Membrane fouling in a submerged membrane bioreactor: Effect of pH and its implications

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Abstract
The effect of pH on membrane fouling in a submerged membrane bioreactor (MBR) was investigated in this study. It was found that, pH increase slightly increased the resistance of virgin membrane and fouled membrane. Pore clogging resistance was quite low, which was not apparently affected by the pH variation. Lower pH resulted in higher adherence of sludge flocs on membrane surface. This energy barrier would decrease with pH decreased, suggesting the existence of a critical pH below which the repulsive energy barrier would disappear, which would facilitate attachment of the foulants. The resistance of the formed cake layer would significantly increase with the feed pH. This result could be explained by the osmotic pressure mechanism. The obtained findings also provided important implications for membrane fouling mitigation in MBRs.

1. Introduction

The distinct advantages offered by membrane bioreactor (MBR) technology over the conventional activated sludge processes, together with increased water reclamation needs, more stringent discharge standards, and steady decrease of membrane costs, have given remarkable impetus to extensive research and application of MBR for wastewater treatment (Le-Clech et al., 2006; Hasar, 2009; Lin et al., 2011b; Wang et al., 2011; Liu et al., 2012). However, membrane fouling, which would lead to trans-membrane pressure (TMP) increase or flux decline, frequent membrane cleaning or replacement, and high energy consumption or costs, remained the major obstacle for the universal application of MBRs (Meng et al., 2009; Lin et al., 2011c, 2013; Wu and He, 2012; Kim and Chung, 2013).

Membrane fouling in a MBR is the result of interactions between membrane and sludge suspension. All the factors affecting membrane or sludge suspension will exert impacts on membrane fouling. Among them, pH is a primary parameter which not only affects membrane properties, but also largely determines sludge suspension properties (Wu et al., 2010). Meanwhile, most real wastewaters treated by MBRs were in the non-pH neutral or pH variation conditions (Lin et al., 2012). Therefore, investigating pH effect on membrane fouling has attracted much attention in recent years (Brinck et al., 2000; Dong et al., 2006; Wu et al., 2010; Sweity et al., 2011). It has been reported that no flux reduction occurred under alkaline conditions, whereas the flux reduction under acidic conditions was severe (Brinck et al., 2000). Similar conclusions have been also drawn by other researchers (Ribau Teixeira and Rosa, 2003; Dong et al., 2006). However, conflicting or inconsistent
phenomena have been also observed. For instances, Sweity et al. (2011) reported that decrease of pH value of sludge suspension from both 6.7 to 5.8 and 7.9 to 6.7 resulted in an obvious increase in filtration permeability in a MBR system. Zhang et al. (2013b) reported that, with pH increase, the specific filtration resistance of sludge quickly increased in pH range of 3–5, while very slowly increased in pH range of 5–8, and then sharply increased in range of 8–10. The causes of these contradictions appeared not well explored. Nevertheless, these studies demonstrated that effect of pH on membrane fouling was complex, and deserved further investigation.

Membrane fouling in MBRs is a process characterized by the initial pore clogging followed by formation of a foulant or cake layer and then foulants changes in cake layer. pH may affect pore clogging fouling in MBRs. Moreover, it is generally accepted that cake layer formation is the main form of membrane fouling in MBRs (Wang and Li, 2008; Lin et al., 2011a). Adhesion of foulants on membrane surface to form a cake layer is a both hydrodynamic and thermodynamic process (Hong et al., 2013). In MBRs, hydrodynamic drag forces cause the foulants approach to the membrane surface, while thermodynamic forces (physico-chemical interactions) are responsible for the binding of the foulants to the membrane surface. Studies have shown that the thermodynamic interactions between foulants and membrane surface can be described through the extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory (Feng et al., 2009; Nguyen et al., 2011). pH is expected to affect adhesion process, and then take a role in membrane fouling. Therefore, XDLVO theory may provide a new approach, were comprehensively analyzed. pH effect based on osmotic pressure mechanism was investigated and discussed. This study led to significant insights into membrane fouling in MBRs.

