SOLID/LIQUID SEPARATION BY A HYBRID MICRO-FILTRATION – FLOTATION PROCESS

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ABSTRACT
A hybrid solid/liquid separation process consisting of a micro-filtration module submerged directly into a flotation cell has been developed. The flotation cell removes solid particles; while the membrane module produces a clean water permeate effluent. The proof of concept for the hybrid solid/liquid separation process has been investigated using synthetic zeolite fines. The effect of air sparging (necessary for the flotation process), air bubble size and solid particle content on the performance of the hybrid process have been studied. Preliminary results indicate that the presence of fine air bubbles and the low zeolite particle content improved the hybrid cell performance.

ΔΙΑΧΩΡΙΣΜΟΣ ΣΤΕΡΕΩΝ /ΥΓΡΩΝ ΜΕ ΥΒΡΙΔΙΚΗ ΔΙΕΡΓΑΣΙΑ ΜΙΚΡΟΔΙΗΘΗΣΗΣ - ΕΠΙΠΛΕΥΣΗΣ
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ΠΕΡΙΛΗΨΗ
Στην εργασία αυτή παρουσιάζεται μια υβριδική συσκευή επίπλευσης και διήθησης με μεμβράνες. Η επίπλευση χρησιμοποιήθηκε στην απομάκρυνση του μεγαλύτερου μέρους του φορτίου των στερεών, ενώ καθαρό νερό παραλαμβάνεται με μικροδιήθηση μέσα από την εμβαπτισμένη μεμβράνη. Το στερεό υλικό που χρησιμοποιήθηκε ήταν συνθετικός ζεόλιθος. Οι παράγοντες που μελετήθηκαν ήταν η επίδραση της παρουσίας του αέρα (απαραίτητου για την επίπλευση), το μέγεθος των φυσαλίδων και η συγκέντρωση των στερεών σωματιδίων. Από τα πειραματικά αποτελέσματα προέκυψε ότι η παρουσία του αέρα, η χαμηλή συγκέντρωση στερεών και το μικρό μέγεθος φυσαλίδων αέρα βελτίωσαν την απόδοση της υβριδικής συσκευής.
1. INTRODUCTION

Environmental problems are gradually becoming more important and public interest towards them is growing. The decreasing availability of fresh water and the fact that in many countries the access to potable water is limited constitutes a critical problem. Research is growing and focusing on the treatment of surface or brackish water for use as potable water as well as for safe disposal and recycling of wastewater.

Flotation is a separation process in which the lifting force of bubbles (usually of air) is used for the removal of suspended matter from solutions. The process is widely applied to the removal of organics from water [e.g., ref. 1], the removal of metal ions, oils, powders, and residual reagents from wastewater [e.g., ref. 2] etc., as well as to the beneficiation of mineral particles in minerals technology. The main disadvantage of flotation is that the removal efficiency can be hampered, due to the fact that some substances either are not retained in the froth or are not sufficiently hydrophobic, thus remaining in the bulk dispersion / solution [3].

Membrane filtration is another solid separation process used in water treatment [3-7]. Membranes are semi-permeable materials, which allow the selective passage of certain species, while obstructing the passage of others. Therefore, using an appropriate membrane, it is possible to control the type and amount of dissolved or dispersed species passing though them, resulting in two streams, one of which is practically free of the undesirable components. Energy efficiency, simplicity of operation and easy scale-up are among the advantages of the membrane separation process. Most of the present membrane processes employ polymer membranes; although ceramic membranes exhibit significant advantages such as excellent mechanical properties, chemical and thermal stability, low fouling tendency, high permeation rates and good recovery behavior [8].

Fouling of membranes is the major factor limiting their use in practice. Fouling is a general term, which describes the gradual deterioration of membrane performance in terms of permeation flux and selectivity, due to the accumulation of solids on its surface or inside its pores. Hydraulic, mechanical, chemical and/or electric methods are commonly used to clean fouled membranes. Membrane fouling can be minimized via feed pre-treatment [9], application of external fields (electric or ultrasound), backflushing [3,10,11], and/or gas sparging [11-15], among others.

