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Model-evaluation of the erosion behavior of activated sludge under shear conditions using a chemical-equilibrium-based model

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Abstract

The primary particles would erode from the sludge surface under shear conditions. As the primary particles have significant effects on the solid–liquid separation process, the erosion behaviors of activated sludge in biological wastewater treatment processes under shear conditions were investigated using a chemical-equilibrium-based model. The equilibrium dispersed mass concentration of the primary particles in the sludge solution was found to nonlinearly increase with the solid content and shear intensity, and could be well described by the model. Compared with other sludge reported in literatures, the activated sludge used in this study was found to be more stable during the shear test, with a high equilibrium constant K^0 of 30.2 and a low Gibbs' free energy of adhesion (ΔG^0) of -3.41 at a shear intensity of 800 s⁻¹. The two parameters could be used to evaluate the strength of the sludge. The negative value of ΔH indicates the energy demand for the erosion process. The low value of ΔH for the activated sludge used in this study.

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1. Introduction

Activated sludge process is widely used in biological wastewater treatment, and mainly employed for the treatment of domestic and municipal wastewater. The properties of sludge regulate the flocculation and settlement of the biomass and the performance of solid-liquid separation in a clarifier [1]. The loose structure of sludge greatly affects the solid-liquid separation efficiency in biological wastewater treatment systems [2,3]. Sludge flocs are a heterogeneous mixture of primary particles, microorganisms, colloids, extracellular polymeric substances and cations [4]. The primary particles have a significant effect on solid-liquid separation process, as a low primary particle concentration would bring a significant decrease in the solid-liquid separation efficiency. Under shear conditions, the primary particles would erode from sludge surface because of hydrodynamic shear force [5]. However, the behaviors of sludge under shear conditions have not been given sufficient attention yet. Although the complexity of sludge constituents and its chaotic structure

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1385-8947/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.cej.2007.10.001 make it difficult to study its behavior under shear conditions, it is of an engineering significance in biological wastewater treatment.

Some efforts have been made to characterize sludge behaviors by measuring the changes of sludge size distribution or sludge volume index under given shear conditions [6,7]. A dissociation constant was also employed to characterize the sludge strength [8,9]. A physically relevant index for describing the total network strength of sludge with rheological tests was proposed [10]. However, these methods may not be adequate for describing such a solid–liquid separation process, in which the primary particle concentration is essential.

A flocculation-deflocculation model was developed by Parker and co-workers [11] based on a mechanistic approach considering the balance of flocculation-deflocculation process. This effort has used to describe the concentration of primary particles in sludge suspension using mathematic methods based on sludge self-flocculation process, and is appropriate for describing the flocculation of activated sludge at low shear intensities [11]. Based on Langmuir adsorption isotherm theory, an adhesion–erosion model was established from a macroscopic viewpoint for quantifying the concentration of dispersed primary particles due to erosion under shear conditions [5,12]. However, these two models for describing the primary particle concentration of sludge suspension under shear conditions had limitations, e.g., the flocculation–deflocculation model was not applicable for describing the process at a high solid content or at a high shear intensity [5], the adhesion–erosion model had some limitation in the conditions of low shear intensity or high sludge content [13]. To solve these problems, a new model based on chemical equilibrium theory, was established to evaluate the behaviors of an anaerobic hydrogen-producing sludge [13]. This model assumed that there was a dynamic equilibrium between the primary particles and flocs under shear conditions, just like a reversible chemical reaction. The model is applicable to more actual conditions, even at high solid contents or low shear intensities.

The main objective of this work was to evaluate the behaviors of activated sludge under shear conditions using the chemical-equilibrium-based model. The relationships between the concentrations of dispersed primary particles and shear intensity or sludge content were investigated. The results of this study are useful for understanding the response of sludge to shear stress and for controlling hydrodynamic conditions in bioreactors.