2. Methods

2.1. Experimental setup and operation

A lab-scale submerged MBR (SMBR) setup with an effective volume of 65 L (0.30 × 0.40 × 0.54 m length × width × height) was used in this study. A schematic of the MBR setup is shown in Fig. 1. A lab-scale submerged MBR (SMBR) setup with an effective volume of 65 L (0.30 × 0.40 × 0.54 m length × width × height) was used in this study. A schematic of the MBR setup is shown in
Fig. S1 (see Electronic Annex in the online version of this article). The MBR tank comprised a down-comer zone and a riser zone separated by a baffle frame. A 0.5 m² flat sheet membrane module (polyvinylidene fluoride (PVDF), 0.3 μm pore size, SINAP Co. Ltd., Shanghai, China) was submerged in the riser zone. The membrane module is one of dominant membrane products used for treatment of industrial and municipal wastewater in China. PVDF material membrane was widely used in MBR applications due to its excellent thermal–mechanical characteristics and chemical resistance (Koehler et al., 1997; Santos and Judd, 2010). This membrane module could therefore be considered as a representative selection in MBRs. The membrane module was intermittently sucked by a peristaltic pump (Baoding Longer, China) to obtain effluent with an intermittent mode (4-min-on and 1-min-off). The sludge concentration indicated as mixed liquid suspended solids (MLSS) was maintained in the range of 9–13 g/L during the operational period. Synthetic wastewater simulating municipal wastewater was used as feed. It is a common operation using synthetic wastewater to test new concepts or study general aspects of membrane fouling (Lin et al., 2013). The composition of the feed was shown in Table 1. Air flow rate of about 50 L/min was applied at bottom of the membrane module to create aeration and shear stress on the membrane surface. Membrane flux was maintained about 30 L m⁻² h⁻¹, which corresponded to an approximate 5.5 h hydraulic retention time (HRT). The MBR set-up was continuously run for over 200 days. The sludge suspension in the stable operation period was used for the following tests.

2.2. XDLVO approach

The particle–substrate interfacial interactions (energy) in aqueous media can be generally described via the XDLVO theory, which consists of three energy components: van der Waals (LW) energy \( U^{LW}_{\text{fwm}}(d) \), Lewis acid–base (AB) energy \( U^{AB}_{\text{fwm}}(d) \) stemming from hydrogen bonding between two surfaces immersed in water, and electrostatic double layer (EL) energy \( U^{EL}_{\text{fwm}}(d) \) (van Oss et al., 1999). According to XDLVO approach, the total interaction energy between foulants and membrane is evaluated as a function of the separation distance \( d \) given as:

\[
U^{\text{XDLVO}}_{\text{fwm}}(d) = U^{LW}_{\text{fwm}}(d) + U^{AB}_{\text{fwm}}(d) + U^{EL}_{\text{fwm}}(d)
\]  

(1)

Surface tension parameters should be experimentally determined in order to calculate above three energy components. The total surface tension parameter \( \gamma^{\text{tot}} \) of a substance is the sum of a dispersive LW \( \gamma^{\text{LW}} \) and polar AB \( \gamma^{\text{AB}} \) components:

\[
\gamma^{\text{tot}} = \gamma^{\text{LW}} + \gamma^{\text{AB}}
\]  

(2)

where \( \gamma^{\text{AB}} \) comprises electron acceptor (\( \gamma^- \)) and non-additive electron donor (\( \gamma^{+} \)) components as indicated in Eq. (3):

\[
\gamma^{\text{AB}} = 2 \sqrt{\gamma^+ \gamma^-}
\]  

(3)

Surface tension parameters of a solid surface can be determined by using contact angle measurement combined with the extended Young’s equation. The extended Young’s equation describes the relationship between the contact angle of a liquid on a solid surface and the surface tension parameters \( \gamma^{\text{LW}}, \gamma^{+}, \gamma^- \) of both the solid (subscript \( s \)) (referring to membrane or foulants in MBRs) and the liquid (subscript \( l \)):

\[
\frac{1 + \cos \theta}{2} \gamma^{\text{tot}} = \sqrt{\gamma^{\text{LW}} l} \sqrt{\gamma^{\text{LW}} s} + \sqrt{\gamma^+ l} \sqrt{\gamma^- s} + \sqrt{\gamma^- l} \sqrt{\gamma^+ s}
\]  