A combination of air sparging and membrane filtration processes integrated into one unit should minimize the adverse effects of each system applied separately for solids removal. Such a system, a hybrid flotation-membrane filtration system, has been studied and results are reported here. The hybrid flotation-membrane filtration system consists of a membrane module submerged inside a flotation column. A suspension of fine-sized adsorbent was fed into the hybrid cell, where the solid particles were partially removed by flotation, while clean water was obtained from the membrane module. Some of the solid particles remaining in the dispersion were deposited on the surface and the pores of the membrane, forming a cake that gradually blocked the pores and caused membrane fouling. The rising gas bubbles were used for the flotation process, while at the same time acting as membrane-surface scrubbers, effectively removing the deposited cake and countering the fouling problem.

2. EXPERIMENTAL APPARATUS & PROCEDURE

The hybrid cell consists of a cylindrical flotation column made of plexiglass, with an inside diameter (D_C) of 100 mm and a cylindrical ceramic porous gas sparger (diameter D_sp = 10 mm,
height 20 mm, average porosity $D_{pore} = 10-16$ µm or 40-100 µm) located close to the bottom of the cell. A membrane module was positioned 60 mm above the gas sparger. The module \(^1\) consists of a twin set of parallel, double-sided ceramic membranes, with a flat sheet multi-channel geometry. The ceramic membrane is characterized by a 0.3 µm mean pore size, a total surface area of 0.021 m\(^2\), hydrophilic surface properties and an initial pure water flow rate capacity ($Q_L$) of about 2 L h\(^{-1}\) \[^{[16]}\].

The clean water permeate flow withdrawn from the membrane module with a peristaltic pump, and the membrane pressure drop (TMP) were measured as a function of time for different experimental conditions. The permeate flow and TMP were used to compute the membrane permeability of the module according to the following equation:

$$Permeability = \frac{Q_L}{S(P_{atm} - TMP)}$$

where $Q_L$ is the liquid flow rate [L h\(^{-1}\)] of the stream pumped out of the membrane and $S$ the surface area of membranes [m\(^2\)].

Air was introduced into the cell through the sparger, at a superficial velocity $U_G = 8.5 \times 10^{-5}$ m s\(^{-1}\). In all experiments, the dispersion height was kept constant at 400 mm.

A small amount of synthetic type-A zeolite (Ineos Silicas Ltd, Warrington, Cheshire, UK), with a chemical formula $\text{Na}_2\text{O}.2\text{SiO}_2.\text{Al}_2\text{O}_3.\text{nH}_2\text{O}$, was dispersed in water; the natural pH of the dispersion varied from 10.0 to 10.5. The homogeneous suspension was continuously fed into the cell using a peristaltic pump at a flow rate corresponding to a superficial liquid velocity $U_L = 7.4 \times 10^{-5}$ m s\(^{-1}\). In the flotation experiments, cetyl trimethyl-ammonium bromide was used as the collector, to render the zeolite particles hydrophobic; its concentration was kept constant at 10 mg L\(^{-1}\).

3. RESULTS AND DISCUSSION

The main objective of this work was to investigate the effect of air flotation on the potential minimization of membrane fouling.

3.1 Micro-filtration experiments

First, experiments were performed by feeding the zeolite suspension into the hybrid cell without any flotation reagents. Experiments were conducted with and without air sparging for two different suspended solid concentrations. The experimental conditions are summarized in Table 1. The effect of time on the trans-membrane pressure and the membrane permeability \(^2\) are shown in Figure 1. The results indicate that the trans-membrane pressure and permeability decrease significantly over time at high feed solid concentration. Air sparging is shown to improve slightly the membrane performance.

