Effect of forward osmosis membrane process on biogas slurry concentration

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Abstract

The use of forward osmosis (FO) for treating biogas slurry was systematically investigated in this study. Membrane performance was investigated with draw solution (DS) concentrations, membrane orientation, solution flow rate, and temperature to identify the optimal conditions. All of the parameters including DS concentration, membrane orientation, solution flow rate, and temperature had significant influence on membrane performance. Results showed that the optimal operation conditions were DS concentration 2 M, flow rate 1.5 L/min, solution temperature 20°C, and FO mode. The recovery rates of total dissolved solids and other substances can reach over 95.6%, no matter how many times concentrated the biogas slurry was. The membrane flux decreased with the increased concentration multiple of biogas slurry. The highest membrane concentration efficiency was about 3 L²/h·m⁻²·g, when biogas slurry was concentrated between 1.5 and 2 times. FO technology which can improve the application value of biogas slurry as fertilizer effectively was feasible to biogas slurry concentration.

Keywords: Forward osmosis; Biogas slurry; Recovery rate; Concentration

1. Introduction

Biogas slurry is the residue of organic substances such as crop straw, the feces of human or livestock after anaerobic fermentation. It is an organic compound fertilizer, which not only contains the tremendously high amount of organic matters but also contains nutrient such as nitrogen (N), phosphorus (P) and potassium (K). Previous research has shown that return the biogas slurry into farmland plays an important role in increasing crop yield, improving agricultural product, and soil quality [1]. Annually, China’s biogas plants produce about 400 million tons of biogas slurry. If biogas slurry cannot be returned to the field or be consumed, it may cause resources wasting. In addition, discharge of untreated biogas slurry poses serious threats to the environment. There are serious doubts such as low nutrient content and high transportation costs with direct application of biogas slurry as liquid fertilizer [2,3]. Therefore, it is significant to concentrate biogas slurry and obtain high-quality liquid fertilizer with easy transport. The main technologies for biogas slurry concentration include humidification–dehumidification, electrodialysis, and membrane treatment [4–6].

Membrane filtration technology has been applied in wastewater treatment as a promising new technology with great development prospects [7–9]. It can be divided by membrane pore size and mechanism into microfiltration, ultrafiltration, nanofiltration, reverse osmosis (RO) and forward osmosis (FO). It is more economical and occupies a smaller area than traditional technology [10]. More importantly, solution can be concentrated, and substances can be rejected by membrane. A pilot dual stage RO membrane process was designed to concentrate, and to recover the nutrient in the biogas slurry [11]. The recovery rates of nutrient and water were 98% and 92.52%, respectively. And the rejection rates of chemical oxygen demand (COD) and ammonia nitrogen (NH₃–N) were over 99%. A hybrid membrane technology was used for biogas slurry concentration. The RO membrane can concentrate the biogas slurry.
slurry with the concentration factor of 5, showed over 97% removal for COD and NH₃-N, which proved the feasibility of the integrated membrane technology in application [12]. Additionally, membrane separation combined with other technologies such as catalytic ozonation can also improve the nutrition of biogas slurry and reduce its ecological risk [13]. However, due to the properties of biogas slurry, serious membrane fouling often appear during membrane process. Thus, the selection of membrane treatment technology with a low fouling tendency has important meanings in biogas slurry.

For the past few years, FO has generated the public’s interest because of the need for more sustainable processes. It depends on a highly concentrated draw solution (DS) as a driving force to extract pure water from the feed solution (FS) based on the difference in osmotic pressure between the DS and FS [14]. Hence, FO has the advantages of low energy consumption, low fouling tendency, high fouling reversibility and high recovery rates compared to the pressure-driven membranes [15–17]. The rejections for most of metal ions under FO process are high [18–20]. FO using NaCl as DS combined with a membrane reactor could reject over 96% total phosphorus (TP), 98% COD and 76% ammonium [21]. Furthermore, FO which can effectively reduce solution volume and realize the reuse of waste is an alternative method for treating high concentration organic wastewater such as landfill leachate [22,23]. It has been used to enrich nutrients from sludge centrate, and membrane performance has also investigated [24–26]. Most of phosphate in sludge centrate was recovered as calcium phosphate precipitates in FO process [24].

