrane bioreactor (SMBR) in one reactor vessel [3]. Contrary to other designs [7–9], the electrocoagulation unit combining with MBR permits a direct interaction with biological processes and membrane filtration. Bani-Melhem and Elektorowicz [3] reported a number of advantages of the designed SMEBR system.

In the previous paper [3], a detailed description of the design constraints and criteria of the new developed method was reported. The main objective of this study is to show the results of performance of the SMEBR system for fouling reduction and wastewater treatment in terms of COD, NH<sub>3</sub>-N and PO<sub>4</sub>-P removal when iron mesh was applied as electrodes.

2. Materials and methods

2.1. Experimental methods

A laboratory scale setup was used in this study (Fig. 2). The setup consisted of an electro-bioreactor with a working volume of 13.4 L, a membrane module ZeeWeed-1 (GE Power & Water/Zenon Mem-
brane Solutions, Canada), a wastewater supply system, an aeration system, and a DC supply system. The membrane module consisted of 80 fibers of 0.2 m in length and a pore size of 0.04 μm, with a total surface area of 0.047 m². The membrane module was fixed vertically in the centre of the electro-bioreactor. The effluent from the membrane module was withdrawn via a peristaltic pump (Model: 13-876-2, Fisher Scientific, Canada) operated at a constant suction pressure. A level sensor was connected to the feeding pump via a level controller system to maintain constant volume in the bioreactor. A cylindrical iron mesh anode (effective surface area = 93 cm²) and a cathode (effective surface area = 106 cm²) were fixed in the centre at a distance of 5.5 cm. The electrodes were connected to a digital external DC power supply maintained at a constant voltage gradient of 1 V/cm. The power supply was connected to a timer to regulate the intermittent DC at an operational mode of 15 min ON–45 min OFF. The aeration was continuous in both zones for maintaining the required dissolved oxygen in the bioreactor (>5 mg/L). In Zone II, an air diffuser was located at the bottom of the membrane module to create a shear stress for effective scouring of the membrane surface, and in Zone I, an aeration tube was used to provide good mixing of the sludge suspension in the bioreactor.

![Fig. 1. Basic idea of the SMEBR system: top view.](image)

### Table 1

| Characteristics of the prepared synthetic wastewater. | 
| --- | --- |
| Water quality index | Average value ± (standard deviation) |
| pH | 6.35 ± (0.36) |
| Temperature (℃) | 20.4 ± (0.5) |
| COD (mg/L) | 334 ± (23) |
| Ammonia-nitrogen (NH3-N) (mg/L) | 30.8 ± (2.1) |
| Nitrate (NO3-N) (mg/L) | Not detected |
| Phosphorus (PO4-P) (mg/L) | 27.2 ± (1.9) |

### 2.2. Wastewater characteristics

To obtain a consistency in the chemical and physical properties of the influent (wastewater composition) during the experimental period, the reactor was fed continuously with a synthetic wastewater mixture. The composition of synthetic wastewater contained (in mg/L): glucose (310), peptone (252), yeast extract (300), (NH4)2SO4 (200), KH2PO4 (37), MgSO4·7H2O (40), MnSO4·H2O (4.5), FeCl3·6H2O (0.4), CaCl2·2H2O (4), KCl (25), and NaHCO3 (25). Table 1 shows the characteristics of the prepared synthetic wastewater. The sludge for inoculation was taken from the secondary clarifier in the municipal wastewater treatment plant in the City of Saint-Hyacinthe (Quebec, Canada). The sludge was acclimatized for 60 days prior to membrane filtration experiments. The fill-and-draw technique was used to cultivate the activated sludge [10].

### 2.3. Analytical methods

Influent, effluents and supernatants in both Zones were sampled daily and analyzed by Hach methods (Hach, DR 2800, USA) for COD, ammonia nitrogen (NH3-N), nitrate nitrogen (NO3-N), and orthophosphate (PO4-P). Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were performed according to Standard Methods [11]. The dissolved oxygen (DO) concentration was measured using a DO meter (YSI, Model 52, US). The values of pH and temperature were measured using a pH meter model 215 (Denver Instrument, US).