2. Experimental

2.1. Sludge

The activated sludge was collected from an aeration tank at the Wangxiaoying Municipal Wastewater Treatment Plant in Hefei, China. Before use, the sludge was passed through 0.45-mm sieves and washed twice with tap water to remove the residual components and dispersed small particles. The sludge was then thickened to approximately $15-18 \text{ g SS L}^{-1}$ (SS: suspended solids). Afterwards, the samples were diluted to $1.5-10 \text{ g SS L}^{-1}$ for the shear tests. The SS of the sludge samples were determined according to the Standard Methods [14].

2.2. Shear tests

In all of the shear tests a baffled paddle-mixing chamber was used at 20-25 °C. The initial testing volume was 1000 mL. Sludge was sheared at a pre-determined shear intensity by mechanical stirring with a flat paddle mixer (JJ-4, JCGS Instrument Co., Jiangsu, China). The shear intensity was quantified by the root-mean-square velocity gradient (G): $G = \sqrt{P/\eta V}$, where P is the power input, η is the fluid viscosity and V is the suspension volume [5]. The actual G during a test was achieved by adjusting the paddle rotation rate in rpm based on a laboratory calibration of G versus rpm. Since the sludge solutions are non-Newtonian fluids, the sludge content has an influence on the sludge viscosity and the calculation of G, especially at a high SS sludge content (above 20 g L^{-1}) [15]. In the present work, the sludge content ranged between 1.2 and 8.0 g L^{-1} only, and previous results demonstrated that a low sludge content would have little influence on the viscosity of sludge solutions. Thus, the viscosity of water was used for the calculation of the shear

intensity *G* in this work. The release of cells and small particles as a result of shear was determined by the change in the supernatant turbidity. Samples of 3 mL were withdrawn from the testing chamber at pre-determined time intervals for the turbidity measurement. The turbidity was measured from the absorbance at 650 nm (UV751GD, Analytical Instrument Co., Shanghai, China) for the supernatant following 2 min of centrifugation at 2200 rpm. The dispersed mass concentration was then estimated using the turbidity/SS-concentration conversion factor given by Wahlberg et al. [11].

2.3. Chemical-equilibrium-based model

In sludge suspension, the particle size distribution is bimodal, mainly containing two particle classes, i.e., primary particles $(0.5-5 \mu m)$ and flocs $(25-100 \mu m)$ [5]. Assuming that there is a dynamic equilibrium between the primary particles and flocs under shear conditions, just like a reversible chemical reaction. The thermodynamic equilibrium constant K^0 at a constant shear intensity could be expressed as follows in terms of mass concentration [13]:

$$K^{0} = \frac{m_{\rm T} - m_{\rm d,\infty}}{m_{\rm d,\infty}^{\alpha}} \tag{1}$$

in which α is the characteristic parameter of sludge, $m_{\rm T}$ is the sludge content, $m_{\rm d,\infty}$ represents the equilibrium mass concentration of dispersed primary particles, and could be estimated using a diffusion equation [5]:

$$m_{d,t} = m_{d,\infty} + (m_{d,0} - m_{d,\infty}) \frac{6}{\pi^2} \sum_{N=1}^{9} \frac{1}{N^2} e^{-N^2 Dt}$$
(2)

where $m_{d,0}$ and $m_{d,t}$ are the dispersed mass concentrations of primary particles at initial time and time *t*, respectively, *N* is an integer and *D* is an effective diffusion constant.

The Gibb's energy of adhesion at a constant shear intensity could be estimated from the following physicochemical equation:

$$\Delta G^0 = -RT \ln K^0 \tag{3}$$

Based on the physicochemical principles, the change in the Gibb's energy can show the direction of equilibrium shift between primary particles and flocs.

Eq. (1) could be rearranged into:

$$m_{\rm T} = m_{\rm d,\infty} + K^0 m_{\rm d,\infty}^{\alpha} \tag{4}$$

From the non-linear regression between $m_{\rm T}$ and $m_{\rm d,\infty}$, the values of K^0 and α could be calculated at a constant shear intensity.

In the experiments for strength testing, the effect of shear intensity could be treated by analogy with that of temperature at a conventional chemical equilibrium [5]. The van't Hoff equation can be integrated into:

$$\ln K^0 = -\frac{\Delta H}{R} \frac{1}{G} + q \tag{5}$$

in which ΔH is the change in enthalpy of sludge adhesion, and is independent of shear intensity, *R* is the gas constant and *q* is a constant without dimension.

