



Respirometric evaluation of biodegradation kinetics for ultrasonic disintegrated domestic sludge

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ABSTRACT

This paper studied the suitability of an internal carbon source for nitrogen removal enhancement with mechanically disintegrated waste activated sludge (WAS) using ultrasonication. In this context, particle size distribution (PSD)-based chemical oxygen demand (COD) fractionation was performed, and denitrification rates of the total, particulate and soluble range of the disintegrated WAS sample were determined. The effect of ultrasonic disintegration on biodegradation characteristics of the domestic WAS was evaluated by respirometry. The ultrasound density of 1 W/mL was applied to the raw WAS, and the specific energy was calculated as 52.8 kJ/g TSS. Two thousand and eight hundred milligram per liter of COD, which corresponded to the 24% of the total COD, was released from the WAS. The PSD-based COD fractionation showed that the COD concentration at the particulate range (65.4%) was significantly high followed by the soluble range (15.5%), and 54% of the solubilized COD was accumulated at the <2 nm size range implying the remarkable effect of disintegration in terms of biodegradability. The maximum denitrification rate was determined as 18.2 mg N/g active VSS h, which is compatible with the results obtained for readily biodegradable fraction of the domestic wastewater. Model calibration results indicated that 33% of the total disintegrated WAS sample was biodegradable which corresponded to the total COD in the disintegrated WAS filtrate collected after 1,600 nm. The maximum hydrolysis rate for X_{S1} was estimated as 5.2/d for the disintegrated samples verifying that ultrasonic disintegration increased the hydrolysis rate of the domestic WAS. The hydrolysis half-saturation constant for X_{S2} was decreased from 0.26 to 0.10 g COD/g COD for the filtrates collected from 1,600-nm and 2-nm filters. The removal of nonbiodegradable COD fraction enhanced the hydrolysis process of the slowly hydrolyzable fraction in the remaining filtrate.

Keywords: Denitrification rate; Domestic waste activated sludge; Particle size distribution; Respirometric evaluation; Ultrasonic disintegration

1. Introduction

The biodegradability characteristics of the organic matter in wastewater affect the rate and extension of the biological nutrient removal (BNR) process. The

most common system to treat the nitrogen from wastewater is nitrification–denitrification process in which shortage of organic matter or a low C/N ratio could be a limiting factor for denitrification in WWTPs

[1]. The performance of BNR systems is directly related to the availability of a carbon source. Mostly, addition of external carbon sources has been applied to improve BNR performance. The studies related to the usage of internal waste carbon sources to enhance the denitrification process have been increased due to the high costs of addition of external carbon sources such as methanol or acetate [2]. Pretreatment methods such as fermentation of wastewater or primary sludge and sludge disintegration to enhance the BNR performance have been considered more recently [3,4]. Pretreated waste activated sludge (WAS) is a promising organic waste that has a potential to increase the treatment efficiency of BNR systems. WAS comprises a variety of microorganisms within organic and inorganic substances in a complex matrix formed by extracellular polymeric substances and cations [5].

Pretreatment of WAS involves the disintegration of the sludge flocs to improve the biodegradability of WAS. Ultrasonic treatment (sonication) is one of the most commonly used mechanical pretreatment methods. Ultrasonic disintegration disrupts the sludge flocs, lyse the cells, and facilitate the release of intracellular matter by hydro-mechanical shear force [6,7]. Ultrasound disintegration has been applied to WAS to improve biogas production in anaerobic digesters, to enhance biodegradability, to reduce the sludge mass, and to produce *in situ* soluble substrate for BNR [1]. Hrustak et al. [8] reported that ultrasonic disintegration increased biogas production by 21% and calculated the increase in the annual profit from the sale of the thermal energy as 18.5%. Research studies mostly focus on the usage of disintegration pretreatment prior to anaerobic stabilization to enhance the biogas production, studies related to the application of pretreated WAS to BNR systems are scarce.