Other parameters (zeta potential and specific resistance to filtration (SRF), which give an indirect indication about the fouling behavior, were also measured. A 50-mL sample of mixed liquor was taken every two days from each zone. Furthermore, the sampled supernatant was taken for zeta potential measurement (Zeta-Meter 3.0”, US) after settling for 30 min. Each sample was measured ten times and the average value was taken as zeta potential with a standard deviation 2–6%. The sample was returned to the electro-bioreactor after taking the measurement. Additionally, about 100 mL were sampled from each zone of the electro-bioreactor every 10 days or at the end of each stage for the SRF tests. The SRF tests were performed as described by Ng and Hermanowicz [12].

### 2.4. Experimental procedure

The strategy of this study was based on operating the SMEBR at a constant transmembrane pressure that was created by withdrawing the effluents via a peristaltic pump operated at a constant suction pressure.

The SMEBR system was working continuously at room temperature without control for a period of 53 consecutive days. For comparison purposes, the SMEBR system was operated in two stages: (i) in Stage I, the bioreactor ran for a period of 26 days without electrokinetcs (electrodes were disconnected); (ii) in Stage II, which lasted for 27 days, the SMEBR was connected to the power supply with an operational mode of 15 min ON–45 min OFF at voltage gradient of 1 V/cm. The fouling behavior was evaluated phenomenologically by measuring the decline of permeate flux.
with time. No backwashing of the membrane module was performed during the operation period; however, in order to enhance the recovery of the membrane permeability during the operating period of each stage, the membrane module was taken out of the electro-bioreactor and externally washed with tap water for a few minutes to remove the attached sludge cake particles over the membrane surface. Before starting Stage II, in order to restore most of the membrane’s permeability, the membrane modules were removed from the bioreactors, and physical and chemical cleaning was applied according to the protocol described by Meng et al. [13]. Moreover, the SMEBR was operated at complete sludge retention time (SRT) to decrease the amount of sludge wasting from the process. Therefore, during the whole experimental period, no sludge was withdrawn from the electro-bioreactor except for the required measurements (supernatants in the electro-bioreactor’s zones, suspended solids, specific resistance to filtration, and zeta potential tests). As a general rule, biomass samples for the zeta potential tests were always returned to the electro-bioreactor.

3. Results and discussion

3.1. Membrane filterability

Since the SMEBR was operated at constant suction pressure, it was stipulated that a decrease of the permeation flux with time would be mostly due to the fouling phenomenon; then, the fouling rate was evaluated by measuring the decline of permeate flux with time. Fig. 3 shows the change in flux ratio ($J/J_0$) during the two stages of the operation period, where $J_0$ is the initial permeate flux (9.792 L/h m²) measured during the first minute, and $J$ is the permeate flux at any time.

It could be assumed that in Stage I, without electrical field, the reactor operated like a conventional submerged membrane bioreactor (SMBR). During the first five days of Stage I, the flux ratio ($J/J_0$) reduced to 0.188, which corresponds to an 81.2% decrease in membrane flux. On day 5, the membrane module was taken out of the electro-bioreactor and externally washed with tap water for a few minutes to remove the attached sludge cake particles over the membrane surface. This event led to enhancing the recovery of the membrane permeability as shown in Fig. 3. The event of membrane washing was repeated on day 13.

In Stage II, when the SMEBR was exposed to intermittently DC field, a significant improvement in regards to membrane permeability was observed in comparison with the performance in Stage I. For example, after five days of continuous operation in Stage II, the flux ratio decreased to 0.32 only, representing a 16.3% improvement in membrane permeability compared with a submerged membrane bioreactor (Stage I).

Fig. 3 demonstrates that the membrane flux can be recovered better after each physical cleaning in Stage II (membrane electro-bioreactor) than in Stage I (membrane bioreactor). Moreover, the membrane permeability can be recovered better in the second washing in Stage II than the first washing. This is attributed to the applied direct current electrical field, which produced less compounds contributing to irreversible membrane fouling.