Introduction of Eqs. (1)–(5) gives:

$$\ln\left(\frac{m_{\rm T} - m_{\rm d,\infty}}{m_{\rm d,\infty}^{\alpha}}\right) = -\frac{\Delta H}{R}\frac{1}{G} + q \tag{6}$$

With this equation, a plot of $\ln[(m_{\rm T} - m_{\rm d,\infty})/m_{\rm d,\infty}^{\alpha}]^{3.98}$ versus 1/*G* is expected to give a straight line with a slope of $-\Delta H/R$ and an intercept of *q*.

3. Results and discussion

3.1. Erosion kinetic curves

A series of shear experiments were conducted to determine the effects of the solid content and shear intensity on the dispersed mass concentration $(m_{d,\infty})$ in the sludge suspensions. The typical sludge erosion curves at various solid contents and shear intensities can be fitted by Eq. (2) as shown in Fig. 1. The supernatant turbidity increased rapidly after the sludge was exposed to the turbulent shear, and then leveled off 3 h later. The erosion rates were significantly affected by both solid content and shear intensity. With an increase in solid content or shear intensity, the erosion rates increased. A regression was performed with the data in Fig. 1 using Eq. (2), and the values of $m_{d,\infty}$ at various solid contents and shear intensities could be estimated, as listed in Table 1. These values could be used to describe the effects of solid content and shear intensity on $m_{d,\infty}$.



Fig. 1. Typical erosion curves of activated sludge obtained at: (a) various solid contents and (b) shear intensities. The lines were regressed using Eq. (2).

Table 1 $m_{d,\infty}$ and standard deviations (in parentheses) calculated from Eq. (2)

$m_{\rm T}$ (g SS L ⁻¹)	$G(s^{-1})$	$m_{\rm d,\infty} ({\rm gSSL^{-1}})$	R^2
1.24	800	0.044 (0.002)	0.748
2.18	800	0.060 (0.001)	0.918
	270	0.023 (0.006)	0.861
	500	0.0785 (0.002)	0.756
	800	0.098 (0.001)	0.903
	1060	0.221 (0.003)	0.957
	1400	0.274 (0.003)	0.974
6.05	800	0.163 (0.004)	0.756
7.96	800	0.236 (0.005)	0.812

3.2. Effect of solid content on $m_{d,\infty}$

The effect of the solid content on $m_{d,\infty}$ for activated sludge at $G = 800 \text{ s}^{-1}$ is illustrated in Fig. 2, in which the curves are drawn with the linear regression results of Eq. (4). The estimates of α and K^0 values at $G = 800 \text{ s}^{-1}$ by the non-linear regression of $m_{d,\infty}$ versus m_T using the Origin 7.0 software are listed in Table 2. The high coefficient of determination indicates that Eq. (4) can be used to describe the effect of solid content on $m_{d,\infty}$. The $m_{d,\infty}$ value significantly increased with increasing solid content.

3.3. Effect of shear intensity on $m_{d,\infty}$

The estimated $m_{d,\infty}$ values at different shear intensities and regression results are shown in Fig. 3. The shear intensity also had a profound effect on the erosion of the cells from the sludge flocs. An increase in shear intensity resulted in a higher $m_{d,\infty}$ for the activated sludge. All the experimental results could be well fitted with the model (Fig. 3). This demonstrates that the present approach was appropriate for describing the effect of shear intensity on $m_{d,\infty}$ under shear conditions. An increase in shear intensity always resulted in a nonlinear increase in $m_{d,\infty}$. However, the shear intensity had a slight effect on $m_{d,\infty}$ at a high shear intensity domain (Fig. 1b). From the linear regression



Fig. 2. Change in $m_{d,\infty}$ as a function of the solid content $m_{\rm T}$ at $G = 800 \,{\rm s}^{-1}$ for the activated sludge.

