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PILOT SUBMERGED MEMBRANE ELECTRO-BIOREACTOR (SMEBR) FOR COD, NUTRIENTS AND HEAVY METALS REMOVAL

PILOTOWE ZASTOSOWANIE ZANURZENIOWEGO MEMBRANOWEGO ELEKTRO-BIOREAKTORA (SMEBR) DO USUWANIA ZWIĄZKÓW OZNACZANYCH JAKO CHZT, BIOGENÓW ORAZ METALI CIĘŻKICH

Submerged Membrane Electro-Bioreactor (SMEBR) is a recently developed technology for wastewater treatment. This paper evaluated the performance of SMEBR pilot system, installed and operated in the City of l'Assomption (Quebec, Canada), with respect to effluent quality. At steady state operation, the removal efficiencies of COD, ammonia (as NH_3^+-N) and phosphorous (as PO_4^{3-}-P) in SMEBR were 92%, 99% and 99%, respectively. Furthermore, high removal rates of Pb (100%), Ni (98.1%), Cu (100%), and Cd (94.6%) were reported.

1. Introduction

Various water resources are commonly used as receptors of effluents from wastewater treatment plants (WWTP); therefore, the quality of such resources depends on the quality of effluents. Then, many technologies have been applied in order to protect water resources from the discharge of undesirable components contained in effluents. Usually, WWTPs consist of many operation units, while each unit is dedicated to the removal of a distinct wastewater component. Subsequently, existing wastewater treatment facilities occupy a huge land and use significant amount of energy. Thus, a new approach which would eliminate many of the operational units (e.g. primary and secondary clarifiers, phosphorous removal) and treat wastewater with high quality effluent is vital.

A newly developed technology called Submerged Membrane Electro-Bioreactor (SMEBR) appeared to fulfill these requirements [1, 2]. SMEBR combines three operational processes; biological treatment, membrane filtration, and electrokinetics in one hybrid reactor. Several laboratory experiments were carried out and the results obtained have proven the feasibility of SMEBR system as an efficient treatment technology [3-7].

The objective of this paper was to demonstrate the results of testing a continuous flow SMEBR in pilot scale, treating raw wastewater and discharge high quality of effluent to l'Assomption River.

2. Methodology

2.1. Experimental Setup

SMEBR pilot facility was located in the WWTP in the City of l'Assomption (Quebec, Canada), and consisted of a

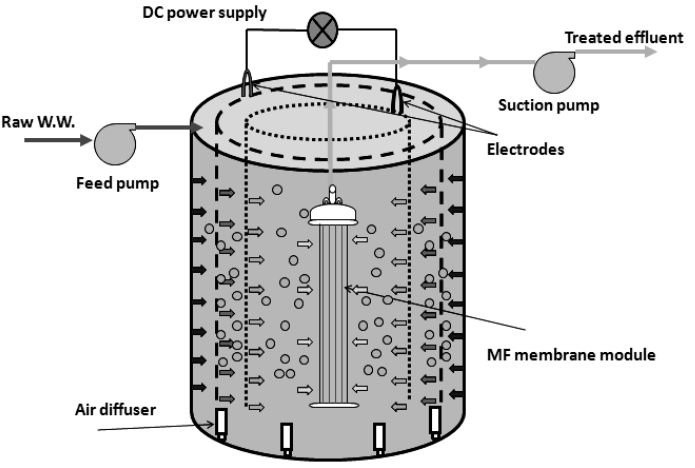

Fig. 1. Principles of SMEBR system

PVC cylindrical reactor (235 L), two cylindrical electrodes connected to a low DC power supply (intermittent supply of electrical field), and a hollow fiber microfiltration membrane (MUNC-600A, Microza, Asahi Kasei Chem. Corp., Japan) (Fig. 1).The membrane has an effective surface area of 12.5 m^2, a pore size of 0.1 μm, and the module was equipped with a built-in bottom air diffuser for scouring. Several fine bubble air diffusers were also placed at the bottom of the reactor to supply the oxygen required for both mixing and microbial activity. SMEBR was continuously fed with pre-screened raw municipal wastewater (see characteristics in Table 1) redirected from the influent channel at a flow rate of 550 L/d for 7 weeks [3, 8]. SRT and HRT were 10 d and 11 h, respectively. SMEBR operated under constant current density.