3.2. Changes in the properties of the mixed liquor

The improvement in the permeation flux in Stage II was associated with significant changes in properties of the mixed liquor in the electro-bioreactor. In this study, the changes in two parameters (zeta potential of floc particles and the specific resistance to filtration – SRF) of the mixed liquor solution, which provide a quantifiable basis for estimating membrane fouling, are shown in Fig. 4. Fig. 4a demonstrates that the zeta potential of the supernatant flocs in both the bioreactor’s zones during Stage I was within the range from −26.5 mV at the beginning of experimental operation to −31.0 mV at the end of Stage I, with an average value of −30.5 mV. A significant variation in zeta potential was observed during Stage II after a DC field was applied on the mixed liquor solution. The zeta potential decreased up to −15.3 mV (Zone I) in Stage II. The magnitude of the zeta potential gives an indication of the stability of the floc particles in the mixed liquor solution. Meng et al. [13] reported a strong correlation between the zeta potential and resistance to membrane fouling, and indicated that the zeta potential is a significant membrane-fouling factor. It was reported that large negative and positive zeta potentials indicate stable suspensions, which prevent the floc’s formation. A dividing line between stable and unstable aqueous suspension can be drawn at zeta potential either +30 or −30 mV [14]. Therefore, the dramatic changes in the zeta potential values in Stage II led to an improvement in permeation flux within the SMEBR system.

On the other hand, the change in the SRF of the activated sludge is considered as another factor representing the filterability of the activated sludge when it is dewatered through a filter medium [12]. It characterizes the fouling as it is related to flocs morphology [15]. It was reported that the SRF increased as well as membrane biofouling due to the presence of colloidal particles [16]. In this study, all measuring filtration resistances were compared with the SRF of the original activated sludge solution ($r_o$) when no DC was applied to the activated sludge that represents the SRF of the mixed liquor solution at the beginning of the operation period. A change of normalized filterability ($r/r_o$) of the activated sludge samples during the operation of SMEBR is shown in Fig. 4b, where $r$ is the SRF of the mixed liquor solution in both zones measured every 10 days or at the end of each stage during the operation period.

The normalized filterability ($r/r_o$) during Stage I did not show a significant change, while a significant decrease ($1 − r/r_o$) in the specific resistance to filtration up to 40% was observed at the end of Stage II (Fig. 4b). According to the Carman–Kozeny equation [3], the specific resistance to filtration of particles is in inverse proportion to the square of particle diameter. It seems that the relatively small particles that are the cause of membrane fouling had undergone flocculation due to the electrocoagulation process; therefore, their effect on membrane fouling was minimized.

Since the SMEBR system was operated under complete SRT in two sequential stages, it is worth mentioning that the MLSS concentration during Stage I was within the range of 2100–3500 mg/L, whereas the fouling rate was higher than the fouling rate in Stage II when the MLSS concentration increased from 3500 mg/L to 5000 mg/L. This result confirms that the MLSS concentration had less effect on the membrane fouling within the above range of concentration (2100–5000 mg/L). The role of the MLSS concentration on membrane fouling was discussed in details in the previous paper.
[3]. Moreover, the ratio of MLVSS/MLSS of sludge in the electro-bioreactor was fluctuated in the range 71% to 83% during Stage I, while this ratio tended to decrease significantly to be less than 70% during the last days of operation of Stage II. This implied that there was an accumulation of inorganic matter in the electro-bioreactor.

