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# Effect of calcium addition on sludge properties and membrane fouling potential of the membrane-coupled expanded granular sludge bed process

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ABSTRACT

The expanded granular sludge bed reactor (EGSB) is considered a promising technology for anaerobic wastewater treatment, and the effluent quality can be further improved by membrane treatments. To mitigate membrane fouling of the membrane-coupled anaerobic process, 2.5 mM $CaCl_2$ was added in a laboratory-scale EGSB reactor (3 L in volume). The effluent was subjected to short-term dead-end ultrafiltration (UF) tests to evaluate the membrane fouling potential. The results showed that $Ca^{2+}$ addition to EGSB efficiently alleviated the fouling of the subsequent UF treatment compared with the control. The fouling potential was not diminished when $Ca^{2+}$ was directly added to the effluent of the control EGSB. Further investigations revealed that the addition of $Ca^{2+}$ to the EGSB resulted in an increase in the content of extracellular polymeric substances (EPS) of the granule by 24.1%. The addition of $Ca^{2+}$ also reduced the concentration of the soluble extracellular polymeric substance (sEPS) (or soluble microbial product, SMP) in the effluent by 47.7–60.7% compared with the control system. Analysis of the fouling model revealed that $Ca^{2+}$ addition reduced the cake resistance ($R_c$) by 42.8% and delayed the transition from the standard pore blocking model to the cake filtration model. The results indicate that fouling-relevant compounds, such as sEPS (aromatic proteins, tryptophan proteins and polysaccharides) and fulvic acids are included in the sludge when $Ca^{2+}$ is added to the reactor, thus preventing them from reaching the membrane surface.

## 1. Introduction

Anaerobic treatment is considered a cost-effective technology for organic matter removal because of the low operation and maintenance costs, as well as the high loading potentials [1]. Application of an upflow anaerobic sludge bed (UASB) and an expanded granular sludge bed (EGSB) to high-strength wastewater treatment is performed primarily because of their high COD loading rate, removal efficiency, recovery of methane as an energy source and low energy consumption compared with aerobic biological processes [2]. Jeison et al. showed that EGSB reactors achieved lower COD effluent concentrations than comparable UASB reactors, especially for treatment of brewery wastewater [1]. Furthermore, EGSB reactors are more effective at low temperatures than UASB reactors [2].

Although anaerobic reactors are effective for the treatment of wastewater, they do not provide complete sludge and particle detention; thus, their effluents often do not meet the standards for water reuse and recycling in terms of COD and of suspended solids (SS) concentrations [3,4]. To improve this tendency, membranes have been integrated in anaerobic processes (Anaerobic MBR, AnMBR) or have been used to treat the effluent of anaerobic reactors (membrane-coupled anaerobic reactors). This leads to nearly absolute detention of SS and biomass and allows for operation at high solids retention times (SRTs), with the potential to generate a high quality effluent [5–7]. It has been reported that membrane-coupled EGSB reactors are capable of removing large amounts of COD (90% COD and TOC removal) while producing a high yield of biogas (0.58 L $L^{-1}$ $d^{-1}$), even at low temperatures [8]. High COD removal values were also obtained for AnMBRs. For example, Smith et al. reported that 92% COD removal, which corresponds to a permeate COD of 36 mg $L^{-1}$, could be obtained with domestic wastewater [7]. However, membrane fouling in membrane-coupled anaerobic bioreactors and AnMBRs is considered more severe than in aerobic

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membrane bioreactors (AeMBR) due to high sludge concentrations and lack of gas (air) shearing. Therefore, it is important to develop measures to reduce membrane fouling in AnMBRs.

The membrane fouling process can be subdivided into three stages. The first stage is rapid fouling caused by initial pore blocking and adsorption of solutes. The second stage is a less rapidly progressing stage (steady fouling) and occurs due to biofilm formation and further blocking. In the third stage, the so-called trans-membrane pressure (TMP) jump occurs, which has been attributed to different mechanisms [9]. To understand the membrane fouling potential and mechanism, dead-end UF tests can be used to investigate the initial stage of membrane filtration, which can help in the development of fouling mitigation strategies [10].

Soluble microbial products (SMP), which are also called soluble extracellular polymeric substances (sEPS), are compounds produced from cell metabolism and lysis and are reported to play an important role in aerobic and anaerobic membrane fouling [11–15]. Based on available literature, these foulants can form an organic layer during the initial stages of membrane filtration, which can then lead to subsequent cake layer development on the membrane surface [16]. The presence of these layers adhered on the membrane surface is a major factor causing the increase of TMP during the following long-term operation. To reduce membrane fouling or to postpone the TMP jump, researchers attempted to optimize the operating conditions (such as temperature, SRT and biogas shear) to reduce the SMP concentrations [6]. However, the dosing of additives has been reported to modify the properties of the bulk solution and the sludge, thus reducing the fouling. For example, it has been confirmed by many studies that the addition of powdered activated carbon (PAC) in an AnMBR resulted in an enhanced membrane performance. The mechanism of fouling mitigation by PAC addition was due to the adsorption of the solutes and colloids in the supernatant and the enlargement of floc size due to the incorporation of PAC in the bioflocs [17,18]. Granular activated carbon (GAC) was also found to efficiently alleviate membrane fouling in membrane-coupled anaerobic reactors [19,20]. These studies describe anaerobic reactors (anaerobic fluidized bed and EGSB) with GAC addition, and the adsorption of SMP by GAC aids the mitigation of fouling.