Sludge	K ^{0a}	$\Delta G^0/RT^a$	α	$\Delta H/R~(\mathrm{s}^{-1})$	q	Reference
AAE sludge ^b	12.3 (0.1)	-2.51 (0.01)	0.74 (0.01)	-438 (20)	1.96 (0.02)	[5]
HS sludge ^b	14.7 (0.5)	-2.69(0.03)	0.65 (0.03)	-436 (21)	2.36 (0.02)	
Hydrogen-producing sludge	6.54 (0.12)	-1.88(0.02)	0.88 (0.07)	-426 (38)	1.22 (0.07)	[13]
Activated sludge	30.2 (4.1)	-3.41 (0.14)	0.93 (0.08)	-717 (1)	2.25 (0.02)	Present study

The estimates and standard deviations (in parentheses) of model	parameters from Eq	ıs. (3), (•	4) and (6) fo	r four types of	sludge
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^a Obtained at $G = 800 \text{ s}^{-1}$.

^b The original data were obtained from Reference [5], and were recalculated according to the chemical-equilibrium-based model.

between $\ln[(m_{\rm T} - m_{\rm d,\infty})/m_{\rm d,\infty}^{\alpha}]$ and 1/G, the values of $\Delta H/R$ and q were estimated and are listed in Table 2. The high coefficient of determination value (0.964) suggests that the present model is valid.

3.4. Comparison with the flocculation–deflocculation model

Based on a mechanistic approach with consideration of the balance in adsorption–erosion process, a flocculation–deflocculation model was developed to describe the sludge flocculation process [11]. From the erosion kinetic curves, the value of equilibrium dispersed primary particles concentration could be estimated as follows:

$$m_{\rm d,t} = m_{\rm d,\infty} + (m_{\rm d,0} - m_{\rm d,\infty}) e^{-k_{\rm A} m_{\rm T} G t}$$
(7)

where k_A is flocculation rate constant. In this equation, the value of $m_{d,\infty}$ could also be expressed as:

$$m_{\rm d,\infty} = \frac{k_{\rm B}G}{k_{\rm A}} \tag{8}$$

Thus, the break-up rate constant $k_{\rm B}$ could be calculated by the following equation:

$$k_{\rm B} = \frac{m_{\rm d,\infty}k_{\rm A}}{G}.$$
(9)

Fig. 4 shows the regression curves of the erosion kinetic curves of the activated sludge under various sludge contents and shear intensities, and Table 3 lists the regression results using Eq. (7). Comparison between the regression results obtained from



Fig. 3. Change in $m_{d,\infty}$ as a function of *G* for the activated sludge at $m_T = 3.98 \text{ g SS L}^{-1}$.

Eqs. (2) and (7) shows that the coefficients of determination using Eq. (2) were higher than those using Eq. (7). This suggests that it was better to model the erosion kinetic curves using Eq. (2). However, there was no significant difference between the values of $m_{d,\infty}$ of sludge estimated from Eqs. (2) and (7).

In the flocculation–deflocculation model, the flocculation and break-up coefficients k_A and k_B were constants relevant to the adhesion energy between sludge cells. Thus, according to Eq. (8), the value of $m_{d,\infty}$ should have a linear relationship with the shear intensity, but had no relationship with the sludge content m_T . However, as listed in Table 3, the values of $m_{d,\infty}$ increased with the increasing sludge content at a shear intensity of $800 \, \text{s}^{-1}$. Furthermore, the values of $m_{d,\infty}$ did not linearly increase with the increasing shear intensity at the same sludge content. This might be explained by the fact that the values of k_A and k_B were not independent of shear intensity and sludge content, as shown in Table 3. These results suggest that the flocculation–deflocculation model might not be appropriate



Fig. 4. Typical erosion curves of activated sludge under shear conditions at: (a) various solid contents and (b) shear intensities. The lines were regressed using Eq. (7).