(4)

The surface tension parameters of the membrane surface \( \gamma^{\text{LW}}, \gamma^{+}, \gamma^- \) and foulants \( \gamma^{\text{LW}}, \gamma^+, \gamma^- \) can be solved through a set of three Young’s equations by measurements of the contact angles using three different probe liquids with known surface tension parameters \( \gamma^{\text{LW}}, \gamma^{+}, \gamma^- \). \( \Delta G^{\text{LW}}, \Delta G^{\text{AB}}, \) and \( \Delta G^{\text{EL}} \) are the LW, AB and EL adhesion free energies per unit area between two infinite planar surfaces when they contact each other, respectively. It has been suggested that the contact of two planar surfaces occurs at a hypothetical minimum equilibrium cut-off distance \( d_0 \) (van Oss et al., 1999). Their values could be calculated through the following equations (Nguyen et al., 2011; Hong et al., 2013).

\[
\Delta G^{\text{LW}}_{d_0} = -2 \left( \sqrt{\gamma^{\text{LW}} l} - \sqrt{\gamma^{\text{LW}} s} \right) \left( \sqrt{\gamma^{\text{LW}} l} - \sqrt{\gamma^{\text{LW}} s} \right)
\]  

(5)

\[
\Delta G^{\text{AB}}_{d_0} = 2 \left( \sqrt{\gamma^+ l} \sqrt{\gamma^- s} + \sqrt{\gamma^- l} \sqrt{\gamma^+ s} \right) \left( \sqrt{\gamma^+ l} \sqrt{\gamma^- s} + \sqrt{\gamma^- l} \sqrt{\gamma^+ s} \right)
\]  

(6)

\[
\Delta G^{\text{EL}}_{d_0} = \frac{\varepsilon_0 \varepsilon \kappa}{d_0} \left( \frac{\varepsilon^2}{\varepsilon^2 + \varepsilon_{\text{m}}^2} \left( 1 - \coth(\kappa d_0) \right) + \frac{2 \varepsilon_0^2 \varepsilon_{\text{m}}^2}{\varepsilon^2 + \varepsilon_{\text{m}}^2} \cosh(\kappa d_0) \right)
\]  

(7)

where, \( \gamma^{\text{LW}}, \gamma^+, \gamma^- \) are the surface tension parameters of membrane (subscript \( m \)), water (subscript \( w \)) and foulants (subscript \( f \)), \( \varepsilon_0 \) is the permittivity of the sludge suspension, \( \varepsilon \) is the surface zeta potential of membrane (subscript \( m \)) and foulants (subscript \( f \)), \( \kappa \) is the reciprocal Debye screening length calculated by Eq. (8):

\[
\kappa = \sqrt{\frac{\varepsilon^2 \sum z_i^2 \varepsilon_{\text{m}}}{\varepsilon_0 \varepsilon_{\text{m}} kT}}
\]  

(8)

where, \( e \) is the electron charge, \( n_i \) is the number concentration of ion \( i \) in solution, \( z_i \) is valence of ion \( i \), \( k \) is Boltzmann’s constant, and \( T \) is temperature.

Eqs. (5)–(7) only apply to planar surfaces, while sperecity is generally assumed for sludge flocs. Therefore, Derjaguin approximation, which integrates plate–plate unit free energies between membrane surface and a series of concentric rings in flocs surface along the separation distance \( d \), is used to calculate the three energy components \( \left( U^{\text{LW}}_{\text{fwm}}(d), U^{\text{AB}}_{\text{fwm}}(d) \right) \) between the membrane surface and sludge flocs. The calculation methods can be expressed as Eqs. (9)–(11):

\[
U^{\text{LW}}_{\text{fwm}}(d) = 2\pi \Delta G^{\text{LW}}_{d_0} \frac{d_0 - d}{d}
\]  