Kampas et al. [6] studied the effect of mechanical disintegration on WAS to release soluble COD (sCOD) and volatile fatty acids as an external carbon source for BNR and proved that phosphorus release and denitrification were significantly improved. The denitrification rates of disintegrated WAS were investigated between 1.5 and 5 mg NO₃-N/g VSS h which was in accordance with the domestic wastewater [9].

The suitability of internal carbon sources for nitrogen removal has been investigated by determining carbon-to-nitrogen ratios [10]. These methods are unreliable to determine the BNR potential of a wastewater, as in many cases there is no correlation between nitrogen (N) removal and the C/N ratio [6]. Nitrate utilization rate (NUR) test is a reliable method to predict the N removal [11]. NUR test is based on denitrification rates with high denitrification rates indicating good denitrification and hence good N

removal. However, NUR test is not enough to evaluate the effect of internal carbon sources on BNR performance. The different fractions of the organic matter should be also determined to evaluate the substrate biodegradation. Respirometry is a useful tool for the assessment of the COD fractionation of the substrate and the process kinetics [12].

This paper examines the suitability of an internal carbon source for nitrogen removal enhancement with mechanically disintegrated WAS using ultrasonication. In this context, the objective of this study was to evaluate the biodegradation characteristics of the disintegrated domestic WAS. For this purpose: (i) Anoxic batch experiments with the disintegrated WAS were conducted, (ii) Particle size distribution (PSD) analysis of disintegrated WAS via sequential filtration/ultrafiltration was performed for COD fractionation (iii) The effect of disintegration on COD fractionation and kinetics was determined by respirometry.

2. Materials and methods

2.1. Ultrasonic and thermochemical treatment

Activated sludge samples were collected from the return line of a full-scale municipal wastewater treatment plant operated for BNR and located in Istanbul, Turkey. The ultrasonic disintegration was performed with an ultrasonic homogenizer (Bandelin Sonopuls HD 2200, Berlin, Germany) equipped with a VS 70T probe. The ultrasonic unit has an operating frequency of 20 kHz and a power supply of 200 W. The sonication density and the specific energy (E_s) provided to the WAS samples were calculated according to Eqs. 1 and 2, respectively. The amplitude of 100% and sonication time of 10 min was applied for a 200 mL of WAS sample, which resulted in a sonication density of 1 W/mL.

$$\text{Sonication density (W/mL)} = \frac{\text{Power input (W)}}{\text{Volume (mL)}} \quad (1)$$

$$E_s \text{ (kJ/kg TS)} = \frac{\text{Power input (W)} \times \text{Sonication time (s)}}{\text{Volume (L)} \times \text{Total solids concentration (kg/L)}} \quad (2)$$

2.2. Denitrification test

For the assessment of the denitrification rate, the sonicated WAS and the non-sonicated WAS samples ultrafiltrated through 1,600- and 2-nm filters were

subjected to batch denitrification test. Batch reactors were initially fed with the sonicated WAS (COD) seeded with appropriate biomass in the range of 0.5–1.0 So/Xo ratios. The seed biomass was obtained from the anoxic tank of a full-scale wastewater treatment plant. The batch reactor designated to determine the endogenous rate was including only anoxic seed sludge. To achieve an initial C/N ratio of 5/1, 1 N stock KNO_3 solution was added to batch reactors as external nitrate source. The batch reactors capped with butyl rubber stopper were purged with nitrogen gas to maintain the anoxic conditions and mixed with magnetic stirrer. Aliquots were taken every 10 or 30 min and immediately filtrated with $0.22\ \mu\text{m}$ for the analyses of nitrate and nitrite. The $\text{NO}_x\text{-N}$ value used for nitrate utilization curve is built of $\text{NO}_3\text{-N} + 0.6 \times \text{NO}_2\text{-N}$. The reduction of 1 g $\text{NO}_2\text{-N}$ to 1 g N_2 requires the same amount of electrons for the reduction of $0.6\ \text{g}\ \text{NO}_3 \pm \text{N}$ to $0.6\ \text{g}\ \text{N}_2$ [11].

