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pH Adjusting to Reduce Fouling Propensity of Activated Sludge Mixed Liquor in Membrane Bioreactors

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The effect of adjusting pH on membrane filterability of activated sludge mixed liquor in membrane bioreactors (MBRs) was studied. The properties of the mixed liquor were analyzed to investigate the mechanisms. The results indicated that moderately adjusting pH was effective to improve the membrane filterability of the mixed liquor. HCl addition provided H^+, which reduced the zeta-potential of the colloidal particles. NaOH addition at pH of 8.0–9.0 released some extractable extra-cellular polymeric substances (eEPS) to the supernatant. Re-flocculation occurred. The fouling propensity of the mixed liquor was therefore reduced. Microbial activity was not significantly affected within the pH of 6.0–9.0.

Keywords activated sludge mixed liquor; fouling propensity; membrane bioreactor; pH adjusting

INTRODUCTION

The membrane bioreactor (MBR) has been considered as one of the most promising processes for wastewater treatment and reclamation. It has many outstanding advantages over the conventional activated sludge processes. However, membrane fouling is a key problem preventing the widespread application of the MBR (1).

In MBRs, the material being filtered is the activated sludge mixed liquor. Foulants originating from the mixed liquor inevitably accumulate on the membrane surface or clog the membrane pores during filtration, causing fouling and an increase in the observed filtration resistance. In most cases, membrane filterability of the mixed liquor is taken as an indirect index representing the fouling propensity of the mixed liquor to the membrane. According to previous reports, many characteristics of the mixed liquor affect membrane fouling (2), such as mixed liquor suspended solids (MLSS) concentration (3,4), viscosity (5), floc size (6), extractable extra-cellular polymeric substances (eEPS) (7), and colloidal and soluble organic substances (8,9).

Some strategies have been proposed to mitigate fouling by modifying the characteristics of mixed liquors in MBRs, for instance, coagulant addition and oxidant addition (10–12). Coagulants, e.g., polymeric ferric sulphate, are able to enhance flocculation by charge neutrality and bridging and removing most of the colloids from the mixed liquor. The fouling propensity of mixed liquor is therefore reduced (10). Oxidants, e.g., ozone, are able to oxidize eEPS, change the surface properties of the sludge flocs and cause re-flocculation in the mixed liquor (12). Therefore, improving flocculability of the mixed liquor can be considered as an effective way to reduce the fouling propensity of the mixed liquor in MBRs.

pH is an important environmental factor. It significantly affects the constituents of eEPS (13), the stability of sludge flocs, and microbial growth (14), and therefore the flocculability and filterability of the mixed liquor (15), which is significantly relative to fouling in MBR. Thus, pH adjusting has been proposed in this study to reduce the fouling propensity of the mixed liquor. Exotic H^+ is expected to provide a positive charge like coagulants and reduce zeta-potential of the flocs. Exotic OH^- is able to release eEPS, which might change the surface properties of sludge flocs like ozone.

In this study, HCl and NaOH addition was applied to adjust the pH of the mixed liquor. Changes in the mixed liquor's membrane filterability under varying pH were first investigated. Changes in the mixed liquor properties with pH were further measured in detail. Accordingly, we proposed a mechanism for how pH adjusting reduces the fouling propensity of the mixed liquor.

MATERIALS AND METHODS

pH Adjusting for the Mixed Liquor

Fresh mixed liquor samples were taken from a pilot MBR in Qinghe municipal wastewater treatment plant in