3.3. COD removal performance

The results show that the SMEBR system could provide a consistently high COD removal efficiency (Fig. 5). Considering Stage I as a reference stage, the removal efficiency of the COD in the electro-bioreactor in both zones increased from 75–90% (Stage I) to 85–95% (Stage II), which can be attributed to the effect of the electrocoagulation phenomenon that occurred during Stage II. Therefore, a high overall COD removal in Stage I can be attributed to the biodegradation and membrane filtration process, which contributes to faster fouling. It was reported that in the electrocoagulation process, the COD removal might involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment [17]. This might explain the improvement in COD removal in the SMEBR system after applying DC in Stage II. This result seems to be significant since it was reported by Yamato et al. [18] that some fractions of organic matter in the mixed liquor have higher affinities with the membrane than other fractions, and consequently cause greater irreversible fouling. It should be emphasized that membrane fouling is caused not only by the microbial flocs, but also by the supernatant containing colloids and solutes [19–21]. The concentration of the colloidal and soluble polysaccharides of the liquid phase was identified as the predominant parameter causing membrane fouling [22]. Other researchers reported that for a microporous pore size membrane, the main components of the activated sludge system that contributed to membrane fouling are small-size soluble and colloid components [23]. Therefore, applying a DC field to the mixed liquor can reduce the contribution load of the dissolved organic matter on membrane fouling. This result may reflect the good performance of the SMEBR system in terms of flux improvement in Stage II where the fouling rate decreased significantly.

3.4. Nitrification process performance

Nitrifying bacteria convert ammonia nitrogen (NH₃-N) to nitrate nitrogen (NO₃-N) in a nitrification reaction. Consequently, the change in ammonia concentration is often used as an indirect measurement in the changes in the nitrification process [24]. In this study, the variations in removal efficiencies of ammonia nitrogen (NH₃-N) concentration in the influent, and the supernatant of the electro-bioreactor’s zones and in the effluent are presented in Fig. 6. The removal efficiency of NH₃-N began with 37% and stabilized at around 97% at the end of Stage I. The lower performance of the nitrification process during the first days of Stage I was attributed to the lower growth rate of nitrifying bacteria since they need more time to establish and reach sufficient concentrations to nitrify the ammonium [25].

During the first days of operation of Stage II, the removal efficiency of NH₃-N decreased significantly. This reflected the lower oxidation rate of ammonia nitrogen in the electro-bioreactor, which may be caused by the rapid increase in the ammonia nitrogen volumetric flow rate after applying physical and chemical cleaning of the membrane before starting Stage II. However, the ammonia removal efficiency increased again after day 31 until day 36. Then, the removal efficiency started to fluctuate between 69% and 82% with an average value around 70% until the end of Stage II.

![Fig. 4. Changes of properties of the mixed liquor during the operation of the SMEBR system: (a) zeta potential and (b) normalized filterability.](image1)

![Fig. 5. Improvement of COD performance due to electro-coagulation process in SMEBR system (Stage II).](image2)

![Fig. 6. Changes in NH₃-N removal in the SMEBR system (Stage II) and in a conventional SMBR (Stage I).](image3)
Although the SMEBR system was able to achieve 82% removal efficiency of ammonia in Stage II, Fig. 6 demonstrates that the performance of nitrification process during Stage II was less efficient than Stage I. This may be caused by two factors: (i) greater sensitivity of nitrifying bacteria to the applied DC field [26]; and/or (ii) accumulation of iron in the electro-bioreactor, raising some inhibitory effects on the activity of nitrifying bacteria [27,28].

The effect of applying a DC on the metabolism of bacteria was an area of research for some investigators [26,29–31]. For example, Li et al. [26] investigated the inhibition of the metabolism of nitrifying bacteria by applying direct electric current using stainless steel electrodes material. At different operating conditions, they found that the metabolism of nitrifying bacteria was inhibited when the applied current was above 2.5 A/m². Even though greater current densities (37.6–57.7 A/m²) were observed in this study (Fig. 7), the inhibitory conditions were attenuated by intermittently exposure of bacteria to DC field. Subsequently, only some fluctuation ammonia nitrification was observed.

On the other hand, if too much iron is added, the iron precipitates might form a barrier that would tend to block the transfer of nutrients and enzymes through the cell membrane [32]. Another study [33] reported that some metal ion complexes with anionic functional groups of extracellular polymers suppressed the respiration and metabolism of bacteria. Furthermore, the adsorption of metal ions onto extracellular ligands is maximized when the pH of mixed liquor is between 6.0 and 8.0; this corresponds to the pH range inside the electro-bioreactor of the SMEBR system during Stage II (data not shown). The above discussion might explain the decrease in ammonia removal performance after applying the DC field into the mixed liquor solution.