(9)

\[
U^{\text{AB}}_{\text{fwm}}(d) = 2\pi d_0 \lambda \Delta G^{\text{AB}}_{d_0} \exp \left[ \frac{d_0 - d}{\lambda} \right]
\]  

(10)

\[
U^{\text{EL}}_{\text{fwm}}(d) = \pi \varepsilon_0 \varepsilon \kappa \left[ \frac{2 \varepsilon_0^2 \varepsilon_{\text{m}}^2}{\varepsilon^2 + \varepsilon_{\text{m}}^2} \ln \left( \frac{1 + e^{-xd}}{1 - e^{-xd}} \right) + \frac{\varepsilon^2}{\varepsilon^2 + \varepsilon_{\text{m}}^2} \ln(1 - e^{-2xd}) \right]
\]  

(11)

where, \( d_0 \) is the fousants or flocs radius, and \( \lambda \) is the decay length of AB energy.

2.3. Analytical methods

2.3.1. EPS extraction and measurement

Extraction of bound extracellular polymeric substances (EPS) of sludge flocs was based on cation exchange resin method. EPS were normalized as the sum of proteins and polysaccharides. Proteins were colorimetrically measured according to phenol/sulphuric acid method with bovine serum albumin (BSA) as proteins standard. Polysaccharides were measured by Folin method with glucose as polysaccharides standard. The operational procedures could refer to Lin et al. (2011a).
2.3.2. Filtration resistance test

Filtration resistance was determined according to Darcy’s law as described in Eqs. (12), (13):

$$ R = \frac{\Delta P}{J \mu} \quad (12) $$

$$ R_t = R_m + R_p + R_c \quad (13) $$

where, $R$ is filtration resistance, $R_t$ is total filtration resistance, $R_m$ membrane filtration resistance, $R_p$ pore clogging filtration resistance and $R_c$ cake layer filtration resistance, respectively, $\Delta P$ is trans-membrane pressure, $J$ is filtration flux and $\mu$ is dynamic viscosity of permeate.

A series pH values (3, 5, 7 and 9) were tested for every resistance component. All the filtration tests were conducted in a stirred cell (model 8200, Amicon) with an applied pressure of 30 kPa. Series waters with different pH (3, 5, 7 and 9) were prepared by adjusting deionized (DI) water with 1 mol/L NaOH or HCl solution. For each pH, values of $R_m$ were obtained by performing tests of filtrating water with same pH value through the virgin membrane. The fouled membrane was obtained by filtering sludge suspension (12.8 gMLSS L$^{-1}$) through virgin membrane for 20 min followed by rinsing with DI water. Values of $R_p$ were estimated by filtration of water with same pH value through the fouled membranes according to Eq. (14):

$$ R_p = \frac{\Delta P}{J \mu} - R_m \quad (14) $$

In order to investigate the effect of pH on $R_c$, the sludge suspension (12.5 gMLSS L$^{-1}$) was firstly adjusted to the desired pH (e.g. pH = 5) with 1 mol/L NaOH or HCl solution. Thereafter, 30 mL adjusted sludge suspension was subjected to filtration in the stirred cell to form a cake layer, then, DI water with the same pH was used to filtrate through the cake layer. $R_c$ was estimated by Eq. (15):

$$ R_c = \frac{\Delta P}{J \mu} - R_m - R_p \quad (15) $$

2.3.3. Microbial adhesion to hydrocarbons (MATH) test

MATH test was used to reflect the adherence of the sludge flocs. A series pH values (3, 5, 7 and 9) were tested. The test procedure for each pH was as follows: The sludge suspension (3.5 gMLSS L$^{-1}$) was firstly adjusted to the desired pH with 1 mol/L NaOH or HCl solution. Thereafter, 30 mL adjusted sludge suspension was used to fill the stirred cell to form a cake layer, then, DI water with the same pH was used to filtrate through the cake layer. $R_c$ was estimated by Eq. (15):

$$ R_c = \frac{\Delta P}{J \mu} - R_m - R_p \quad (15) $$

2.3.4. Contact angle measurement

Ultrapure water, glycerol and diiodomethane were used as probe liquids in the contact angle measurement. The contact angles between the three probe liquids and membrane, foulants were measured by using a contact angle meter (Tantec Inc.).