Calcium salts are low-cost reagents, which can also be used as an additive to improve the properties of sludge and mixed liquor. Arabi and Nakhla [21] have reported that the addition of 7 mM $Ca^{2+}$ in an aerobic membrane bioreactor (AeMBR) improved the permeability by 35%, which could be attributed to the binding of EPS to the flocs by cationic bridges. However, when the dosage was increased to 21 mM, the membrane permeability decreased due to inorganic fouling. Additionally, Thiele et al. [22] investigated the effect of influent $Ca^{2+}$ (25 mM) on the performance of volatile fatty acid (VFA)-degrading anaerobic granules. The high $Ca^{2+}$ concentration caused a decrease in the specific degradation rate of acetate, propionate and butyrate. A high $Ca^{2+}$ concentration, however, not only exacerbates membrane fouling but also inhibits the activity of anaerobic bacteria. It has been reported by Johng-Hwa et al. that the calcium concentrations of 5–7 g/l (125–175 mM) had an inhibitory effect on anaerobiosis for anaerobic digestion of swine wastewater [23]. Therefore, there should be an optimal range for $Ca^{2+}$ addition. Similarly, adding 2.5 mM $Ca^{2+}$ in an aerobic sequencing batch reactor (SBR) could strongly reduce the amount of fine particles, colloids and sEPS, leading to less membrane fouling [24]. Furthermore, studies have shown that $Ca^{2+}$ addition could improve the properties of granular sludge (such as settling velocity and sludge volume index, SVI) in an aerobic reactor [25]. However, the influences of $Ca^{2+}$ on the effluent properties of the anaerobic process as well as the influence on membrane fouling of the effluent have not yet been described.

To investigate these influences, we added 2.5 mM $CaCl_2$ (which was under the inhibition level) to a laboratory-scale expanded granular sludge bed (EGSB) and measured the fouling potential of the effluent as well as the sludge properties. The results were compared with an EGSB without this addition. A dead-end ultrafiltration (UF) cell was used to investigate the membrane fouling potential and fouling mechanisms, while EPS extraction and excitation-emission matrix (EEM) measurements were performed to understand the influence of $Ca^{2+}$ addition on the composition of organics in the effluent.

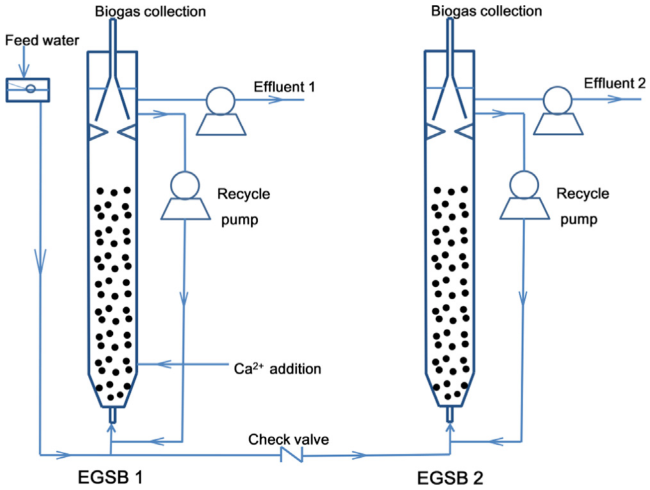

**Fig. 1.** Schematic presentation of the two Expanded Granular Sludge Bed (EGSB) systems (EGSB1: with $Ca^{2+}$ addition; EGSB 2: the control reactor).

## 2. Experimental

### 2.1. EGSB setup

As shown in Fig. 1, two lab-scale EGSBs (EGSB1 and EGSB2) were operated in parallel with synthetic wastewater for nearly three months. $CaCl_2$ was added into EGSB1 continuously with a final concentration of 2.5 mM. We selected this value based on the literature [24] in which 2.5 mM $Ca^{2+}$ was added in an SBR reactor. These results revealed that the supplementation of $Ca^{2+}$ at 100 mg $L^{-1}$ (2.5 mM) in a granulation process could greatly reduce the amounts of fine particles, colloids and sEPS, leading to less membrane fouling. Additionally, the concentration falls below the inhibition level of calcium ions, as mentioned in Section 1. EGSB2 was the control reactor without $Ca^{2+}$ addition. The diameter of the reactor was 50 mm, and the height of the reactor was 1800 mm. The effective working volume of EGSB was 3 L, and the effluent flow rate was set at 0.75 L $h^{-1}$, corresponding to a hydraulic retention time (HRT) of 4 h. There was recycling of the effluent (Fig. 1) with a liquid up-flow velocity of 10 m $h^{-1}$. Therefore, the recirculation flow ratio (recirculation flow /influent flow) was 13.3. The reactors were inoculated with 10 g $L^{-1}$ granular sludge originating from the bottom of a large-scale up-flow anaerobic sludge blanket (UASB) of a soybean wastewater treatment plant in Harbin, China. The SRTs were infinite in both of the reactors, as no sludge was removed. The synthetic wastewater consisted of glucose (200 mg $L^{-1}$), sodium acetate (150 mg $L^{-1}$), $NH_4Cl$ (150 mg $L^{-1}$), $KH_2PO_4$ (22 mg $L^{-1}$), $NaHCO_3$ (400 mg $L^{-1}$), and a mixture of trace elements. Prior documentation was used to determine the amount and composition of the trace elements used [26]. The synthetic wastewater contained 310–360 mg COD $L^{-1}$, 35–45 mg $NH_4^+$–N $L^{-1}$ and 4–5 mg TP $L^{-1}$, and had a pH value of 7.0–7.5.

### 2.2. Short-term UF tests

Bench-scale dead-end UF tests were conducted to study the membrane fouling potential and behavior of EGSB effluents. The