Journal of Hazardous Materials B123 (2005) 145–150

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration

Fen Wang [a,*], Yong Wang [b], Min Ji [a]

[a] School of Environmental Science and Technology, Tianjin University, Weijin Road 92, Nankai District, Tianjin 300072, China

[b] North China Municipal Engineering Design & Research Institute, Tianjin 300074, China

Received 28 October 2004; received in revised form 3 March 2005; accepted 14 March 2005
Available online 29 April 2005

Abstract

Ultrasonic energy can be applied as pre-treatment to disintegrate sludge flocs and disrupt bacterial cells' walls, and the hydrolysis can be improved, so that the rate of sludge digestion and methane production is improved. In this paper, by adding $NaHCO_3$ to mask the oxidizing effect of $^{\bullet}OH$, the mechanisms of disintegration are investigated. In addition, kinetics models for ultrasonic sludge disintegration are established by applying multi-variable linear regression method. It has been found that hydro-mechanical shear forces predominantly responsible for the disintegration, and the contribution of oxidizing effect of $^{\bullet}OH$ increases with the amount of the ultrasonic density and ultrasonic intensity. It has also been inferred from the kinetics model which dependent variable is $SCOD_+$ that both sludge pH and sludge concentration significantly affect the disintegration.

Keywords: Ultrasound; Disintegration; Waste activated sludge; $NaHCO_3$; Multi-variables linear regression

1. Introduction

Anaerobic digestion is widely used for sewage sludge stabilization, resulting in the reduction of sludge and the production of biogas. However, the anaerobic digestion is a slow process, which results in a long residence time in the digestion tank and the requirement of a large tank volume. It had been identified by Eastman and Ferguson [1] and Shimizu et al. [2] that the hydrolysis of waste activated sludge (WAS) is the rate-limiting step. Therefore, pre-treatment of waste activated sludge has been developed to improve anaerobic digestion, and it includes mechanical [3–7], chemical [8–13] and thermal [14] disintegration.

Ultrasound is well known to disintegrate sludge flocs and disrupt microbial cell walls, and it causes the release of soluble substances. Tiehm et al. [5] showed that applying ultrasound (3.6 kW, 31 kHz, 64 s) to sludge disintegration can release the organic substances into the sludge, so that the soluble chemical oxygen demand (SCOD) in the supernatant increases from 630 to 2270 mg/L. Moreover, the digestion time could be reduced to 8 days. Lee and co-workers [7] demonstrated that "weak" ultrasound pre-treatment greatly increased both the production rate and ultimate yield of methane. Chiu et al. [12] observed simultaneous alkaline and ultrasound pre-treatment was more effective in releasing SCOD.

As for the mechanisms of ultrasonic disintegration, Tiehm et al. [5] noted that hydromechanical shear forces produced by ultrasonic cavitation were predominantly responsible for sludge disintegration. However, it is still unclear about the other contributions to the ultrasonic waste activated sludge disintegration. In the article, we obtain more sight into the mechanisms of ultrasonic sludge disintegration. Based on the test data, the kinetics models for ultrasonic sludge disintegration have been established.

* Corresponding author. Tel.: +86 22 27404005; fax: +86 22 27406057.
E-mail addresses: tjuwf@163.com (F. Wang), jimin@tju.edu.cn (M. Ji).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.03.033

2. Materials and methods

2.1. Waste activated sludge

The WAS in the disintegration study was obtained from a laboratory sequencing batch reactor (SBR). The seeding sludge was collected from a membrane bioreactor (MBR), which handles washing and bathing wastewater in Tianjin University. The SBR was operated three cycles per day, and the solid residence time (SRT) was maintained at 13.3 days. Synthetic wastewater was used for the operation; carbon, nitrogen and phosphorous sources were from glucose, ammonium chloride (or ammonium sulfate) and potassium dihydrogen phosphate (or dipotassium hydrogen phosphate), respectively. The influent BOD was about 420 mg/L. The ratio of biological oxygen demand (BOD): N:P was kept at 100:5:1. During the steady state, the mix-liquor suspended solids (MLSS) concentration was maintained at about 5000–6000 mg/L. The sludge at the end of the cycle, solid content about 0.5%, was taken for the study, or the sludge is precipitated gravitationally until the volume of sludge was reduced by 50%. Then the supernatant is decanted and the thickened sludge (solid content of about 1%) is used for the pre-treatment. The total chemical oxygen demand (TCOD) of the raw sludge in the end of the cycle and the thickened sludge were 6000–6500 and 10,000–12,000 mg/L, respectively.