Table 2

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Table 3 $m_{d,\infty}$ and standard deviations (in parentheses) calculated from Eq. (7)

$\overline{m_{\rm T}~({\rm g~SS~L^{-1}})}$	$G(s^{-1})$	$k_{\rm A} (\times 10^{-7}{\rm Lg^{-1}})$	$k_{\rm B}~(\times 10^{-11}~{\rm s})$	$k_{\rm B}/k_{\rm A}~(\times 10^{-4}{\rm sgL^{-1}})$	$m_{\rm d,\infty} ({\rm gSSL^{-1}})$	R^2
1.24	800	8.01 (3.24)	4.42 (1.96)	0.55 (0.03)	0.044 (0.002)	0.683
2.18	800	3.84 (0.75)	2.92 (0.63)	0.76 (0.02)	0.061 (0.001)	0.903
	270	33.73 12.02	64.84 (24.60)	1.92 (0.04)	0.052 (0.001)	0.711
	500	3.83 (1.25)	6.01 (2.12)	1.57 (0.04)	0.078 (0.002)	0.742
3.98	800	4.33 (0.83)	5.51 (1.13)	1.27 (0.02)	0.102 (0.001)	0.902
	1060	2.75 (0.44)	5.68 (1.00)	2.06 (0.04)	0.219 (0.004)	0.931
	1400	1.76 (0.23)	3.42 (0.49)	1.94 (0.03)	0.272 (0.004)	0.955
6.05	800	3.10 (0.92)	6.26 (2.00)	2.02 (0.05)	0.161 (0.004)	0.779
7.96	800	1.59 (0.52)	4.20 (1.49)	2.64 (0.06)	0.211 (0.005)	0.773

for describing the erosion phenomena of activated sludge under shear conditions.

3.5. Significance of the model

The shear tests were used to evaluate the erosion behavior of microbial sludge in many studies. Several types of sludge were used to confirm that the model was appropriate for studying sludge erosion behavior [13]. For comparison, the parameters of sludge used in other works are also listed in Table 2. The K of the activated sludge used in the present study was larger than those of other sludge, including the activated sludge reported by Mikkelsen and Keiding [5], and the hydrogen-producing sludge tested by Sheng and Yu [13]. These results imply that the erosion of the activated sludge used in this study was lower than those of the various sludges in other studies. This might be associated with the sludge structure and cultivation conditions. The erosion behavior of sludge under shear conditions would be related to the free energy, enthalpy and equilibrium constant of adhesion. The negative value of ΔH indicates the energy demand for the erosion process. The lower value of ΔH for the sludge used in this study suggests that the erosion process was more energy demanding than the other sludges, which in turn made the erosion process less shear dependent. This implies that an increase in shear had a relatively low effect on the sludge. According to the chemical-equilibrium-based model, with an increase in shear intensity G, the ΔG^0 value increased, but the K^0 value decreased, whereas the ΔH value was independent of G. The ΔG^0 value could reflect the stability of sludge against shear [13]. As shown in Table 2, the $\Delta G^0/RT$ value for the sludge used in this study was lower than those of other sludges reported previously, implying that the sludge used in this study had a greater stability.

In addition to the sludge type, the sludge solution conditions (e.g., pH, and ionic strength) could also influence the sludge erosion behavior. The binding between bacterial cells is attributed to various types of intermolecular interactions, such as van der Waal's force, electrostatic forces, ion bridging interaction, and hydrophobic interaction, etc. [3]. An increase in solution pH will induce ionization of many charged functional groups on cell surfaces. This would result in a stronger repulsion between the cells and hence weakens the sludge stability. An increase in solution ionic strength could compress the thickness of the double electric layer and reduce the repulsive electrostatic force, which make sludge become stable.

In the present study, a macroscopic approach based on chemical equilibrium theory was used to evaluate the erosion phenomena of sludge, which has crucial effects on the solid-liquid separation efficiency and the effluent quality in a biological wastewater treatment system. Even a small amount of primary particles eroded from sludge induced by hydrodynamic or mechanic shears would have a significant impact on the solid-liquid separation efficient and the SS concentration in the effluent. Thus, an investigation into the erosion phenomena of sludge under shear conditions would provide useful information for reducing the effluent SS level. In order to operate the treatment systems efficiently, sludge with a high strength should be selected to withstand the turbulent shear. To obtain goodquantity effluent, the shear intensity and solid content should be controlled in accordance with the sludge characteristics. The application of the chemical-equilibrium-based model can provide one approach to evaluate the erosion phenomena of sludge under shear conditions. The estimates of $m_{d,\infty}$ at various G values would be useful for monitoring the effluent quantity of a wastewater treatment plant. The model parameters reflected the characteristics of sludge and could be used to calculate the primary particle concentration in sludge suspension. Thus, the solid-liquid separation efficiency in the wastewater treatment plants could also be evaluated quantitatively from the sludge characteristics.