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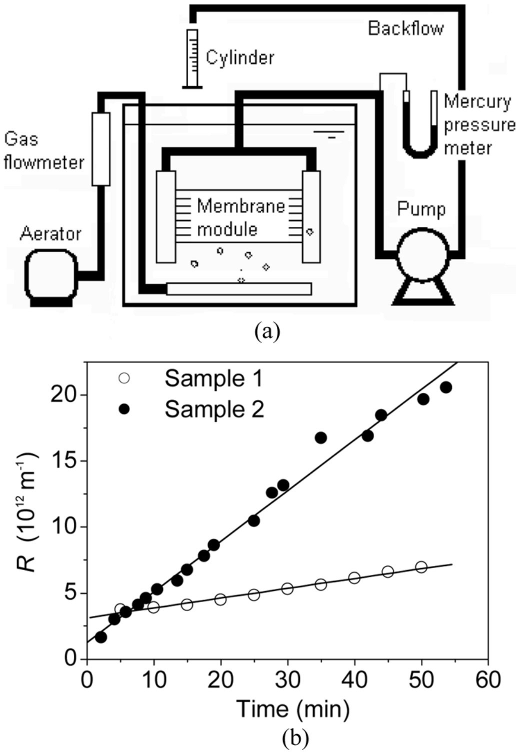
Beijing. The mixed liquor samples at pH of 7.0–7.5 were acidified with HCl solutions to pH of 4.0, 5.0, and 6.0 or alkalized with NaOH solution to the pH of 8.0, 9.0, and 10.0. At each pH, the membrane filterability and other physical, chemical, and biological properties of the mixed liquor samples were determined. After the membrane filterability measurement, the mixed liquor properties were measured again because aeration performed in the filterability tests might have caused the change in some of the properties. All the properties were analyzed in triplicate using parallel samples.

Measurement of the Mixed Liquor's Membrane Filterability

Membrane filterability of mixed liquors was determined using a mini-hollow fiber membrane module with a nominal pore size of 0.4 μm and a filtration area of 0.033 m^2. The module was set in a reactor with an effective volume of 3.0 L, as shown in Fig. 1a. The membrane material was polyethylene (Mitsubishi Rayon Co. Ltd., Japan). The mixed liquor sample was introduced to the reactor, aerated with a flow rate of $0.4\,m^3\,h^{-1}$ through a porous stone located beneath the module, and filtered through the membrane under the suction of a pump connected to the module. Aeration was performed to prevent sludge particles from being deposited on the membrane surface. The filtrate was returned to the reactor to maintain a stable liquid level and constant sludge concentration. With the mixed liquor filtered at a constant flux of $36\,L\,m^{-2}\,h^{-1}$, trans-membrane pressure (TMP) was monitored with time using a mercury pressure meter for about 30 min during the entire filtration process. Filtration resistances were then calculated using Darcy's equation:

$$R = \frac{\Delta P}{\mu J} \tag{1}$$

where R is the filtration resistance, m^{-1}; ΔP is the trans-membrane pressure, kPa; μ is the viscosity of the filtrate, Pa s; and J is constant flux, $36\,L\,m^{-2}\,h^{-1}$. A curve representing the increase of filtration resistance over time (R versus time) was obtained (Fig. 1b). The increase rate of filtration resistance with time (k_R, the slope coefficient of the trend line) was calculated as an indicator for the fouling propensity of the mixed liquor: the higher the k_R value, the poorer the membrane filterability of the mixed liquor.



(a)

(b)

FIG. 1. Membrane filterability evaluation test of mixed liquor: (a) Schematic representation of the mini-membrane filtration reactor; (b) Increase of filtration resistance over time for two samples.

Measurement of the Mixed Liquor Properties

Mixed liquor suspended solids (MLSS) and volatile suspended solids (MLVSS) were determined according to the standard methods (16). The eEPS was extracted using the formaldehyde-NaOH process, and then analyzed for total organic carbon (TOC) (17). The methods for determining colloidal and soluble organic materials were as described by Bouhabila et al. (18). Direct centrifugation (4500 rpm) for 1 min produced the supernatant, which contained colloidal and soluble materials. Flocculation with $Al_2(SO_4)_3$ at 250 mg L^{-1} and a second centrifugation (4500 rpm for 10 min) of the supernatant removed the colloids. In this way, two supernatant samples were available for TOC determination, which were the supernatant total organic concentration (TOC) and the soluble organic concentration (SOC). The difference between them is the colloidal organic concentration (COC). Separated from suspended solids, the supernatant sample was available for zeta-potential determination (ZetaPlus, Brook Heaven Co., USA). The settleability of the mixed liquors was evaluated by the sludge volume index (SVI), which was measured according to the standard methods (16) in a 1 L settling cylinder. The microbial activity of the activated sludge was measured in terms of specific oxygen uptake rate (SOUR) as described by Surmacz-Gorska et al. (19). The deviation of the measuring values of SOURs was less than 10%.