In general, membrane filtration efficiency in FO process is impacted by various factors, including operating conditions, water conditions and membrane structure. The concentration effect of biogas slurry in FO membrane can be effectively improved by optimizing operating conditions and solution properties. The parameters including type of DS and its concentration, flow rate and solution temperature can affect the concentration of FO membrane, especially the separation temperature. Biogas slurry is a product of anaerobic fermentation. The temperature of anaerobic fermentation is usually divided into three categories: low temperature (less than 20°C), medium temperature (20°C–45°C), and high temperature (45°C–60°C) [27]. The temperature of biogas slurry is related to the type of anaerobic fermentation. Furthermore, solution temperature can influence the key characteristics in membrane separation processes such as solute mass transfer, water viscosity, water transportation, concentration polarization (CP) and membrane fouling [28]. To date, there has been relatively little research conducted on optimizing operating conditions during the FO membrane treatment of biogas slurry [29–31]. Therefore, it is very important to obtain optimized operating conditions for the concentration of biogas slurry by FO membrane treatment. Further research is needed.

The objective of this study is to evaluate the feasibility of FO for biogas slurry concentration. The effects of operating conditions including DS concentration, membrane orientation, water velocity, solution temperature and concentration multiple were investigated. Furthermore, membrane concentration efficiency of biogas slurry was also studied. The recovery rates of organic matters and nutrients were analyzed. This study has potential implications on FO membrane in biogas slurry treatment.

2. Materials and methods

2.1. Membrane and solution

Cellulose triacetate (CTA) membranes (CTA-ES) for FO used in this study was obtained from the Hydration Technology Innovations (HTI, Albany, USA). The membrane at pH ranges (3–8) had a filtration area of 40 cm². The limit of membrane temperature were 71°C. The raw biogas slurry came from the effluent of hoggy wastewater after biogas fermentation. The characteristics are displayed in Table 1. The biogas slurry contained large quantities of N, P, K and organic matters. The DS was sodium chloride solution (NaCl, Beijing Chemical Works, China).

2.2. FO membrane set-up

A schematic diagram of the FO performance are shown in Fig. 1. It consisted of a membrane cell, a FS tank and a DS tank, two peristaltic pumps, a temperature control device, an electric balance and a computer. Membrane cell had symmetric channels on both sides, which allowed for both the FS and DS to flow tangential to the membrane. Two peristaltic pumps were used to recirculate the feed and draw liquids under different flow rates in a closed loop. The temperature control device was used to control the solution temperature. An electronic balance was placed under the DS tank, which connected to the computer to record the weight of the DS. Prior to each experiment, a virgin membrane was soaked in deionized water for 24 h in order to remove the protective solution. To obtain a satisfied filtrate flux, the FO membrane was initially stabilized for 24 h with deionized water as the FS and NaCl as the DS (baseline test). After that membrane experiments were performed. The experiment conditions are shown in Table 2, and the baseline test conditions were consistent with the membrane experiment. A virgin membrane was used in each experiment in order to compare the results under the same condition. All the tests had been repeated three times.

2.3. Analytical methods

Total organic carbon (TOC) was measured with a TOC analyzer (TOC-VCPH, Shimadzu, Japan). Total potassium was detected by the inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA-2000, PerkinElmer, USA). The total dissolved solids (TDS), nitrogen and phosphorus were analyzed according to Chinese National Standards.

Membrane flux can be expressed using Eq. (1):

\[ Q = \frac{V_f - V_s}{T \times A} \]  

where \( Q \) is the flux (L/h·m², LMH); \( V_f \) and \( V_s \) are the volume of biogas slurry before and after treatment (L); \( T \) is the filtration time (h); \( A \) is the membrane area (m²).
Table 1
Characteristics of raw biogas slurry

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH</th>
<th>Conductivity (µS/cm)</th>
<th>TDS (g/L)</th>
<th>TK (mg/L)</th>
<th>TP (mg/L)</th>
<th>NH₄-N (mg/L)</th>
<th>TN (mg/L)</th>
<th>TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas slurry</td>
<td>7.63</td>
<td>7,735 ± 81</td>
<td>4.98 ± 0.51</td>
<td>712 ± 31</td>
<td>253 ± 23</td>
<td>776 ± 18</td>
<td>2,118 ± 40</td>
<td>1,501 ± 65</td>
</tr>
</tbody>
</table>

TK - Total potassium; TN – Total nitrogen; TP – Total phosphorus

Fig. 1. Schematic diagram of the forward osmosis system.