2.3. Sequential filtration/ultrafiltration

The PSD analysis was conducted on the supernatant of the sonicated WAS samples. The sequential filtration/ultrafiltration assay was performed with a stirred cell (Amicon, Model 8400) operated under positive pressure (0.6–1.2 atm, N_2 gas). The filtration/ultrafiltration experiments were conducted as described in Doğruel [13]. Conventional filters with pore sizes of 1,200–1,600 nm (Millipore AP40, glass fiber), 450 nm (Durapore HV, PVDF), and 220 nm (Durapore HV, PVDF) were used for sequential filtration. The ultrafiltration membranes with nominal molecular weight cutoff values of 100, 30, 10, 3, and 1 kDa (Millipore, MA) were used for sequential ultrafiltration. The particle size was distributed as particulate ($>1,600\ \text{nm}$), colloidal (1,600–2 nm), and soluble ($<2\ \text{nm}$) fractions [14].

2.4. Respirometric analyses

Oxygen uptake rate (OUR) measurements were conducted on sonicated WAS samples, and the sonicated WAS samples ultrafiltrated through 1,600-nm and 2-nm filters. OUR data were analyzed in the modeling studies using the modified Activated Sludge Model No. 1 [15]. The model parameters and initial state variables were estimated in accordance with the method proposed by Insel et al. [16] and Dochain et al. [17]. Model simulations and parameter estimation were carried out using AQUASIM [18]. The OUR measurements were performed using Applitek

Ra-Combo Continuous Respirometer. A nitrification inhibitor (Formula 2533, Hach Company, USA) was used at all OUR runs to prevent possible interference of nitrification. The sample was continuously aerated with compressed air in order to keep the dissolved oxygen level above $5\ \text{mg}\ \text{O}_2/\text{L}$ in the aeration vessel. The batch OUR experiments were initiated with anoxic sludge samples seeded with disintegrated WAS in a 2-L vessel. All respirometric experiments were conducted at 20°C .

2.5. Analytical work

Total solids (TS), suspended solids (SS), volatile suspended solids (VSS), total Kjeldahl nitrogen (TKN), and ammonium nitrogen ($\text{NH}_4^+\text{-N}$) parameters were analyzed according to standard methods [19]. Chemical oxygen demand (COD) was measured as described in ISO 6060 [20]. Samples for sCOD were filtered through $0.45\ \mu\text{m}$ membrane filter for conventional characterization. TOC and DOC were measured using high-temperature combustion using a Shimadzu TOC-5000A analyzer (Shimadzu Corporation, Kyoto, Japan). The minimum detection limit for TOC was $0.6\ \text{mg/L}$. Standard deviations of measurements were all around 2–3%. Nitrate (NO_3^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) concentrations were determined by ion chromatography (Dionex ICS-1500 unit, Sunnyvale, CA) equipped with a conductivity detector and an analytical column AS14A (Dionex IonPac). The unit was operated in autosuppression mode with $1\ \text{mM}\ \text{NaHCO}_3/8\ \text{mM}\ \text{Na}_2\text{CO}_3$ eluent with a flow rate of $1\ \text{mL/min}$. All standards and samples were filtered through $0.22\ \mu\text{m}$ membrane filters prior to injection. The minimum detection limits for NO_3^- , NO_2^- , and PO_4^{3-} were 0.03 ± 0.05 , 0.05 ± 0.07 , and $0.12 \pm 0.06\ \text{mg/L}$, respectively. Samples were analyzed in duplicate for each parameter.

3. Results and discussion

3.1. Sludge disintegration

The effect of sludge disintegration on the solubilization of organic matter as an external carbon source for denitrification was investigated by applying ultrasonication on WAS. The ultrasound density of $1.0\ \text{W/mL}$ was used, and the specific energy provided to the sample was calculated as $52.8\ \text{kJ/g TSS}$ for the raw WAS. The optimum specific energy input for sludge disintegration is reported as $50\ \text{kJ/g TSS}$ considering the disintegration performance, sludge settleability, and optimization of the energy requirements [7]. The release in sCOD may slow down due to the

increment rate of protein, polysaccharides, and DNA at an energy input of over 50 kJ/kg TS, and also sludge dewaterability may deteriorated at higher energy inputs [21].