2.2. Ultrasonic setup

Fig. 1 shows the diagram of the ultrasonic waste activated sludge disintegration. It was produced in Xinzhi Bio-instrument Ltd. The ultrasonic energy output is 300–200 W, its frequency is set at 20 kHz, and its probe diameter is 20 mm. The probe is immersed 10 mm into the sludge during disintegrating. To investigate the disintegration results under alkaline condition, 1 M NaOH and 1 M H_2SO_4 are used to adjust pH of sludge sample before disintegrated.

The degree of sludge disintegration is assessed by determining the COD difference in the sludge supernatant, and the augment of SCOD is defined as the SCOD difference before and after disintegration ($SCOD_+$). The physical meaning for $SCOD_+$ is the substance that can be readily used to produce methane in the anaerobic digestion. The percentage of releasing SCOD is calculated as the ratio of $SCOD_+$ to the TCOD, and it is abbreviated as $SCOD_{\%}$. The physical meaning for $SCOD_{\%}$ is the degree of sludge disintegration.

2.3. Analytical procedures

COD and TS were determined according to *standard methods* [15].

2.4. Disintegration mechanisms

There are four paths, which are shown as following, responsible for the ultrasonic activated sludge disintegration:

- hydro-mechanical shear forces;
- oxidizing effect of •OH, •H, •N and •O produced under the ultrasonic radiation;
- thermal decomposition of volatile hydrophobic substances in the sludge;
- increase of temperature during ultrasonic activated sludge disintegration.

If the sludge temperature improved, the lipid on the cytoplasmic membrane can be decomposed, which results in the generation of little holes on the membrane. The intracellular substances can release through the holes, which causes the increase of SCOD in the supernatant.

Because the quantity of volatile hydrophobic substances in the sludge is very low, so the third path can be ignored. The increment speed in sludge temperature is slow. In this research, the longest disintegration time is 60 min and the disintegrated sludge temperature is increased to 82 °C. According to our study on thermal sludge disintegration, improving the sludge temperature to 80 °C in 1 h produces low $SCOD_+$ and $SCOD_{\%}$. Therefore, the forth can also be neglected. As for the second path, Hart [16,17] has demonstrated that the amount of •OH is much more than the one of •H, •N and •O. Accordingly, the oxidizing effect of •H, •N and •O can be ignored. From the above analysis, we know there are two

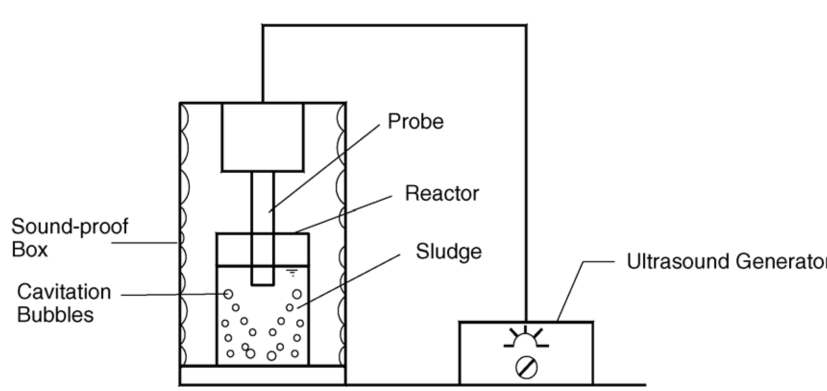

Fig. 1. Scheme of ultrasonic activated sludge disintegration.

main paths attributed to the ultrasonic sludge disintegration, namely hydro-mechanical shear forces and the oxidizing effect of •OH.

In this paper, $NaHCO_3$ is added to the sludge before disintegration to mask the oxidizing effect of HO•. By observing the difference of $SCOD_{\%}$ before and after disintegration, the mechanisms of ultrasonic activated sludge disintegration are identified. The chemical relationship between •OH and $NaHCO_3$ is shown as Eq. (1).

$$HCO_3{}^- + HO \rightarrow CO_3{}^{2-} + H_2O \quad (1)$$

The reason that choosing $NaHCO_3$ as masking agent is that the above reaction rate constant k is $8.5 \times 10^6\ M^{-1}\ S^{-1}$, while the constant for the reaction between $NaHCO_3$ and activated sludge is very low. Therefore, during ultrasonic disintegration, the reaction between •OH and $NaHCO_3$ is a high-priority one. For the amount of •OH produced is low, which is only several hundreds micromolar [18], the amount of $NaHCO_3$ added to the sludge is enough to react with •OH, and the reaction between •OH and activated sludge is almost inhibited. Consequently, after adding enough amount of $NaHCO_3$ to the sludge before disintegration, the disintegration can be thought to be the effect of hydro-mechanical shear forces only.