Table 2
List of the experimental conditions

<table>
<thead>
<tr>
<th>Feed solution (FS)</th>
<th>Draw solution (DS)</th>
<th>Solution temperatures (°C)</th>
<th>Flow rate (L/min)</th>
<th>Membrane orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Biogas slurry</td>
<td>1 M NaCl</td>
<td>20</td>
<td>1.5</td>
<td>FO</td>
</tr>
<tr>
<td></td>
<td>2 M NaCl</td>
<td></td>
<td></td>
<td>FO</td>
</tr>
<tr>
<td></td>
<td>3 M NaCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 M NaCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Biogas slurry</td>
<td>2 M NaCl</td>
<td>20</td>
<td>1.5</td>
<td>FO</td>
</tr>
<tr>
<td>3 Biogas slurry</td>
<td>2 M NaCl</td>
<td>20</td>
<td>0.5</td>
<td>Pressure retarded osmosis (PRO)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>FO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>4 Biogas slurry</td>
<td>2 M NaCl</td>
<td>10</td>
<td>1.5</td>
<td>FO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
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<td></td>
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<td>30</td>
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<td></td>
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<td>40</td>
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<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Baseline test conditions were consistent with the membrane experiment.
Recovery rate of substance after membrane treatment is given by Eq. (2):

$$R = \frac{M_2 - V}{M_1} \times \frac{V}{V_1} \times 100$$

(2)

where $R$ is the recovery rate (%); $M_2$ is the concentration of substance after treatment (mg/L); $V_2$ is the volume of biogas slurry after treatment (L); $M_1$ is the concentration of substance before treatment (mg/L); $V_1$ is the volume of biogas slurry before treatment (L).

The membrane concentration efficiency depended on the membrane flux when it concentrated per unit TDS. The concentration efficiency is calculated:

$$Z = \frac{Q'}{\Delta TDS}$$

(3)

where $Z$ is membrane concentration efficiency ($L^2/h/m^2/g$); $Q'$ is flux at different stages ($L/h/m^2$, LMH); $\Delta TDS$ is the variation of TDS during different stages (g/L).

3. Results and discussion

3.1. Influence of DS concentration

Previous research have been reported that NaCl with low-cost had a high osmotic pressure [32]. Therefore, it was an ideal DS. Membrane behavior under different NaCl concentrations was studied as shown in Fig. 2. High concentration DS possessed high osmotic pressure. Thus, the highest pure water flux was observed with 4 M NaCl in the FO mode. The DS was diluted, resulting in osmotic pressure reduced. The pure water flux gradually decreased with filtration time. In order to keep a constant osmotic pressure, the DS was replaced every hour. So, the pure water flux remained basically unchanged. More membrane flux loss was observed in the filtration of biogas slurry. At the end of the filtration, membrane fluxes with different concentrations of NaCl were 1.65, 2.78, 2.06 and 2.36 LMH, respectively. The reductions of flux were 73.39%, 65.98%, 81.30% and 80.93%, respectively. Biogas slurry were continuously concentrated, causing the osmotic pressure of FS increased. In addition, membrane fouling was another reason for flux decrease. Fouling can blocked membrane pores.
and deposited on membrane surface, formed fouling layer, which increased the membrane resistance, leading the flux decrease. It had reported that high membrane flux can cause membrane flux decrease sharply, which meant a fast-fouling rate [33]. According to the experimental results, 2 M NaCl was selected as the appropriate concentration.

3.2. Characteristics of membrane orientation in flux decline

Membrane orientation had influence on membrane performance and fouling. Therefore, the filtration of biogas slurry in FO mode and pressure retarded osmosis (PRO) mode were evaluated, as displayed in Fig. 3. The pure water flux in PRO mode was higher than that of the FO mode. It was due to more severe dilutive internal concentration polarization (ICP) in the FO mode, compared to the concentrative ICP in the PRO mode [34,35]. Sharp decline of flux was observed in the PRO mode compared with that of the FO mode, while the biogas slurry was selected as FS. The flux was decreased by 75.4% in the PRO mode, higher than that of the FO mode with flux decreased by 64.89%. In addition, the slopes of the curves can be obtained through linear fitting. The slopes of the filtration of the biogas slurry were \(-3.28 \times 10^{-3}\) and \(-4.93 \times 10^{-3}\) in FO and PRO modes, respectively, showed severe fouling in PRO mode. According to previous research, three factors, the porous layer morphology (pore size, porosity and roughness), enhanced ICP and cake enhanced osmotic pressure (CEOP) due to pore blocking, contributed to rapid flux decline in the PRO mode [36].