RESULTS AND DISCUSSION

Membrane Filterability of the Acidified Mixed Liquor at Various pHs

Figure 2 gives membrane filterability of the mixed liquor at various pHs when the mixed liquor samples were acidified by HCl. The increase rate of resistance k_R gradually decreased as the pH of the mixed liquor was reduced. In view of too low pH weakening the microbial activity, the lowest pH adjusted by HCl was set at 4.0. At this pH, k_R decreased 35% to $8.3 \times 10^{10}\,m^{-1}\,s^{-1}$, which was not too far different from k_R of $9.0 \times 10^{10}\,m^{-1}s^{-1}$, where the pH was adjusted to 6.0. It indicated that a small HCl amount (pH 6.0) was able to improve the membrane filterability of the mixed liquor. When compared to fouling limitation by coagulants and oxidants (10,12), the effectiveness of acidification did not appear to be that significant.

Characterization of the Acidified Mixed Liquor

In order to understand the performance of H^+ with the particles in the acidified mixed liquor, the mixed liquors at various pHs were characterized in terms of physical and chemical properties. Figure 3 exhibits two of them: the zeta-potential of the colloids and colloidal organic concentration. As the pH reduced by HCl addition, the absolute value of the zeta-potential of the colloids decreased, which implied the occurrence of an electric double layer compression. The colloidal organic concentration (COC) was reduced accordingly. The mechanisms could be proposed thus: HCl addition provided H^+ to the colloidal particles of negative charges in the mixed liquor. The zeta-potential of the colloidal particles was accordingly reduced by the electric double layer compression. The colloids lost stability and were removed from the supernatant. The reduction of the colloid amount reduced the fouling propensity of the acidified mixed liquor. Although HCl provided positive charge-like coagulants, its effect on the fouling limitation was not as significant as the coagulants' effect because coagulants, e.g., polymeric ferric sulphate, of macro-molecular weight are able to cause bridging as well.

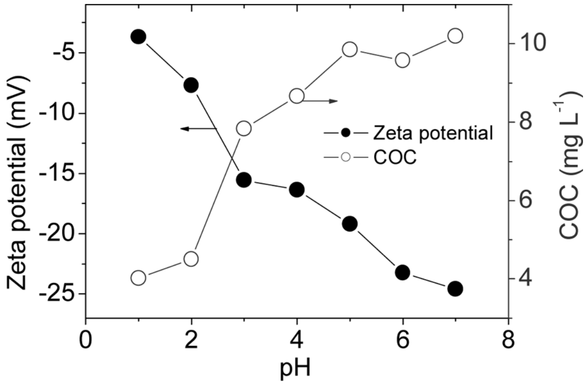


FIG. 3. Zeta-potential of the colloids and colloidal organic concentration in the acidified mixed liquor at various pHs.

Membrane Filterability of the Alkalified Mixed Liquor at Various pHs

Figure 4 gives membrane filterability of the mixed liquor at various pHs when the mixed liquor samples were alkalified by NaOH. In view of too high pH weakening the microbial activity, the highest pH adjusted by NaOH was set at 10.0. The increase rate of resistance k_R first decreased as the pH increased, reached the lowest value of $7.4 \times 10^{10}\,m^{-1}\,s^{-1}$ at pH of 8.5, and then increased back. At pH of 8.0–9.0, the membrane filterability of the mixed liquor was improved.

Characterization of the Alkalified Mixed Liquor

Improvement of Sludge Settleability

Change of SVI of the mixed liquor at various pHs is shown in Fig. 5. The lowest SVI and the lowest k_R value occurred at an almost the same pH (Fig. 4 and 5), which suggested the improvement of the membrane filterability

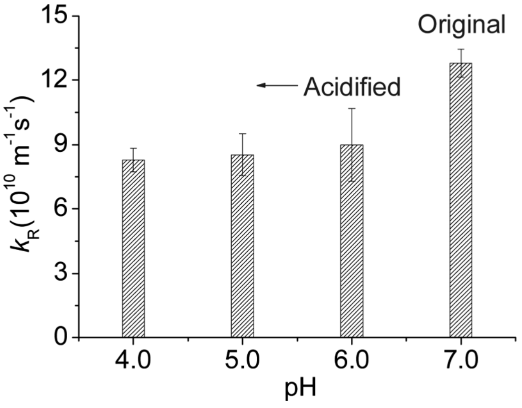


FIG. 2. Membrane filterability of the acidified mixed liquor by HCl at various pHs.