The characterization of the raw WAS and disintegrated WAS is depicted in Table 1. Since ultrasonication disintegrates the sludge flocs and increases the sCOD by releasing the intracellular matter, the performance of the ultrasonic disintegration is determined by measuring sCOD [22]. Two thousand and eight hundred milligram per liter of COD, which corresponded to the 24% of the total COD, was released from the WAS. Observed sCOD release was in accordance with the literature findings for 1% TS content. Akin et al. [23] reported that sCOD release increased from 1,000 to 1,800, 4,000, 5,800, and 3,200 mg/L at the TS content of 0.98, 1.7, 2.6, and 3.6% w/v, respectively.

The ultrasonic disintegration enhances VSS reduction, and in this study, VSS reduction was observed as 63%, and the VSS/SS ratio was increased from 67 to 79.5%. As expected, ultrasonic disintegration increased the solubilization of nitrogen and phosphate release along with the organic compounds. Soluble TKN concentration was increased from 18 to 280 mg/L with a percentage of 94%, and the ammonium nitrogen concentrations were also increased during the ultrasonication. Phosphate concentration in the aqueous phase increased from 7.95 to 75 mg/L. The solubilization of nitrogen and phosphorus results obtained in this study were in agreement with the results obtained by previous studies [5,24]. It should be noted that findings in the literature related to the ultrasound

disintegration are very scattered since too many variables have impact on sonication.

3.2. PSD based COD fractionation

PSD-based COD fractionation was performed to determine the distribution of organic carbon content of the disintegrated WAS. The overall results of the PSD based COD fractionation are given in Table 2. The cumulative COD corresponds to the measured COD values in aliquots of each filtration/ultrafiltration step, and the differential COD is the difference between COD values of two sequential filtration step [13].

The COD concentration at the particulate range (>1,600 nm) was measured as 65.4% of the total influent COD. COD values at colloidal range (1,600–2 nm) were 19.1% of the total influent COD. At soluble range (<2 nm), 15.5% of the total influent COD was observed (Fig. 1(a)). The differential COD values of disintegrated WAS are illustrated in Fig. 1(b). The COD concentration at the particulate range was significantly high followed by the soluble range.

Based on the conventional characterization, the overall solubilized COD via disintegration was measured as 2,800 mg/L. PSD-based characterization revealed that 54% of the solubilized COD was accumulated at the <2 nm size range (1,495 mg/L COD). A significant portion of the sCOD was observed at the <2 nm size range after the ultrasonic disintegration, and this result implies the remarkable effect of disintegration in terms of biodegradability. As well PSD-based characterization provides a better interpretation of the efficiency of the pretreatment methods in terms of biodegradability. The COD profile of the disintegrated WAS was in agreement with the studies performed for domestic wastewater [14]. Similar to the results of this study, 65% of the COD concentration was accumulated at the particulate range (>1,600 nm), and 14% of the COD was observed at the soluble range (<2 nm) for the raw domestic wastewater.

3.3. Batch denitrification tests

Anoxic batch tests were performed to determine the denitrification rates of the disintegrated WAS. Beside total disintegrated WAS, the disintegrated samples filtered through 1,600- and 2-nm filters resembling particulate and soluble range, respectively, selected for the batch tests due to the results of the PSD analyses. PSD analysis clearly showed that the organic content of the disintegrated WAS was remarkably high at particulate and soluble range (Fig. 1).