3. Results and discussions

3.1. Disintegration mechanisms

In this article, the ultrasonic density ranges between 0.096 and 0.72 W/mL. Correspondingly, the ultrasonic intensity ranges between 30.56 and 229.2 W/cm^2. $NaHCO_3$ with a quantity of 10 or 50 mM is added to the sludge with solid content of 0.5%.

When the applied ultrasonic density is 0.096 W/mL and ultrasonic intensity is 30.56 W/cm^2, $SCOD_{\%}$ with $NaHCO_3$ addition, the oxidation effect is a little more than the one without $NaHCO_3$ addition. This indicates that there barely exists an oxidizing effect of •OH. The increase of $SCOD_{\%}$ is a result of the improvement of sludge pH (about 7.1–7.4).

Before $NaHCO_3$ is added to the sludge, the $HCO_3{}^-$ concentration is very low; the disintegration is a result of hydro-mechanical shear forces and oxidizing effect of •OH. As can be seen from Fig. 2, when $HCO_3{}^-$ concentration is 10 or 50 mM, it is the hydro-mechanical shear forces that are predominantly responsible for the disintegration. The reaction of disintegration is a first-order one, and the reaction of disintegration under the effect of hydro-mechanical shear forces is also a first-order one. So the reaction under oxidizing effect only is also a first-order one.

The total reaction rate constant u can be expressed as Eq. (2):

$$u = u_{\bullet OH} + u_{HSF} \quad (2)$$

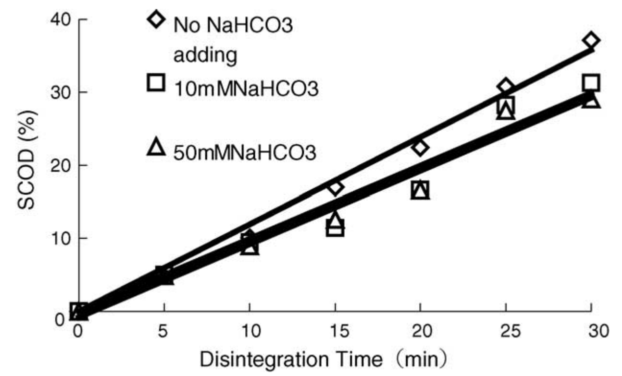

Fig. 2. Comparison of $SCOD_{\%}$ between $NaHCO_3$ adding and no $NaHCO_3$ addition, when the applied ultrasonic density is 0.384 W/mL and ultrasonic intensity is 122.23 W/cm^2.

where, $u_{\bullet OH}$ is the reaction constant under oxidizing effect only and u_{HSF} is the reaction constant under the effect of hydro-mechanical shear forces.

When $HCO_3{}^-$ concentration is 10 or 50 mM, Eq. (2) can be simplified to Eq. (3).

$$u = u_{HSF} \quad (3)$$

In Table 1, the reaction constant at different $HCO_3{}^-$ concentration is shown.

As shown in Table 1, u, $u_{\bullet OH}$ and u_{HSF} can be calculated. It can be concluded that when the sludge is disintegrated at the ultrasonic density of 0.384 W/mL, the contributions of hydro-mechanical shear forces and the oxidizing effect of •OH are 80.85% and 19.15%, respectively; when the applied ultrasonic density is 0.72 W/mL, the contributions of the two factors are 74.14% and 25.86%, respectively. However, when the applied ultrasonic density is 0.096 W/mL, the predominant contribution to the disintegration is hydro-mechanical shear forces, and oxidizing effect of •OH has almost no impact on the disintegration. It can be inferred that the contribution of oxidizing effect of •OH becomes more and more as the augment of ultrasonic intensity.