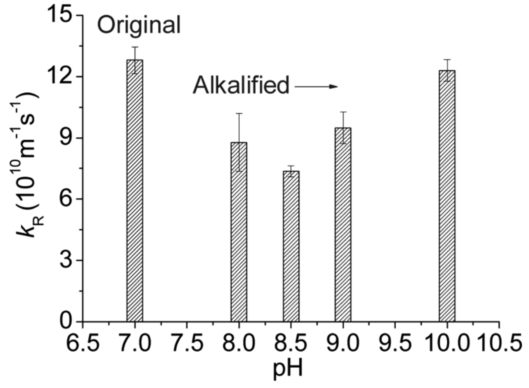


FIG. 4. Membrane filterability of the alkalified mixed liquor by NaOH at various pHs.

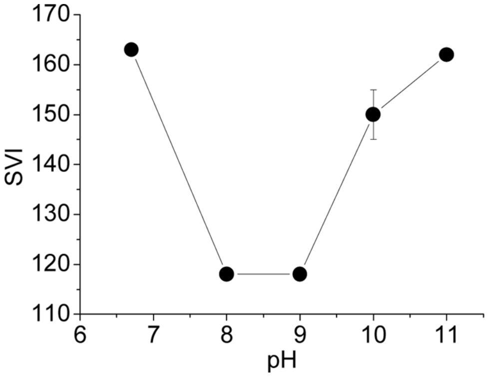


FIG. 5. SVI of the alkalified mixed liquor by NaOH at various pHs.

and the setteability of the mixed liquor at the same pH range.

Release of eEPS

Figure 6 shows that eEPS and the supernatant organic content in the alkalified mixed liquor at various pHs. As the pH increased, eEPS content significantly decreased; and the supernatant TOC concentration accordingly increased. It was confirmed that NaOH was effective in releasing eEPS, which has been applied to EPS extraction (17). More supernatant organics after alkalization was from the released eEPS.

Re-flocculation Caused by Released eEPS

In order to find out the reason that the membrane filterability of the alkalified mixed liquor was improved, the performance of the released eEPS was further studied. Figure 7 shows the zeta-potential of colloids in the supernatant of the alkalified mixed liquor. The absolute value of the zeta-potential was initially reduced and then increased as the pH increased. Thus, the mechanisms on alkalization were totally different from those of acidification.

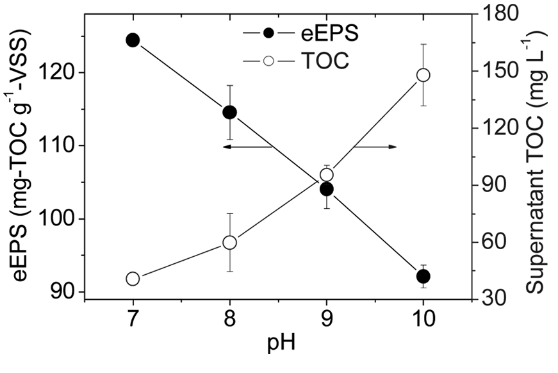


FIG. 6. eEPS and supernatant TOC concentration in the alkalified mixed liquor by NaOH at various pHs.

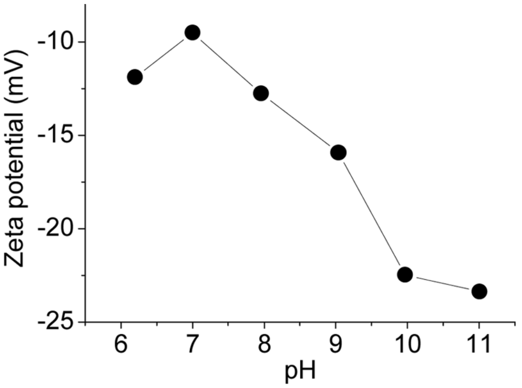


FIG. 7. Zeta-potential of the alkalified mixed liquor by NaOH at various pHs.