Table 1
Characterization of the raw and disintegrated WAS

Parameter	Unit	WAS	Disintegrated WAS
SS	mg/L	12,110	3,800
VSS	mg/L	8,120	3,020
TS	mg/L	12,635	7,695
TVS	mg/L	8,065	5,540
VSS/SS	–	67.0	79.5
VS/TS	–	63.8	72.0
TCOD	mg/L	11,595	9,650
sCOD	mg/L	21.0	2,802
TOC	mg C/L	1,782	2,584
DOC	mg C/L	4.9	1,203
TKN	mg N/L	632	ND*
STKN	mg N/L	18.0	280
NH ₄ -N	mg N/L	34.0	63.0
PO ₄ -P	mg P/L	7.95	75.0
NO ₃ -N	mg N/L	1.75	1.78
NO ₂ -N	mg N/L	0.82	1.18

*Not determined.

Table 2
PSD based COD fractionation of sonicated WAS

Separation	Particle size (nm)	Cumulative COD	Size category (nm)	Differential COD	% of total influent COD
Total		9,650			
AP40 filter	1,200–1,600	3,342	>1,600	6,309	65.4
HV filter	450	2,802	450–1,600	540	5.6
GV filter	220	2,213	220–450	588	6.1
100 kDa	13	1,918	13–220	295	3.1
30 kDa	8	1,827	8–13	91	0.9
10 kDa	5	1,805	5–8	22	0.2
3 kDa	3	1,611	3–5	194	2.0
1 kDa	2	1,495	2–3	116	1.2
			<2	1,495	15.5

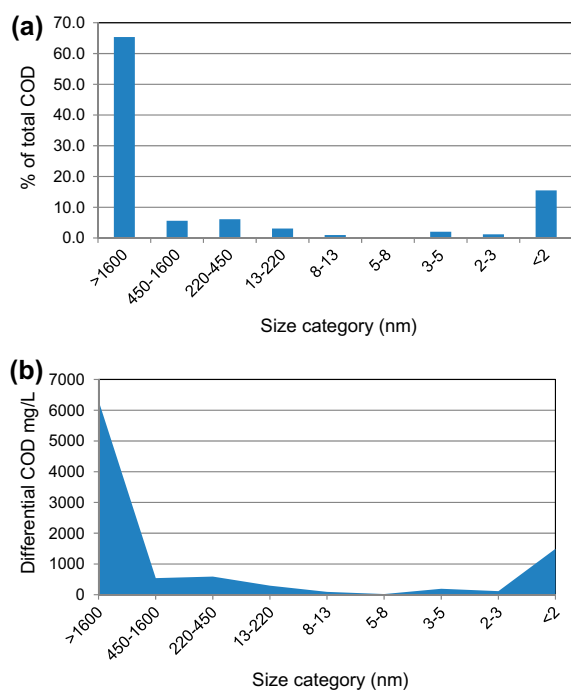


Fig. 1. PSD-based COD fractionation of disintegrated WAS (a) % of total COD (b) differential COD values.

The denitrification rates determined from the total disintegrated WAS are shown in Fig. 2(a). Hereby, the initial phase of the total disintegrated WAS was controlled by the readily biodegradable COD, and specific denitrification rate was determined as 18.2 mg N/g active VSS h (K_1). The second and third phases were associated with rapidly and slowly hydrolyzable COD, and specific denitrification rates were calculated as 8.3 mg N/g active VSS h (K_2) and 2.2 mg N/g active VSS h (K_3), respectively. The last phase was controlled by the endogenous biomass, but endoge-

nous denitrification could not be determined from this graph as the duration of the anoxic batch test was not long enough to calculate the rate.

The denitrification rates determined from the disintegrated WAS filtrate collected after 1,600-nm filter (particulate range) are illustrated in Fig. 3(b). The initial phase was associated with the readily biodegradable COD, and specific denitrification rate was calculated as 18.2 mg N/g active VSS h (K_1). The second and third phases were controlled by the rapidly and slowly hydrolyzable COD, and specific denitrification rates were determined as 8 mg N/g active VSS h (K_2) and 3.8 mg N/g active VSS h (K_3), respectively. Similar to the total disintegrated WAS, the endogenous denitrification rate could not be determined. The maximum specific denitrification rate was also calculated as 18.2 mg N/L h from the disintegrated WAS filtrate collected after 2-nm filter (Fig. 3(c)). The anoxic batch test designated to determine the endogenous rate was including only anoxic seed sludge with the deficiency of organic matter, and the endogenous denitrification rate was calculated as 1.35 mg N/g VSS h.