Next, the effect of air bubble size on the trans-membrane pressure and membrane permeability has been studied using two different diffusers. The porosity ranges for the spargers used are 1-16 µm and 40-100 µm. Experiments were carried out with an initial solids concentration of 3 g/L. The experimental conditions and results are shown in Table 2 and Figure 2, respectively. Figure 2 indicates that air sparging reduces membrane fouling which results in a slower decline in the trans-

\(^1\) Kindly provided by the Institute of Environmentally Compatible Process Technology (UPT) of the University of Saarland (Saarbrücken, Germany).

\(^2\) Both are presented as relative values, i.e., divided by their initial value.
membrane pressure and water permeability with time. The air bubbles hinder membrane fouling by scouring the zeolite particles deposited on its surface, and by reducing the probability of particles to get deposited on the membrane surface and its pores.

**TABLE 1.** Experimental conditions for micro-filtration process – effect of gas presence and solids concentration.

<table>
<thead>
<tr>
<th>(x_{\text{zeolite}}) [g L(^{-1})]</th>
<th>(U_G) [m s(^{-1})]</th>
<th>(U_L) [m s(^{-1})]</th>
<th>(\text{TMP}_{\text{initial}}) [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.5(\times)10(^{-4})</td>
<td>7.4(\times)10(^{-5})</td>
<td>0.900</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>7.4(\times)10(^{-5})</td>
<td>0.900</td>
</tr>
<tr>
<td>5</td>
<td>8.5(\times)10(^{-4})</td>
<td>7.4(\times)10(^{-5})</td>
<td>0.875</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>7.4(\times)10(^{-5})</td>
<td>0.900</td>
</tr>
</tbody>
</table>

**TABLE 2.** Experimental conditions for micro-filtration process – effect of bubbles size.

<table>
<thead>
<tr>
<th>(x_{\text{zeolite}}) [g L(^{-1})]</th>
<th>(U_G) [m s(^{-1})]</th>
<th>(U_L) [m s(^{-1})]</th>
<th>Diffuser type [-]</th>
<th>Frother–ethanol (% v/v)</th>
<th>(\text{TMP}_{\text{initial}}) [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>8.5(\times)10(^{-4})</td>
<td>7.4(\times)10(^{-5})</td>
<td>D4</td>
<td>0.1</td>
<td>0.900</td>
</tr>
<tr>
<td>3</td>
<td>8.5(\times)10(^{-4})</td>
<td>7.4(\times)10(^{-5})</td>
<td>D4</td>
<td>-</td>
<td>0.900</td>
</tr>
<tr>
<td>3</td>
<td>8.5(\times)10(^{-4})</td>
<td>7.4(\times)10(^{-5})</td>
<td>D2</td>
<td>-</td>
<td>0.900</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>7.4(\times)10(^{-5})</td>
<td>-</td>
<td>-</td>
<td>0.900</td>
</tr>
</tbody>
</table>

The type / porosity of the ceramic gas sparger does not seem to affect substantially the “fouling-avoiding” process: the profiles of relative TMP and permeability with time are practically identical for the two spargers used. However, the addition of a surfactant, in this case a frother – ethanol 0.1% v/v – yields much smaller gas bubbles, slightly improved the membrane performance.

**Figure 1.** Evolution of the relative trans-membrane pressure and membrane permeability with time; \(U_L = 7.4\times10^{-5}\) m/s, \(U_G = 8.5\times10^{-4}\) m/s (where applicable).
Figure 2. Effect of air addition and of the presence of a surfactant (frother) on the evolution of relative trans-membrane pressure and relative membrane permeability with time; $x_{\text{zeol}} = 3 \text{ g/L}$, $U_L = 7.4 \times 10^{-5} \text{ m/s}$, $U_G = 8.5 \times 10^{-4} \text{ m/s}$ (where applicable).