2.2. Analytical Methods

Dissolved oxygen (DO), pH values, temperature, electrical current and voltage were continuously monitored. Samples from influent raw wastewater and treated effluent were collected four times per week and tested for COD, phosphorus, and ammonia using Hach TNT vials. Samples were repeated twice and an average value was recorded. At the last stage of the SMEBR pilot test, metals such as Ni, Pb, Cd, Cu, Fe, Ca, Mg and Zn were also measured in nitric acid digested samples of influent and effluent using an Atomic Absorption Spectrometer (Perkin Elmer, Analyst 100). Readings were repeated three times for each sample and average values were reported. The handheld NITON XRF analyzer was used to identify the elements present in electrode deposits as well as in the biosolids.

3. Results and Discussion

At steady state operation, the removal efficiencies of COD, ammonia (as NH_3^+-N) and phosphorous (as PO_4^{3-}-P) were 92%, 99% and 99%, respectively. The concentrations of COD, ammonia and phosphorus in the treated effluent were < 25, < 0.9, and < 0.5 mg/L, respectively (Fig. 2). The significant increase in the removal efficiency could be attributed to electrokinetic phenomena. When the DC field is applied, in situ Al^{3+} metal ions (coagulation agent) are generated due to the electrooxidation of the sacrificial aluminum anode. These ions destabilize the negatively charged particles found in the bulk solution through which the van der Waals attraction forces are dominant; hence, this permits the flocs to aggregate. The destabilization mechanism occurs in two different ways: charge neutralization of the ionic species present in the bulk solution by the counter ions produced by the electro-oxidation of the anode, or compressions of the double layer formed around the particle. The oxidation of water produces hydrogen (H^+) and oxygen gas at the anode whereas hydrogen gas and hydrogen oxide (OH^-), due to the water reduction, are generated at the cathode. The electrolytic dissolution (electrooxidation) of the aluminum anode produces cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ at acidic conditions. At suitable pH values, they are first transformed to $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$.

After the biological oxidation in zone 1, wastewater entered zone 2 (as demonstrated in Fig. 1) where electrokinetics (including oxidation) generated more available substrates, resulting in high COD removal. Ammonia could be removed by some oxidants such as chlorine generated from the electrooxidation of the aluminum anode, or ammonia might have been stripped as the pH increased between 8 and 9 in the SMEBR [8]. Nitrification was also enhanced in SMEBR resulting in higher rates of ammonia conversion [3, 8]. The complete removal of phosphorus could be explained in several ways:

- Chemically, through which Al^{3+} ions would react with the available phosphate and form insoluble aluminum phosphate ($AlPO_4$ – eq. 1), or the formation of calcium hydroxyapatite in the presence of calcium, which would also precipitate (eq. 2):

$$Al^{3+} + HnPO_4^{3-n} \leftrightarrow AlPO_4 + nH^+ \quad (1)$$

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (2)$$

- Deposition on electrodes as 113and 4 mg PO_4^{3-}-P/m^2 were reported on the surface of the cathode as well as on the surface of the anode, respectively [8].

At the last stage of the pilot test, results showed that the SMEBR without any additional units was able to remove undesirable metals from wastewater (Table 1). High removal rates of Pb (100%), Ni (98.1%), Cu (100%), and Cd (94.6%) were reported at this range of pH (8-9) with very low concentrations in the treated effluent (0.0, 0.24, 0.0 and 0.04 mg/L for Pb, Ni, Cu, and Cd, respectively), while the removal rates of Mg, Zn, and Fe were 87.5%, 80.4%, and 85%, respectively. SMEBR produced a very high quality effluent where the concentrations of Ca, Mg, Zn, and Fe in the treated effluent were significantly low (0.0, 0.009, 0.09, and 0.27 mg/L, respectively).