3.2. Establishment of reaction kinetics models

As demonstrated in Fig. 3, when the disintegration time is 10 min at 1.44 W/mL, the $SCOD_+$ can reach 2785 and

Table 1
The value of u under different $HCO_3{}^-$ concentration when the ultrasonic density is 0.384 and 0.72 W/mL

	u	R^2
0.384 W/mL		
0	1.1921	0.9911
10 mM	0.9956	0.9545
50 mM	0.9638	0.9688
0.72 W/mL		
0	1.7648	0.9377
10 mM	1.283	0.9909
50 mM	1.3084	0.9618

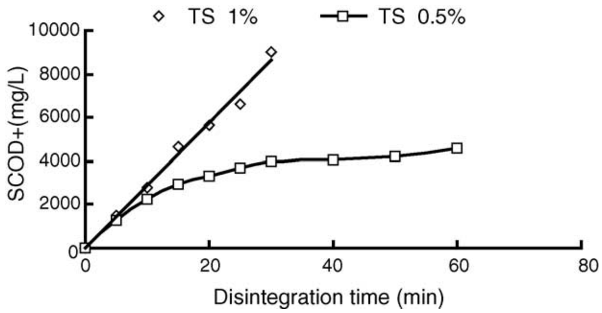

Fig. 3. SCOD change at ultrasonic density of 1.44 W/mL for two different solid contents.

2261 mg/L for the solid content of 1% and 0.5%, respectively. And when the disintegration time is 30 min at 1.44 W/mL, the $SCOD_+$ can reach 9019 and 3966 mg/L for the solid content of 1% and 0.5%, respectively. Therefore, sludge concentration has significant impact on the $SCOD_+$. In this research, we found that the reaction of disintegration fits well with a first-order kinetic equation within 30 min. However, as indicated in Fig. 3, applying ultrasonic density of 1.44 W/mL to the disintegration the sludge with solid content of 0.5% for 20 min, $SCOD_+$ reaches 3000 mg/L. The trend of the increase of $SCOD_+$ becomes slow as the disintegration time increases. However, to unify the disintegration time, only the data in which disintegration time is within 30 min were chosen as the samples to establish the models. In this research, the disintegration of sludge with solid content 0.5% at 1.44 W/mL is considered as an approximate first-order one. As can be seen in Figs. 4–6, ultrasonic intensity, ultrasonic density and pH all have impact on the sludge disintegration. Therefore, sludge concentration, ultrasonic intensity, ultrasonic density, pH and disintegration time are chosen as the independent variables, and $SCOD_+$ and $SCOD_{\%}$ are chosen as dependent variables. The mathematical forms are shown as Eqs. (4) and (5):

$$\frac{\mathrm{d}(SCOD_+)}{\mathrm{d}t} = k \tag{4}$$

$$\frac{\mathrm{d}(SCOD_{\%})}{\mathrm{d}t} = u \tag{5}$$

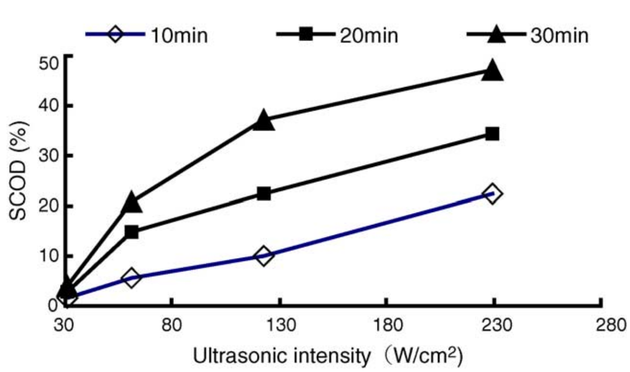

Fig. 4. $SCOD_{\%}$ at different ultrasonic intensity, when the solid content of disintegrated sludge is 0.5%.

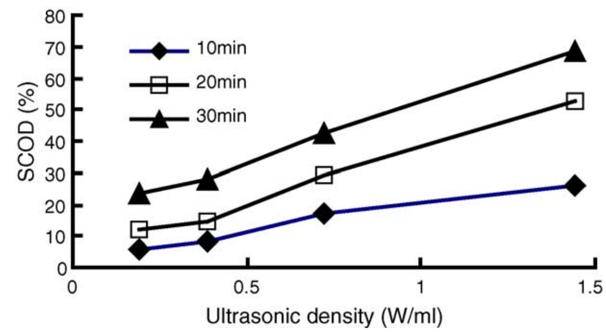

Fig. 5. $SCOD_{\%}$ at different ultrasonic density, when the solid content of disintegrated sludge is 1%.