A further study on flocculation was carried out. The alkalified mixed liquors at pHs of 8.0 and 9.0 were mixed with the original mixed liquor without any treatment by 1:1. The determination of membrane filterability and supernatant organic concentration was carried out for the mixed samples (Table 1). The mixed samples featured a little better membrane filterability and less supernatant organics than the alkalified ones. Less supernatant organics indicated that re-flocculation occurred in the mixed samples.

The released eEPS played an important role in the re-flocculation process. eEPS are responsible for the structural and functional integrity of the aggregates (20). Abundant eEPS can hinder free bacterial solids suspended in the mixed liquor from coming into close contact with each other to integrate, while the decrease of abundant eEPS content can allow close contact between cells through aggregate restructuring (21). Thus, the extraction of eEPS by alkalization might be a possible reason for re-flocculation.

The mechanisms on alkalization could be proposed thus: at pH of 8.0–9.0, some eEPSs of much negative charges were released to the supernatant, which led to a change of the zeta-potential and re-flocculability of the sludge flocs. The fouling propensity of the mixed liquor was therefore reduced. On the other hand, excess supernatant organics and loose flocs at high pH resulted in severe fouling. Therefore, pH is recommended to 8.0–9.0.

Effect of pH Adjusting on Microbial Activity

Change of pH might adversely affect the microbial activity. Table 2 listed the effect of pH adjusting on microbial activity. From Table 2, it can be obviously be observed that all the acidified and alkalified samples attempted to recover their pH in 24 h. SOUR of the activated sludge was determined in order to know the effect of pH adjusting on microbial activity. The results indicated

TABLE 1
Membrane filterability and supernatant organic concentration of the mixed liquor mixed by alkalified and original mixed liquor at 1:1

Sample		$k_R(10^{10}\,m^{-1}min^{-1})$	Supernatant TOC ($mg\,L^{-1}$)
pH 8.0	Alkalified	9.90	58.12
	Mixed with original liquor	9.62	50.37
pH 9.0	Alkalified	10.72	71.10
	Mixed with original liquor	10.58	63.39

TABLE 2
SOUR of the activated sludge in the original, acidified and alkalified mixed liquor

Sample	Original	Acidified 1	Acidified 2	Alkalified
pH when adjusting	7.07	4.18	5.88	8.88
pH after 24 h	7.74	5.09	6.72	8.58
SOUR when adjusting (mg-O_2 g^{-1}-VSS d^{-1})	0.508	0.213	0.444	0.445
SOUR after 24 h (mg-O_2 g^{-1}-VSS d^{-1})	0.488	0.279	0.476	0.444

that the microbial activity of the mixed liquor adjusted at the pH of 4 was significantly weakened by acidification. However, microbial activity at pHs of 5.88 and 8.88 was reduced below 13%, which was a little higher than the deviation of the measuring SOURs (10%). Therefore, adjusting pH within 6.0–9.0 would not influence the wastewater treatment performance of an MBR system.

CONCLUSIONS

pH adjusting was able to reduce the fouling propensity of the mixed liquor in MBRs. The membrane filterability could be enhanced 35–45% when the mixed liquor was modified by HCl at pH 6.0 or by NaOH at pH 8.5.

When the mixed liquor was acidified by HCl at pH 6.0, HCl addition provided H^+ to the colloidal particles of negative charges in the mixed liquor. The zeta-potential of the colloidal particles was reduced by electric double layer compression. The colloids lost stability and were removed from the supernatant. Reduction of the colloid amount reduced the fouling propensity of the acidified mixed liquor.

When the mixed liquor was alkalified by NaOH at pH of 8.0–9.0, some eEPSs of much negative charges were released to the supernatant, which led to the increase of zeta-potential and improvement of re-flocculation. The fouling propensity of the mixed liquor was therefore reduced.

Microbial activity was affected by pH adjusting. Therefore, pH was recommended as 6.0 for acidification and 8.5 for alkalization. At the two pHs, SOUR was reduced blow 13%.

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