3.3. Influence of flow rate

The influence of different flow rate on membrane flux has been investigated. The results are shown in Fig. 4. The flow rate had a little effect on membrane pure water flux. As the solution flow rate increased from 0.5 to 2.0 L/min, average flux of pure water was gradually increased from 6.23 to 9.65 LMH. Nevertheless, a noticeable influence in flux was observed in the filtration of biogas slurry, as Fig. 5 shows. membrane fluxes decreased from 6.17, 7.55, 8.15 and 9.35 LMH to 1.78, 1.93, 2.58 and 2.64 LMH, respectively. The decline rates were respectively 71.15%, 74.36%, 68.34% and 71.76%. The influence of external concentration polarization...
(ECP) can be mitigated with the increasing of flow rate, causing the flux increased. Moreover, a high liquid flow rate can increase the shear force of the membrane surface, alleviate the foulants deposition effectively. However, an excessive flow rate will damage the membrane surface, shorten membrane life. And as mentioned earlier, high membrane flux may cause a high flux reduction. Therefore, 1.5 L/min was selected as the optimum flow velocity with considering various factors.

3.4. Membrane performance under different solution temperatures

Temperature influenced the thermodynamic characteristics of solution and the membrane properties, which directly influenced the water permeability, salt permeability and reverse solute flux selectivity [28,35]. The pure water flux was increased by 145.66%, when the solution temperature (both FS and DS) was increased from 10°C to 50°C, as shown in Fig. 6a. The net bulk osmotic pressure directly influenced the water permeability, salt permeability of solution and the membrane properties, which was a positive influence on water flux with the temperature increasing. And further research would be conducted to understand the effect of temperature on biogas slurry concentration during FO membrane.

Membrane behavior influenced by temperature was also investigated during the biogas slurry filtration process, as displayed in Fig. 6b. The flux decreased with the filtration time increased. Furthermore, there was significant difference on the flux decline as the temperature increased from 10°C to 50°C. At the filtration time between 0 to 600 min, membrane flux decreased to 3.15, 5.06, 5.38, 6.74 and 9.19 LMH with the solution temperature increased from 10°C to 50°C, respectively (Fig. 6b). It showed a declined tendency. The decline rates of membrane flux were 49.35%, 39.87%, 51.31%, 48.07% and 40.17%. Subsequently, flux was dropped further. At the end of the filtration, fluxes were down by 62.08%, 69.34%, 76.11%, 77.04% and 79.56%, respectively, when the solution temperatures were 10°C, 20°C, 30°C, 40°C and 50°C. The fastest decline rate was 79.56% with the solution temperatures 50°C. The results was due to the joint influence of both organic convection and temperature polarization [41]. It suggested temperature had a significant effect on FO membrane performance.

3.5. Variation of flux under different concentration multiple of biogas slurry

There were obvious changes in membrane performance under different conditions. Under the condition of solution flow rate of 1.5 L/min, solution temperature of 20°C, FO mode, the variation of membrane flux in different concentration multiple of biogas slurry were investigated, as shown in Fig. 7. As the concentration multiple of biogas slurry increased, membrane flux decreased gradually. When the FS was raw biogas slurry, the maximum membrane flux was 8.4 LMH. When the biogas slurry was concentrated from 2.5 to 3 times, membrane flux decreased sharply from 6.76 to 3.58 LMH. When biogas slurry was concentrated 4 times, membrane flux was decreased to 2.15 LMH. membrane flux decrease rate was 74.4%, comparison to that of raw biogas slurry. As the increase of concentration multiple, the concentration of the substance in biogas slurry was increased. Due to a decrease of driving force on both sides of the membrane and the serious fouling, membrane flux decreases evidently. Previous research had shown a similar result [42].

The concentrations of the main substances were detected respectively and the recovery rate was calculated under different concentration multiple as shown in Table 3. The recovery rates of phosphorus, nitrogen and potassium
were above 98%, no matter how many times concentrated the biogas slurry was. The recovery rate of TDS gradually decreased from 99.3% to 95.6% with the concentration multiple increased. However, it still can keep a high recovery rate over 95%. In addition, the recovery rates of TOC were also to keep above 98%. The results indicated that FO membrane can reject most of ions and organic matters. FO membrane with tiny pores had the advantage of high retention rate for solute. Solution–diffusion was the main mechanism for ions transport across the FO membrane. The Donnan equilibrium effect may hinder ionic permeation degrees of the feed ions across the active layer due to the presence of highly concentrated DS [43]. Furthermore, Metal ions with larger hydrated radius can be rejected for diffusivity decreases with increasing hydrated radius. Hence, it can be used as an effective treatment for biogas slurry concentration.