2.3.5. Zeta potential measurement

Zeta potential measurement based on laser Doppler electrophoresis technique was conducted for sludge suspension at various pH values by using a Zetasizer Nano ZS electrophoretic light scattering spectrophotometer (Malvern Instruments, UK). The background electrolyte was 0.01 mol/L NaCl solution, and the desired pH of sludge suspension was adjusted by using 0.01 mol/L HCl or 0.01 mol/L NaOH solution. The zeta potential of the membrane surface was determined by using a Zeta 90 Plus Particle Size Analyzer (Brookhaven Instruments, Worcestershire, UK). The measurement procedure could refer to Mahendran et al. (2011).

2.3.6. Other items measurements

Water quality parameters including chemical oxygen demand (COD) and mixed liquor suspended solids (MLSS) were analyzed according to the standard methods (APHA, 2005). The supernatant was obtained by centrifuging the sludge suspension for 10 min at 8000 rpm (GTR16-2 high-speed refrigerated centrifuge, Beijing Era Beili Centrifuge Co., Ltd., China). Particle size distribution (PSD) of sludge suspension was determined by a Malvern Mastersizer 2000 instrument with a detection range of 0.02–2000 μm.

3. Results and discussion

3.1. Effect of pH on membrane and pore clogging resistance

Both virgin membrane and fouled membrane were performed to filtrate a series of DI waters with different pH. The filtration results are shown in Fig. 1. With pH increased, the filtration resistance of the virgin membrane and fouled membrane slightly increased, implying that pH slightly affected the permeability of virgin membrane and fouled membrane. This result might be attributed to the membrane properties. Polymeric membrane is generally prepared with addition of some non-solvent additives in casting solution. At high pH, the non-solvent additives entrapped in the membrane polymer matrix will swell due to the stronger repulsive force in them, which may slightly reduce the membrane pore size, and thus reduce the permeability of membrane. The swelling phenomena in polymeric membrane have been reported by other researchers (Yang et al., 2001; Hashim et al., 2009). Moreover, the filtration resistance due to pore clogging was leveled at 5 × 10$^{-9}$–9 × 10$^{-9}$ m$^{-1}$, which was only about 2.5–5% of that of the virgin membrane. At such low resistance levels, pH appeared to have no apparent impact on pore clogging fouling (Fig. 1). This phenomenon may be ascribed to the PS and the low soluble microbial products (SMP) of sludge suspension in the MBR. Analysis of PS showed that almost all the particles in the sludge suspension had size larger than 0.3 μm, a value same to the mean pore size of the PVDF membrane used in the MBR system. Meanwhile, supernatant COD was measured to be as low as
8.3 ± 2.2 mg/L (20 measurements during 160 days), which can be generally regarded to mostly consist of SMP due to the easily degradable property of influent organics. It was therefore expected that pore clogging was minor, let alone partial blockage was reversible.

3.2. Effect of pH on adherence of sludge flocs

A general model of sludge flocs is bacteria aggregation in a three-dimensional hydrated matrix formed by EPS. Therefore, EPS highly determined surface properties of sludge flocs including adherence capacity. In this study, proteins and polysaccharides in EPS were measured as 17.3 ± 3.6 and 5.0 ± 1.7 mg/kg MLSS (25 measurements during 122 days), respectively. MATH test was used to quantitatively describe the adherence capacity of sludge flocs in this study. Fig. S2 (see Electronic Annex in the online version of this article) shows how pH affects $r_s$. $r_s$ increased with the decrease of pH, indicating that low pH could significantly enhance the adherence capacity of sludge flocs. For example, a pH decrease from 7 to 3 corresponded to approximately a 70% increase in $r_s$. Fig. 2 illustrates the variation of zeta potential of membrane and sludge flocs with pH. It can be seen from Fig. 2, both membrane and sludge flocs were negatively charged over the entire investigated pH range. Moreover, the absolute value of zeta potential decreases with pH decreased for the two materials. It is therefore intuitively deduced that, at lower pH, the repulsive forces between sludge flocs and membrane surface would decrease, which would facilitate the adhesion of sludge flocs on membrane surface. By nature, adhesion of sludge flocs on membrane surface in MBR is a thermodynamic process which is determined by the thermodynamic interactions between membrane and sludge (Hong et al., 2013). Therefore, the thermodynamic interactions were analyzed to comprehensively assess the pH effects on foulants adherence in Section 3.3.