3.2 Hybrid flotation – micro-filtration process

The addition of a surfactant in the liquid solution renders the solid particles hydrophobic. Thus, when the suspension is brought into contact with gas bubbles, the solid particles collide with the ascending bubbles; some of these collisions result in the solid particles adhering to the bubbles, thus being removed to the surface of the 3-phase system. Consequently, fewer solid particles reach the surface and the pores of the membrane, which results in less pronounced membrane fouling.

Experiments were conducted to validate the above assumption. The performance of the hybrid micro-filtration – flotation process has been compared to the performance of a simple micro-filtration system. The experimental conditions are summarized in Table 3; and results are shown in Figure 3. The results indicate that the hybrid micro-filtration – flotation process has a higher performance. Over 500 min of operation, the TMP drops only by 5% as compared to a 40% drop for the simple micro-filtration system. At the same time, the membrane water permeability dropped only by 40% as compared to an 80% drop for the simple micro-filtration system. It is evident that the removal of the solid particles by flotation is beneficial to the overall process, since it reduces considerably the fouling of the membrane. Figure 3 indicates also, that the addition of a surfactant which renders the particles hydrophobic is an important operating parameters. In the absence of froth, the hybrid micro-filtration – flotation process does not yield a significant improvement as compared to the simple micro-filtration system.

TABLE 3. Experimental conditions for the hybrid process.

<table>
<thead>
<tr>
<th>$x_{\text{zeolite}}$ [g L$^{-1}$]</th>
<th>Process</th>
<th>$U_G$ [m s$^{-1}$]</th>
<th>$U_L$ [m s$^{-1}$]</th>
<th>Diffuser type [-]</th>
<th>Frother-ethanol (% v/v)</th>
<th>$\text{TMP}_{\text{initial}}$ [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>simple MF</td>
<td>0</td>
<td>$7.4 \times 10^{-5}$</td>
<td>-</td>
<td>-</td>
<td>0.900</td>
</tr>
<tr>
<td>5</td>
<td>hybrid MF-flotation</td>
<td>$8.5 \times 10^{-4}$</td>
<td>$7.4 \times 10^{-5}$</td>
<td>D4</td>
<td>-</td>
<td>0.875</td>
</tr>
<tr>
<td>5</td>
<td>hybrid MF-flotation</td>
<td>$8.5 \times 10^{-4}$</td>
<td>$7.4 \times 10^{-5}$</td>
<td>D4</td>
<td>0.1</td>
<td>0.920</td>
</tr>
</tbody>
</table>
Figure 3. Effect of the presence or absence of air on the evolution of the relative trans-membrane pressure and membrane permeability with time; $x_{\text{zeol}} = 5 \text{ g/L}, U_L = 7.4 \times 10^{-5} \text{ m/s}, U_G = 8.5 \times 10^{-4} \text{ m/s}$ (where applicable).

4. CONCLUSIONS

Membranes are very useful in producing clarified water from solid suspensions. However the fouling of the membrane surface and its pores hampers their operation.

In this work, it has been demonstrated that it is possible to reduce substantially the fouling process by combining membrane micro-filtration with flotation. In such a process flotation removes effectively a major part of the solid particles responsible for membrane fouling. The addition of surfactants has been to improve substantially the system performance. These results in a longer membrane operation time with less frequent membrane cleaning.

NOTATION

$D_C$: column diameter [m]  
$D_{\text{por}}$: mean diameter of gas sparger pores [µm]  
$D_{\text{sp}}$: gas sparger diameter [m]  
$Q_L$: liquid volumetric flow rate $[\text{m}^3 \text{ s}^{-1}]$  
$S$: surface area of membranes $[\text{m}^2]$  
$TMP$: transmembrane pressure [bar]  
$U_G$: superficial gas velocity $[\text{m s}^{-1}]$  
$U_L$: superficial liquid velocity $[\text{m s}^{-1}]$  
$x_{\text{zeol}}$: zeolite concentration $[\text{g/L}]$

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REFERENCES