where

$$k = k_0[I]^{\alpha}[\mathrm{pH}]^{\beta}[D]^{\gamma}[C]^{\delta}; \qquad u = u_0[I]^{\varphi}[\mathrm{pH}]^{\nu}[D]^{\lambda}[C]^{\theta}$$

in which, I is the ultrasonic intensity, pH is the pH of experimental sludge, D the ultrasonic density, C the sludge concentration, α, Φ the influence indexes for ultrasonic density, β, ν the influence indexes for the pH of experimental sludge, γ, λ the influence indexes for ultrasonic intensity, δ, θ the influence indexes for the sludge concentration and k_0, u_0 are the intrinsic kinetics constants and they are related to reaction temperature. According to the Arrhenius law, k_0 and u_0 can be defined as Eq. (6).

$$k_0 = A \exp\left(\frac{-\Delta E_a}{RT}\right) \tag{6}$$

Referring to Shirgaonkar and Pandit [19] and Cheung and Kurup [20] research, temperature does not have significant impact on the ultrasonic disintegration. Hence, it is concluded that temperature does not impact on the reaction rate. As a result, activation energy and pre-exponential factor cannot be figured out. Whereas, k_0 and u_0 can be taken as constants, and be calculated by the method of multi-variable linear regression. The procedure is shown as following.

Integrating Eqs. (4) and (5), then transforming the integrated equations logarithmically, Eqs. (7) and (8) can be obtained.

$$\ln(SCOD_+) = \ln(k_0) + \alpha\ln(I) + \beta\ln(\mathrm{pH}) + \gamma\ln(D) + \delta\ln(C) + \ln t \tag{7}$$

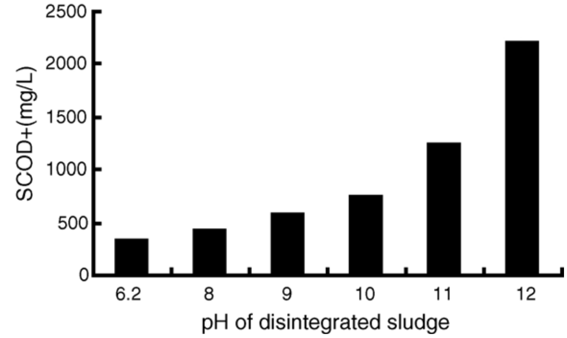

Fig. 6. $SCOD_+$ at different pH when the disintegration time is 30 min.

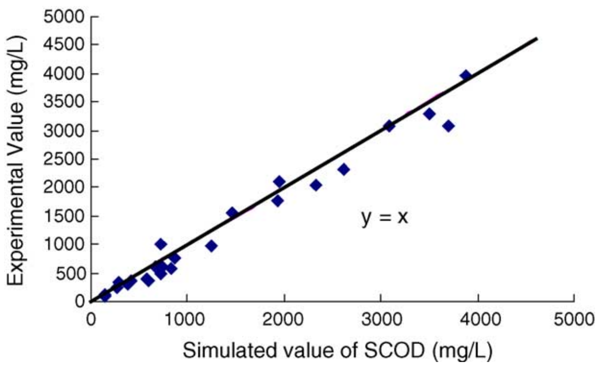

Fig. 7. Relation between simulated data and true data for $SCOD_+$.

$$\ln(SCOD_{\%}) = \ln(k_0) + \phi\ln(I) + \nu\ln(pH) + \lambda\ln(D) + \theta\ln(C) + \ln t \quad (8)$$

By doing this, the equations are linearized. In Eqs. (7) and (8), $SCOD_+$, $SCOD_{\%}$, I, pH, D and C are known quantities, and α, Φ; β, ν; γ, λ; γ, λ; k_0, u_0 can be gained by multi-variables linear regression method.

The sample can be divided into 14 groups according to the difference of sludge concentration, pH and ultrasonic density. Taking 10 groups in the 14 ones as the sample to establish the models, and the other 4 groups are used to verify the models. To ensure that the model has the largest applicability, the chosen 10 groups must include the boundary groups.