Due to the driving force of FO membrane originated from the concentration gradient of both sides of the membrane, the relationship between TDS concentration in biogas slurry and membrane flux was also analyzed. As Fig. 8a shown, membrane flux reduced gradually with the TDS concentration of biogas slurry increased. While the TDS concentration was above 12 g/L, membrane flux rapidly decreases. There were two reasons for membrane flux reduction. Firstly, concentration gradient across the membrane gradually reduced with the TDS concentration of

**Table 3**

<table>
<thead>
<tr>
<th>Concentration multiple</th>
<th>1 (raw biogas slurry)</th>
<th>1.5</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>4.98 ± 0.51</td>
<td>7.39</td>
<td>9.84</td>
<td>12.3</td>
<td>14.46</td>
<td>19.92</td>
<td>19.82</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>–</td>
<td>99.3</td>
<td>98.1</td>
<td>98.1</td>
<td>97.9</td>
<td>97.3</td>
<td>95.6</td>
</tr>
<tr>
<td>TK</td>
<td>712 ± 31</td>
<td>1,053</td>
<td>1,413</td>
<td>1,766</td>
<td>2,129</td>
<td>2,434</td>
<td>2,823</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>–</td>
<td>98.9</td>
<td>98.9</td>
<td>98.7</td>
<td>99.1</td>
<td>99.1</td>
<td>98.6</td>
</tr>
<tr>
<td>TP</td>
<td>253 ± 23</td>
<td>373</td>
<td>502</td>
<td>630</td>
<td>745</td>
<td>870</td>
<td>993</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>–</td>
<td>98.7</td>
<td>98.8</td>
<td>98.4</td>
<td>98.7</td>
<td>98.8</td>
<td>98.1</td>
</tr>
<tr>
<td>TN</td>
<td>2,118 ± 40</td>
<td>3,157</td>
<td>4,221</td>
<td>5,275</td>
<td>6,301</td>
<td>7,360</td>
<td>8,419</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>–</td>
<td>99.1</td>
<td>99.2</td>
<td>99.2</td>
<td>98.5</td>
<td>98.4</td>
<td>98.7</td>
</tr>
<tr>
<td>TOC</td>
<td>1,501 ± 65</td>
<td>2,216</td>
<td>2,995</td>
<td>3,741</td>
<td>4,473</td>
<td>5,209</td>
<td>5,951</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>–</td>
<td>99.1</td>
<td>99.4</td>
<td>99.1</td>
<td>98.5</td>
<td>98.7</td>
<td>98.4</td>
</tr>
</tbody>
</table>

TK – Total potassium; TN – Total nitrogen; TP – Total phosphorus
biogas slurry increased. As a result, the driving force of the membrane showed a little decline, resulting in a continuous decrease in membrane flux. The variation of membrane flux at different concentrations multiple of biogas slurry also exhibited the same trend. Secondly, membrane fouling gradually became serious, resulting in a sharp decrease in flux. In fact, the latter was more important.

By calculating the ratio of membrane flux and the variation of TDS at different stages, membrane concentration efficiency can be obtained as shown in Fig. 8b. With the increase of TDS concentration, membrane concentration efficiency displayed a decreasing trend. When the TDS concentration was less than 9.84 g/L, membrane concentration efficiency had little change. The change rate was just only 6%. The highest concentration efficiency 3.08 L/h·m²·g was observed with the TDS concentration 7.39 g/L. As the TDS concentration increased, membrane concentration efficiency declined sharply. When the TDS concentration was 19.82 g/L, the minimum concentration efficiency was only 0.74 L/h·m²·g. According to the results, it can be concluded that a high concentration efficiency was obtained while biogas slurry was concentrated between 1.5 and 2 times.

4. Conclusions

In this study, some influence factors were investigated in FO process for biogas slurry recovery. According to the results, conclusions can be drawn:

- Properties of DS concentration, membrane orientation, solution flow rate and temperature had significant influence on membrane performance. Water flux was higher in PRO mode than that of the FO mode. But more rapid flux decline was also observed in the PRO mode. Increased liquid flow rate was favor to the membrane process because of the increasing shear force, which alleviated the foulants deposition effectively. However, an excessive flow rate could damage membrane surface and shorten membrane life. Higher temperature results more rapid flux decline rate. Although operation at higher temperature may yield higher pure water flux. Through the investigation, the optimum operation conditions with DS concentration 2 M, flow rate 1.5 L/min, temperature 20°C and FO mode can be obtained. The optimum operating conditions should be changed based on the use case required, when the bench scales up.

- Under the optimum conditions, the maximum membrane flux was about 8.4 LMH, when the FS was raw biogas slurry. The recovery rates of TDS and other substances can reach over 95.6%, no matter how many times concentrated the biogas slurry was. The membrane flux decreased with the increased concentration multiple of biogas slurry. The maximum membrane concentration efficiency was about 3 L/h·m²·g, when the concentration time of biogas slurry was between 1.5 and 2. FO technology was feasible to concentrate biogas slurry. It can improve the application value of biogas slurry as fertilizer effectively.

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References


