論文の内容の要旨

論文題目

Mitigation of membrane fouling by applying the electrochemical oxidation process in a membrane bioreactor

（メンブレンバイオリアクターにおける電気化学的酸化法による膜ファウリング抑制に関する研究）

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（本文）

Membrane bioreactors (MBRs) offer many advantages for the treatment of municipal and industrial wastewater compared to conventional wastewater treatment processes. It is expected that the demand for MBRs will further increase, with more than double-digit growth annually over the next decade (Santos et al., 2011). However, one of the main drawbacks of the widespread use of MBRs is membrane fouling, which can result in severe flux decline or a rapid trans-membrane pressure (TMP) increase that subsequently increases the net operation cost due to frequent membrane replacements and/or cleaning (Le-Clech et al., 2006). The problems associated with membrane fouling must be addressed before large-scale practical application of MBRs can occur. Thus, methods to prevent or reduce membrane fouling have been the subject of intense research.

In this study, we proposed an electrochemical oxidation (EO) process used to generate highly reactive oxidants as a new cleaning method for the mitigation of membrane fouling in a MBR. The motivation of this study is an initial attempt to evaluate the potential use of integrating the EO process with the membrane filtration process in one reactor, with a focus on membrane fouling reduction. The EO process is a promising and attractive technique for the effective oxidation of wastewater containing organic compounds. During electrolysis, organic compounds are destroyed by either direct or indirect oxidation processes via the main oxidizing agents, such as reactive oxygen species (i.e., $^{\bullet}OH$, H_2O_2 and O_3) and free chlorine species (mainly ClO^- or HClO) produced from chloride ions (Comninellis, 1994; Chen, 2004). In particular, the indirect oxidation of organic compounds mediated by free chlorine species that are electrochemically generated on dimensional stable (DSA) anodes (e.g., RuO_2, IrO_2 and Pt) has proven effective for the degradation of organic compounds (Chen, 2004; Costa et al., 2008; Khelifa et al., 2009). The extensive use of free chlorine species in the EO process is due to the ubiquitous presence of chloride in wastewater and to its effectiveness and long lifetime.

The aforementioned characteristics of the EO process enabled us to hypothesize that organic

membrane foulants accumulating on the membrane surface or clogging the inside of the membrane pores during filtration could be reduced through the electro-generated oxidants in the region close to the anode surface and/or bulk solution. The principle objective of this study was to evaluate the potential use of integrating the EO process with a micro-filtration process, with a focus on the role of the EO process in mitigating membrane fouling in the MBR. To achieve above objective, the newly designed MBRs, called the EO-MBR and modified EO-MBR, were developed by applying a direct current between perforated Ti/IrO_2 anodes and Ti/Pt cathodes around a membrane module and its performance was investigated. The main empirical findings derived from this study can be summarized as follows.

First, batch cell electrolysis experiments revealed, as evidenced by linear sweep voltammetry measurements and the quantities of reactive oxygen species and free chlorine species generated, that organic membrane foulants on the Ti/IrO_2 anode can be degraded by direct and indirect oxidation by free chlorine species, while other electro-generated oxidants (e.g., $^{\bullet}OH$, H_2O_2 and O_3) play a less important role. Furthermore, the Ti/IrO_2 anode is energetically more efficient than other anodes (e.g., Ti/RuO_2, Ti/IrO_2+RuO_2, Ti/Pt and boron-doped diamond (BDD)), which are widely applied in the EO process, in presence of chloride ion because it leads to COD removal of organic membrane foulants with lowest energy consumption due to the higher electrocatalytic activity for free chlorine species evolution, although good results in terms of COD removal are obtained with the BDD anode.

Second, batch cell electrolysis experiments with the Ti/IrO_2 anode carried out using chloride as supporting electrolyte resulted in more efficient degradations by reaction with the electro-generated free chlorine species, while phosphate, sulphate and carbonate did not influence on the performance of the EO process. Furthermore, the current density plays a key role on degradation kinetics and lower current density was considered as the suitable operating condition in terms of the lower energy consumption. Additionally, the Ti/IrO_2 anode proved to be the efficient anode material as an advanced treatment of various organic membrane foulants (i.e., humic acid, bovine serum albumin, starch and alginic acid) and ammonia, which might be additional advantage of the EO process integrated with activated sludge process.

Third, scale deposition on the cathode surface caused gradually an increase of voltage and average bubble size, whereas scale deposition did not influence on the performance of the EO process in terms of the quantity of free chlorine species production and bubble generation efficiency. The SEM-EDS analysis characterized scale deposition as a cluster of $CaCO_3$, $Mg(OH)_2$ and phosphorus compounds. However, current switching after scale growth proved to be an efficient control strategy of scale deposition.

Forth, batch cell electrolysis experiments revealed that organic compounds in the mixed liquor, such as protein, humic acid and fulvic acid, were effectively reduced by the EO process. Moreover, the zeta-potential of the mixed liquor was decreased, increasing the size distribution of the sludge floc. These are some of the factors that may be responsible for the EO process via direct or indirect oxidation mediated by free chlorine species. In the microbial activity experiments, a current density of 0.4 mA/cm^2 was determined to be adequate for the EO process; this current does not inhibit the activities of the heterotrophic and autotrophic biomasses. Further increases in the current density, however, resulted in a significant decrease in biomass activity.

Fifth, the continuous experiments confirmed that compared to the increase in the TMP observed in the control MBR, incorporating the EO process into the EO-MBR system effectively suppressed the increase in the TMP with a current density of 0.4 mA/cm^2. The cleaning cycle of the EO-MBR was almost twice as long as that of the control MBR. According to the hydraulic and chemical analyses of the cake sludge layer, the reduction of fouling observed in the EO-MBR is largely due to the electro-generated free chlorine species on the Ti/IrO_2 anode, which reduced the physically irremovable membrane fouling and was effective at degrading organic membrane foulants, such as SMP, proteins, and humic acid, in the cake sludge layer that accumulate on the membrane. In terms of effluent quality, the DOC concentration of effluent from the EO-MBR did not show a significant difference compared with the control MBR, implying that most of the microorganisms do not lose their activity with the EO process. However, the variation in the microbial community observed in the EO-MBR was significantly influenced by the EO process compared to control MBR. The energy consumption for the EO process was 0.029 – 0.034 kWh/m^3 (permeate), which was much lower than the overall operation costs of the conventional MBRs (0.7 – 1.2 kWh/m^3 kWh/m^3 (permeate)), supporting the economic feasibility of using the EO process as a new control method for fouling reduction in MBRs.

Sixth, the modified EO-MBR system, which was comprised of placing the membrane module combined with perforated anodes inside non-woven fabric filter (as a pre-filter), was found to effectively reduce the increased TMP at intermittent current density of 5 mA/cm^2 ("30 s on, 2 min 30 s off" mode) and simultaneously the wastewater treatment efficiency of the MBR in terms of ammonia removal was improved. Moreover, the energy consumption of the modified EO-MBR was approximately 0.028 kWh/m^3 (permeate), which was identical to that of the EO-MBR in which the applied current density was 0.4 mA/cm^2.

Keywords: membrane bioreactor; membrane fouling; electrochemical oxidation process; free chlorine species.