3.2.1. Establishment of kinetics model which dependent variable is $SCOD_+$

Analyzing every 10 groups by the method of multi-variables linear regression (the program is conducted with Matlab), 21 results can be obtained. For every result, the partial correlation coefficient ν is all more than 90%, which indicates that every independent variable correlates well with dependent variable. Moreover, value of t can pass the t check with a degree of confidence of 90%, which shows that every independent variable has significant impact on the dependent variable. Ultrasonic density and ultrasonic intensity are inter-related. The model without ultrasonic density or ultrasonic intensity as independent variable is established, but the model is not quite accurate when it is verified. So it is not necessary to eliminate some independent variables to establish a new model. Comparing the multiple correlation coefficients, the standard deviation (S), and average value of relative errors, the best result demonstrated as Eq. (9) is obtained.

$$\frac{d(SCOD+)}{dt} = 0.09727[D]^{0.4896}[pH]^{1.2692}[I]^{0.6559}[C]^{0.8680} \quad (9)$$

To verify the model, the left four groups of data substituted it, and some simulated data are obtained. The relation between experiment data and the simulated data is demonstrated in Fig. 7. In Fig. 7, the nearer the coordinate point to the straight line "$y = x$", the smaller the difference between the two values is. From Fig. 7, we can conclude that the two groups of data fit well.

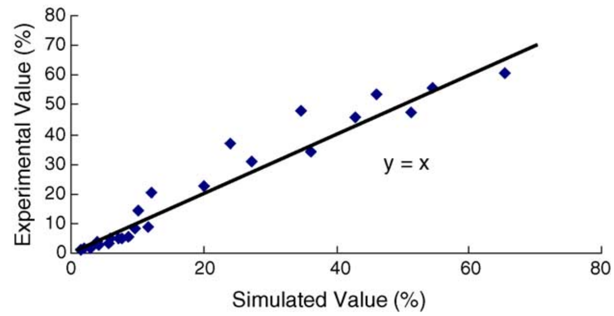

Fig. 8. Relation between simulated data and true data for $SCOD_{\%}$.

Generally, the more the influence index is, the larger its impact on the disintegration is [21,22]. Inferred from Eq. (7), the magnitude of the effect of each parameter is given below: sludge pH > sludge concentration > ultrasonic intensity > ultrasonic density.

3.2.2. Establishment of kinetics model which dependent variable is $SCOD_{\%}$

Analyzing every 10 groups by the method of multi-variables linear regression (the procedure was conducted with Matlab), 21 results can be obtained. For every result, ν between sludge concentration and $SCOD_{\%}$ is low, while ν between every the other three independent variables and the dependent variable are all more than 80%, which indicates that the sludge concentration does not correlate well with $SCOD_{\%}$ and the other three independent variables correlate well with the dependent variable $SCOD_{\%}$. Moreover, t between sludge concentration and $SCOD_{\%}$ is low, While t between every the other three independent variables and the dependent variable all can pass the t check with a degree of confidence of 90%, which indicates that sludge concentration has little impact on $SCOD_{\%}$, and the other three independent variables have significant impact on $SCOD_{\%}$. The reason is that the TCOD for the thickened sludge with the solid content of 1% is twice as much as one for the raw sludge with the solid content of 0.5%. The $SCOD_+$ for disintegrating the thickened sludge is about twice as much as one for the raw sludge with the solid content of 0.5%. As a result, there is not much difference between the two $SCOD_{\%}$ for the two concentrations. Therefore, the dependent variable of sludge concentration must be eliminated to re-establish a simpler model, and u in Eq. (5) can be simplified as following.

$$u = u_0[I]^{\varphi}[pH]^{\nu}[D]^{\lambda}$$

Comparing the multiple correlation coefficients, S, and average value of relative errors, we get the best result demonstrated as Eq. (10).

$$\frac{d(SCOD_{\%})}{dt} = 0.009474[D]^{0.5867}[pH]^{1.4024}[I]^{0.5436} \quad (10)$$

The model is also verified, and as Fig. 8 shown, the simulated data and the experimental data fit well.

4. Conclusions

- By adding $NaHCO_3$ to mask the oxidizing effect of $^{\bullet}OH$, the mechanisms of disintegration were investigated. It was determined that hydro-mechanical shear forces are predominantly responsible for ultrasonic activated sludge disintegration, and the contribution of the oxidizing effect of $^{\bullet}OH$ becomes more and more as the ultrasonic intensity is increased.
- Ultrasonic density, ultrasonic intensity, disintegrated sludge pH and sludge concentration have impact on the sludge disintegration. By the method of multi-variable linear regression, the disintegration kinetics models with the dependent variables of $SCOD_+$ and $SCOD_{\%}$ were established. From the kinetics model with $SCOD_+$ as dependent variable, the magnitude of the effect of each parameter was obtained, which is shown as follows: sludge pH > sludge concentration > ultrasonic intensity > ultrasonic density.