3.3. Effect of pH on thermodynamic interactions between sludge and membrane

The surface thermodynamic parameters including contact angle and zeta potential of the membrane and sludge flocs were measured in order to assess thermodynamic interactions between them. The results at pH 7.0 are presented in Table 1. The possessed high negative charge renders this membrane a certain anti-fouling ability as reported by Mahendran et al. (2011) due to the strong electrostatic repulsion between the membrane and sludge flocs. Fig. 3 shows the variations of interaction free energies with the separation distance between membrane and sludge flocs based on the XDLVO approach by using the data in Table 2. The profiles of the three type interaction energies are significantly different. LW and AB interactions are continuously attractive (Fig. 3(a) and (b)), while EL interaction is continuously repulsive (Fig. 3(c)) with the separation distance. Moreover, the AB interaction is much stronger and more short-ranged than LW and EL interactions (Fig. 3). With the separation distance decreases, the total interaction energy decreases.
Fig. 2. Because pH has almost no short-term effect on the surface tension of a solid material, the measured zeta potential and surface tension values were used to calculate the thermodynamic interactions between membrane and sludge flocs. Fig. 3 shows the variation of the total interaction energy with the separation distance and pH value. The interaction becomes more attractive when pH decreases from 9 to 3. At pH 3 and 4, the interactions covering the whole separation distance are totally attractive. pH decrease also significantly reduces the value of the energy barrier. This means that sludge flocs would more easily adhere to membrane surface to form cake layer at low pH conditions, causing more severe membrane fouling. Thus, analysis of thermodynamic interactions provides a solid explanation for the enhanced adhesion of sludge flocs at low pH in Fig. S2. This result also shows that there exists a critical pH value below which the repulsive energy barrier will disappear. Such a situation will be very unfavorable to membrane fouling control. The critical pH value was approximately 4.3 in this study, indicating that pH should be controlled to be at least higher than this value from standpoint of fouling mitigation. Generally, the lower the critical pH value, the better for membrane fouling control is. It can be seen that the critical pH value for a MBR system rather depends on the surface properties of membrane and sludge flocs. Therefore, the finding regarding the critical pH provides a guideline for membrane selection and sludge properties modification in MBRs.

3.4. Effect of pH on the filtration resistance of cake layer

Continuous operation of MBR eventually led to a cake layer formed on membrane surface in this study. Under the conditions in this study, an apparent cake layer formed on membrane surface in stable operation period typically required 30–50 days. Once a cake layer formed on membrane surface, a TMP (trans-membrane pressure) rise or filtration resistance rise would be observed in the following short period. At pH of around 7.0, the cake layer formed in the dead-end filtration test possessed a filtration resistance of 6.3 × 10⁻¹² m⁻¹, which is about 30 times higher than that of fouled membrane (2.0 × 10⁻¹¹ m⁻¹). This result confirmed the frequently reported phenomenon that cake layer formation rather than pore clogging is the predominate form of membrane fouling in MBRs. As shown in Fig. S3 (see Electronic Annex in the online version of this article), the filtration resistance of cake layer formed in the dead-end filtration test is remarkably affected by the feed pH. The cake layer resistance continuously increased with pH, and the filtration resistance at pH 9.0 was about 12 times of that at pH 3.0 for the same cake layer.