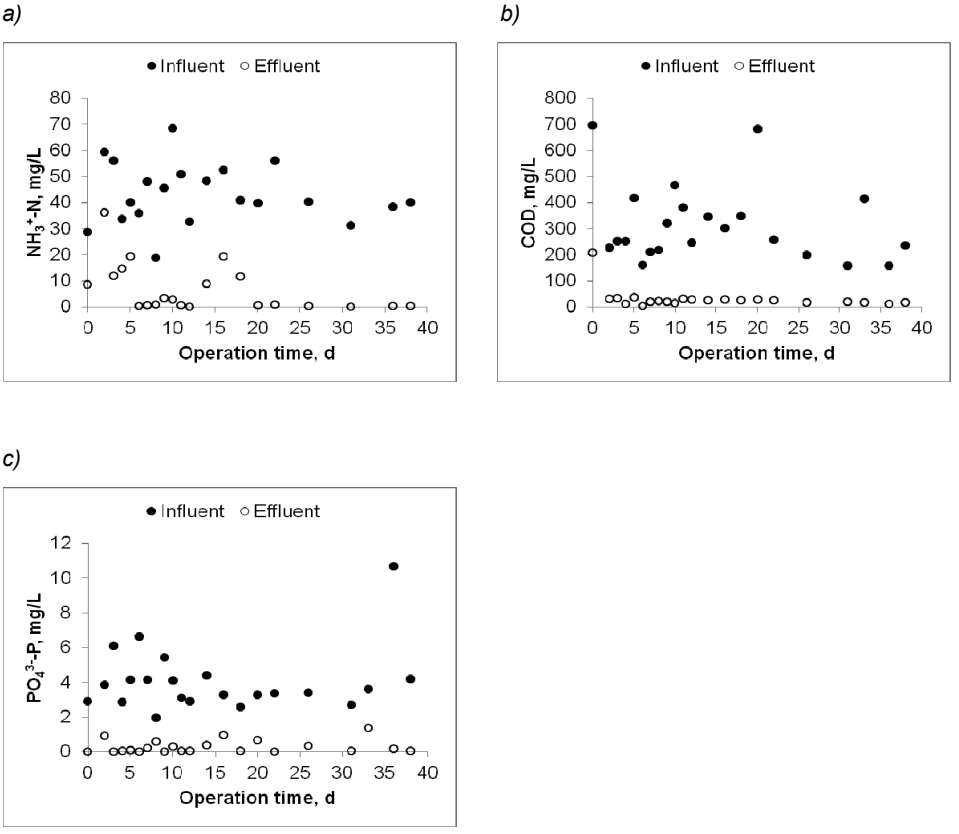

Fig. 2. Influent and SMEBR treated effluent concentrations of (a) COD, (b) ammonia, and (c) phosphorus

Tab. 1. Average concentrations of metals in influent and SMEBR treated effluent streams

Contaminant	Influent, mg/L	Effluent, mg/L	Removal efficiency %
Pb	0.009	0.0	100
Cu	0.05	0.0	100
Ni	12.5	0.24	98.1
Cd	0.75	0.04	94.6
Mg	0.072	0.009	87.5
Zn	0.46	0.09	80.4
Fe	1.8	0.27	85
Ca	5.9	0.0	100

The removal mechanisms of several metals could be attributed to the precipitation of the metal hydroxides, absorption by sludge flocs, or deposition on the surface of the electrodes, mainly on the surface of the cathode [8]. For example, when the DC voltage was applied, the transportation of polar molecules towards the electrodes was expected through electromigration phenomenon. Furthermore, metal complexes found adequate conditions to precipitate in reducing conditions (presence of OH^- and H_2 gas) produced by the stainless steel cathode. Therefore, the hydroxide ions produced under the electrical field would react with metals and insoluble metal hydroxides such as $Ni(OH)_2$, $Zn(OH)_2$, $Pb(OH)_2$, $Cd(OH)_2$, and $Cr(OH)_3$ might have precipitated or deposited on the surface of the electrodes (resulting in the high removal rates as demonstrated in Table 2).

The pH in SMEBR system did not change noticeably (around 8-9) since the generated OH^- ions at the cathode were consumed by the aluminum ions generated at the anode, consequently forming the desired $Al(OH)_3$ flocs. The removal of metals was associated with the solution pH, and previous studies reported the impact of the solution pH on the removal efficiency [9, 10]. It was reported that the removal of metal ions was pH dependent as the adsorption capacity increases with increasing the pH value of the solution, and at a particular pH the order of increasing the removal percentage was $Cu^{2+} < Cr^{3+} < Cd^{2+} < Zn^{2+} < Pb^{2+} < Fe^{3+}$ [11]. At low pH, poor removal rates were reported as the hydrogen ions were dominant over the metal hydrolysis products, whereas at high pH hydroxide ions would compete with organic compounds for metal adsorption sites and the precipitation of the metal hydroxides. These findings were in line with Dermentzis et al. [12] who investigated the removal of metals using electrocoagulation; and reported low removal rates of Ni^{2+}, Zn^{2+}, Cu^{2+} at low pH (less than 2), while more than 97% removal efficiencies were reported in the pH range of 4-9.

The removal of metals in SMEBR could be also attributed to the large number of the negatively charged functional groups in EPS matrix [13-15] which could form multiple complexes with many metals. As a result, this had a significant impact on geochemical behavior, bioavailability and toxicity of heavy metal ions [16].

4. Conclusions

The pilot SMEBR system operated successfully despite the daily and seasonal variations in the characteristics of the raw wastewater, and produced excellent effluent quality. SMEBR is a compact unit which includes three operational units in one hybrid reactor, without primary treatment and thus has a much smaller footprint. SMEBR could be also placed on a mobile unit and used in different applications such as at exploration bases and mining sites.

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