References

[1] J.A. Eastman, J.F. Ferguson, Solubilization of particulate organic carbon during the acid phase of anaerobic digestion, J. WPCF 53 (3) (1981) 352–366.

[2] T. Shimizu, K. Kudo, Y. Nasu, Anaerobic waste activated sludge digestion—a bioconversion and kinetic model, Biotechnol. Bioeng. 41 (1993) 1082–1091.

[3] H.B. Chio, K.Y. Hwang, E.B. Shin, Effect on anaerobic digestion of sewage sludge pretreatment, J. Water Sci. Technol. 35 (10) (1997) 207–211.

[4] J. Muller, Disintegration as a key-step in sewage sludge treatment, Water Sci. Technol. 41 (8) (2001) 123–130.

[5] A. Tiehm, K. Nickel, M. Zellhorn, U. Neis, Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization, J. Water Res. 35 (8) (2001) 2003–2009.

[6] A. Tiehm, K. Nickel, U. Neis, The use of ultrasound to accelerate the anaerobic digestion of sewage sludge, Water Sci. Technol. 36 (11) (1997) 121–128.

[7] C.P. Chu, D.J. Lee, C.S. You, J.H. Tay, weak ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids, Water Res. 36 (2002) 2681–2688.

[8] Y. Sakai, T. Fukase, H. Yasui, M. Shibata, An activated sludge process without excess sludge production, Water Sci. Technol. 36 (11) (1997) 163–170.

[9] S. Deleris, J.M. Rouston, Effect of ozonation on activated sludge solubilization and mineralization, Ozone Sci. Eng. 22 (2000) 473–486.

[10] S. Saby, M. Djafer, G.H. Chen, Feasibility of using a chlorination step to reduce excess sludge in activated sludge process, Water Res. 36 (2002) 656–666.

[11] T. Lendormi, C. Prevot, F. Doppenberg, M. Serandio, H. De Bellefontaine, Wet oxidation of domestic sludge and process integration: the mineralis process, Water Sci. Technol. 44 (10) (2001) 163–169.

[12] Y.C. Chiu, C.N. Chang, J.G. Lin, S.J. Huang, Alkaline and ultrasonic pre-treatment of sludge before anaerobic digestion, Water Sci. Technol. 36 (11) (1997) 155–162.

[13] S. Tanaka, K. Kamiyama, Thermochemical pretreatment in the anaerobic digestion of waste activated sludge, Water Sci. Technol. 46 (10) (2002) 173–179.

[14] P. Camacho, S. Deleris, V. Geaugey, P. Ginestet, E. Paul, A comparative study between mechanical,thermal and oxidative disintegration techniques of waste activated sludge, Water Sci. Technol. 46 (10) (2002) 79–87.

[15] APHA, AWWA, WEF, Standards Methods for the Examination of Water and Wastewater, 19th ed., 1995.

[16] E.J. Hart, Isotopic exchange in the sonolysis of aqueous solutions containing 14,14N2 and 15,15N2, J. Phys. Chem. 90 (1986) 5989–5991.

[17] E.J. Hart, A. Henglein, Sonolytic decomposition of nitrous oxide in aqueous solutions, J. Phys. Chem. 90 (1986) 5992.

[18] I.I. Hua, M.R. Hoffmann, Optimization of ultrasonic irradiation as an advanced oxidation technology, Environ. Sci. Technol. 31 (1997) 2237–2243.

[19] I.Z. Shirgaonkar, A.B. Pandit, Degradation of aqueous solution of potassium iodide and sodium cyanide in the presence of carbon tetrachloride, Ultrason. Sonochem. 4 (1997) 245–253.

[20] H.M. Cheung, S. Kurup, Sonochemical destruction of CFC 11 and CFC 113 in dilute aqueous solution, Environ. Sci. Technol. 28 (1994) 1619–1622.

[21] P.E. Savage, M.A. Smith, Kinetics of acetic acid oxidation in supercritical water, Environ. Sci. Technol. 29 (1995) 216–221.

[22] J.-G. Lin, Y.-S. Ma, Magnitude of effect of reaction parameters on 2-chlorophenol decomposition by ultrasonic process, J. Hazard. Mater. B 66 (1999) 291–305.