The first and second denitrification rates (K_1 and K_2) obtained from the total disintegrated WAS, disintegrated WAS filtrate collected after 1,600-nm and 2-nm filters were in agreement except for the third denitrification rate (K_3). The third denitrification rate associated with the slowly hydrolyzable fraction of the COD was higher in the disintegrated WAS filtrate collected from 1,600-nm filters compared to the total disintegrated WAS as a consequence of the removal of slowly biodegradable particulate matter when filtered through the 1,600 nm.

The denitrification rates of the disintegrated WAS are comparable with results obtained for domestic wastewater. Sözen and Orhon [25] determined the maximum denitrification rate K_1 associated with

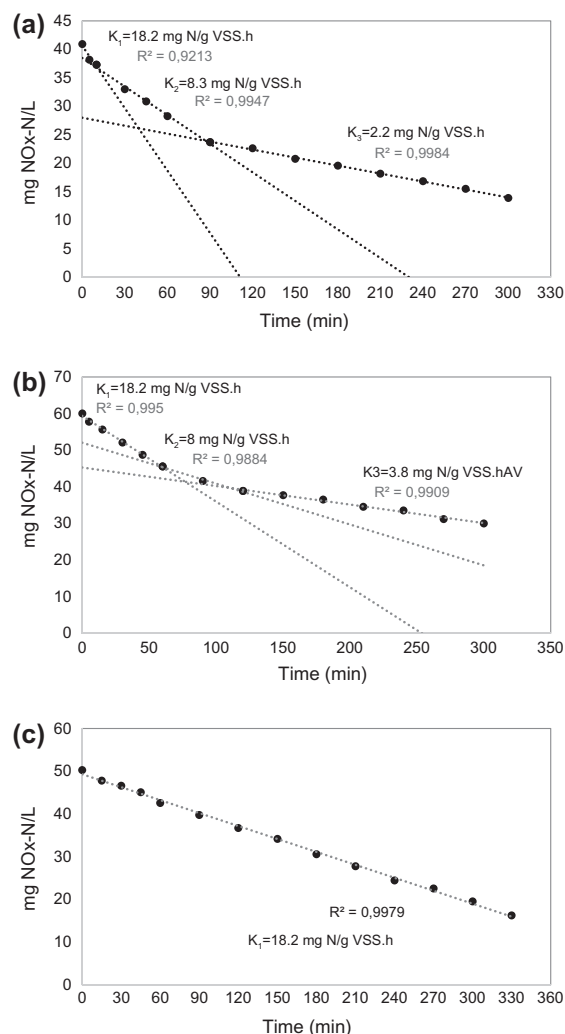


Fig. 2. Denitrification rate of the disintegrated WAS (a) total disintegrated WAS (b) disintegrated WAS filtrate collected after 1,600-nm filter (c) disintegrated WAS filtrate collected from 2-nm filter.

the readily biodegradable COD in the range of 10–55 mg N/g active VSS h, K_2 defining hydrolysis-limited denitrification in the range of 5–38 mg N/g active VSS h, and K_3 reflecting endogenous denitrification rate between 5 and 19 mg N/g active VSS h. The effect of disintegrated sewage sludge as internal carbon source for BNR was studied, and maximum denitrification rate was obtained as 2.4 mg N/g VSS h for mechanically disintegrated surplus activated sludge using deflaker [26]. Peng et al. [27] reported the maximum denitrification rates of ethanol, acetate, and methanol as 9.6, 12, and 3.2 mg N/g VSS h, respectively. The results were also compared with the reported values of industrial wastewater. De Lucas et al. [28] reported the maximum denitrification rates in the range of 1.3–1.8 mg N/g VSS h for agro-food