To further confirm the impact of the SMEBR operation on the nitrification process, another indicator, the nitrate nitrogen (NO₃-N) concentration in the effluent, is presented with the concentration of NH₃-N in Fig. 8. The nitrification rate in the reference stage (Stage I) was observed during the starting stages. Although the nitrification rate was low during the first five days, the oxidation of ammonia to nitrate increased up to more than 97% at the end of the Stage I (Fig. 6). When DC was applied in the SMEBR system, the nitrification rate in the Stage II fluctuated around 70%.

3.5. Phosphorous removal performance

Although the SMEBR system was operated with minimum sludge removal, the results demonstrate that the overall PO₄-P removal efficiency in Stage I varied between 75% to almost 96% before applying DC (Fig. 9), which is higher than the normal phosphorus removal in SMBR application at long sludge retention time.

It was reported that when membrane bioreactor (MBR) systems operate with minimum sludge removal, enhanced biological phosphorus removal are limited in MBR applications [34,35]. The increase in phosphorus removal at the end of Stage I might be attributed to a rapid increase in the HRT and the decrease in F/M ratio. However, the overall PO₄-P removal efficiency increased significantly after applying the DC field in Stage II. The SMEBR system had excellent and stable PO₄-P overall removal performance (over 98% on average), and a significant and stable improvement in PO₄-P removal in Zones I and II. It should be emphasized that the phosphorous removal efficiency in the SMEBR system was higher than other studies on MBR without electrokinetics.

This improvement was attributed to the electro-coagulation phenomenon that occurred in Zone I. This improvement likely resulted from the chemical reactions that occurred in the SMEBR system between iron ions and soluble phosphorus. When the iron ions began to appear on the anode side of SMEBR, it reacted with hydroxide ion (OH⁻) produced on cathode, and then iron hydroxide was produced according to the following reactions [36]:

At the anode:

\[
4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^- \tag{1}
\]

At the cathode:

\[
2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \tag{2}
\]

And with dissolved oxygen in solution:

\[
4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^+(aq) \tag{3}
\]

Overall reaction:

\[
4Fe(s) + 10H_2O(l) + O_2(g) \rightarrow Fe(OH)_3(s) + 4H_2(g) \tag{4}
\]
The produced iron hydroxide is beneficial for the rapid adsorption of soluble phosphorus in the bioreactor. On the other hand, any excess iron ion (Fe³⁺) has the opportunity to react with phosphorous ions to form FePO₄(s) that precipitates out in the reactor according to the following reaction:

\[
\text{Fe}^{3+} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4(s)
\]

The above mechanisms explain the significant improvement in phosphorus reduction in the SMEBR system.

4. Conclusions

The results of 53 days of investigating the performance of the SMEBR system demonstrated that the novel design of SMEBR was found to be an efficient method not only for reducing the membrane fouling, but also for increasing the quality of the treated wastewater. In comparison with traditional MBR, the novel SMEBR system can offer several advantages: (i) in contrast to other studies where chemical coagulation was used with MBR to improve the filtration process, in this study, since electrocoagulation was integrated with the membrane filtration system in one hybrid unit, no liquid chemicals were added or coagulation agents were required, leading to a decrease in the operating cost and reducing the amount of sludge produced; (ii) the SMEBR system achieved a 16.3% (on average) reduction in membrane fouling without any backwashing of the membrane module compared with traditional SMBR; (iii) SMEBR treatment managed to remove more than 98% of dissolved orthophosphates, which was substantially higher than other studies on MBR applications; and (iv) the SMEBR also increased removal of COD to 96%.

Conversely, ammonia nitrogen (NH₃-N) reduction through biological nitrification was reduced in the SMEBR operation; this may be an indication that the microbial community in the SMEBR system is sensitive to the magnitude of the applied DC and/or to the operational mode of applying the DC field. Accordingly, the electrolysis conditions in the SMEBR should be optimized so as not to impede biological treatment.

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