Our recent studies revealed a new membrane fouling mechanism: osmotic pressure effect during cake layer filtration process (Chen et al., 2012; Zhang et al., 2013b). The negatively charged functional groups, such as carboxyl, hydroxyl and phosphoric groups, contained in EPS matrix would lead to large concentration of counter-ions presented in cake layer for reason of electro-neutrality (Keiding et al., 2001). As a result, the water chemical potential of cake layer is much lower than that of permeate due to the higher entropy (Curvers et al., 2009; Zhang et al., 2013a). It was

Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>Contact angle (°)</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure water</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Virgin PVDF membrane</td>
<td>58.62 (±0.27)</td>
<td>53.70 (±1.27)</td>
</tr>
<tr>
<td>Sludge flocs</td>
<td>70.68 (±1.41)</td>
<td>68.55 (±1.09)</td>
</tr>
</tbody>
</table>

Contact angle and zeta potential data for membrane and sludge flocs.

![Figure 4](image-url)
suggested that filtration through cake layer should overcome an osmotic pressure which was originated from the difference of water chemical potential between cake layer and permeate. The high cake resistance has been reported to be mostly contributed by the osmotic pressure effect (Chen et al., 2012; Zhang et al., 2013b). According to this mechanism, it can be deduced that the significant of osmotic pressure effect was highly determined by the dissociation of these functional groups which is directly controlled by the pH conditions. At lower pH, the functional groups in cake layer will be less dissociated, which will result in less counter-ions presented in cake layer, and reduce osmotic pressure and filtration resistance consequently, and vice versa. Therefore, the osmotic pressure mechanism could well predict the change trend of cake resistance with pH, and serve as a plausible explanation for pH effect on cake resistance.

3.5. Combined effect of pH on membrane fouling and its implications

The experiment results indicated that pH affected membrane fouling in different forms in a MBR. Increase in pH slightly increased the filtration resistance of virgin membrane. Pore clogging resistance was quite low, and was not apparently affected by pH variation. Elevated pH reduced adherence capacity of foulants, while improved cake filtration resistance. Therefore, the combined effect of pH on membrane fouling in MBRs was complicated, which depended on the main stage of membrane fouling in MBRs. In initial MBR operation, pore clogging was generally the predominated fouling form, pH would slightly affect membrane fouling in this stage. As stated above, the adhesion of sludge foulants on membrane surface was generally a prolonged process. In this prolonged stage, pH would exert a negative impact on membrane fouling. Finally, as an apparent cake layer was formed on membrane surface, pH would positively influence membrane fouling due to the effect of osmotic pressure mechanism. Such a combined effect would be much helpful to explain the contradictions regarding pH effect in literature. For example, some researchers reported that membrane fouling was serious in acidic conditions (Brinck et al., 2000; Ribau Teixeira and Rosa, 2003; Dong et al., 2006), and this could be attributed to the improved adherence capacity of sludge flocs in acidic conditions. Sweity et al. (2011) observed that pH decrease from 6.7 to 5.8 by dosing HCl solution corresponded to a significantly enhanced filtration permeability of a MBR system. The underlying cause should lie in the reduced osmotic pressure when a cake layer was formed on membrane surface.

It should be noted that synthetic wastewater was used as influent in this study, which may induce sludge flocs with different properties from those generated by real wastewater. However, the general structure of sludge flocs and the change trend of their properties with affecting factors should be similar, e.g., they all consist of cells and EPS, and their surface properties are affected by pH and other factors. It can be seen from above analysis, the main conclusions regarding pH effect are derived from the general structure of sludge flocs and the change trend of their characteristics.

4. Conclusion

Increase in pH slightly increased the resistance of virgin membrane. Pore clogging resistance was minor and not apparently affected by pH changes. pH increase reduced the adherence of sludge flocs on membrane surface. It was found that a repulsive energy barrier exists when the flocs got close to membrane surface. This energy barrier would decrease with pH decreased, facilitating attachment of the foulants. The resistance of cake layer significantly increased with pH due to the effect of osmotic pressure mechanism. The obtained findings also provided important implications for membrane fouling mitigation in MBRs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.10.096.

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