4. Conclusions

Experiments were carried out to investigate the erosion behavior of activated sludge in a full-scale municipal wastewater treatment plant under shear conditions using a chemicalequilibrium-based model. The equilibrium dispersed mass concentration of the primary particles in the sludge solution was found to nonlinearly increase with the solid content and shear intensity, and could be well described by the model. Compared with other types of sludge reported in literatures, the activated sludge used in this study was found to be more stable during the shear test, with a high equilibrium constant K^0 of 30.2 and a low Gibbs' free energy of adhesion (ΔG^0) of -3.41 at a shear intensity of 800 s⁻¹. The negative value of ΔH indicates the energy demand for the erosion process.

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References

- B. Jin, B.M. Wilen, P. Lant, A comprehensive insight into floc characteristics and their impact on compressibility and settleability of activated sludge, Chem. Eng. J. 95 (2003) 221–234.
- [2] B.M. Wilen, B. Jin, P. Lant, Impacts of structural characteristics on activated sludge floc stability, Water Res. 37 (2003) 3632–3645.
- [3] G.P. Sheng, H.Q. Yu, X.Y. Li, Stability of sludge flocs under shear conditions: roles of extracellular polymeric substances (EPS), Biotechnol. Bioeng. 93 (2006) 1095–1102.
- [4] J. Wingender, T.R. Neu, H.C. Flemming, Microbial Extracellular Polymeric Substances: Characterization, Structures and Function, Springer-Verlag, Berlin, Heidelberg, 1999.
- [5] L.H. Mikkelsen, K. Keiding, Equilibrium aspects of the effects of shear and solids content on aggregate deflocculation, Adv. Colloid. Interface Sci. 80 (1999) 151–182.
- [6] C.A. Biggs, P.A. Lant, Activated sludge flocculation: on-line determination of floc size and the effect of shear, Water Res. 34 (2000) 2542–2550.

- [7] M.A. Seka, W. Verstraete, Test for assessing shear sensitivity of activated sludge flocs: a feasibility study, Water Res. 37 (2003) 3327– 3334.
- [8] A. Zita, M. Hermannsson, Effects of ionic strength on bacterial adhesion and stability of flocs in a wastewater activated sludge system, Appl. Environ. Microbiol. 60 (1994) 3041–3048.
- [9] B.Q. Liao, D.G. Allen, G.G. Leppard, I.G. Droppo, S.N. Liss, Interparticle interactions affecting the stability of sludge flocs, J. Colloid. Interface Sci. 249 (2002) 280–372.
- [10] P.S. Yen, L.C. Chen, C.Y. Chien, R.M. Wu, D.J. Lee, Network strength and dewaterability of flocculated activated sludge, Water Res. 36 (2002) 539–550.
- [11] E.J. Wahlberg, T.M. Keinath, D.S. Parker, Influence of activated sludge flocculation time on secondary clarification, Water Environ. Res. 66 (1994) 779–786.
- [12] T. Mascarenhas, L.H. Mikkelsen, P.H. Nielsen, Effects of chlorination on the adhesion strength and deflocculation of sludge flocs, Water Environ. Res. 76 (2004) 327–333.
- [13] G.P. Sheng, H.Q. Yu, Chemical-equilibrium-based model for describing the strength of sludge: taking hydrogen-producing sludge as an example, Environ. Sci. Technol. 40 (2006) 1280–1285.
- [14] APHA, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, New York, 1995.
- [15] I. Seyssiecq, J.H. Ferasse, N. Roche, State-of-the-art: rheological characterization of wastewater treatment sludge, Biochem. Eng. J. 16 (2003) 41–56.