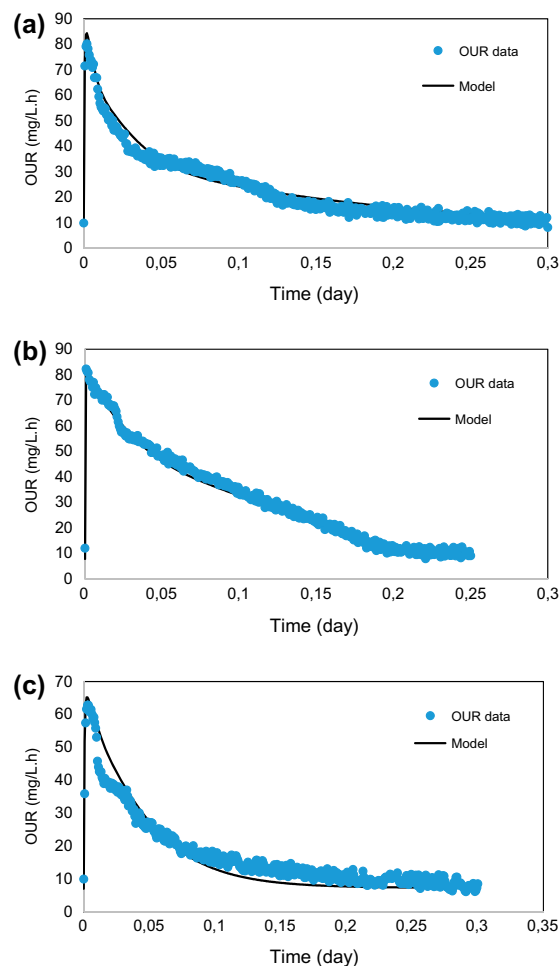


Fig. 3. Model calibration results obtained for total disintegrated WAS (a) disintegrated WAS filtered through 1,600-nm filter (b) disintegrated WAS filtered through 2-nm filter (c).

wastewaters including slaughterhouses, potato and tomato processing, and winery industries. The results of the reported studies indicate that enhancement of denitrification potential with the ultrasonically treated is a promising treatment. It should be noted that the variation in the findings is closely related to the activity of the seed sludge.

3.4. Respirometric analyses

The kinetic constants and the magnitude of the readily and slowly biodegradable substrates are determined by respirometric analyses of the activated sludge. Model calibration results obtained for total disintegrated WAS and filtrates collected from 1,600- and 2-nm filters are given in Fig. 3.

The calibrated model provided a close fit with the experimental OUR profile. The results of the model calibration are outlined in Table 3. The hydrolyzable COD fraction used in the model (X_{S1} and X_{S2}) reflects the particulate and the sCOD fractions. The conventional characterization revealed that ultrasonic disintegration increased the sCOD from 20 to 2,800 mg/L. Model calibration results indicated that almost whole COD in the disintegrated WAS filtrate collected from 1,600-nm filter was essentially biodegradable and remaining portion in the total disintegrated WAS sample was nonbiodegradable. The total COD was measured as 3,340 mg/L for the filtrate collected after 1,600 nm, and the total biodegradable COD fraction was determined as 3,210 mg/L COD showing that 33% of the total disintegrated WAS sample was biodegradable. The readily biodegradable fraction was corresponded to the 3.1% of the total biodegradable COD for the total disintegrated WAS and filtrate collected after 1,600 nm. The rapidly and slowly hydrolyzable COD fractions were accounted for the 18.1% and 78.8% of the total biodegradable COD and filtrate collected after 1,600 nm, respectively. The COD fractions revealed different patterns for the disintegrated WAS

samples. The concentration of readily biodegradable COD, S_{S1} , and rapidly hydrolyzable COD, X_{S1} , did not change but the ratio of these fractions to the total biodegradable COD was increased when the disintegrated WAS sample was filtered through 2-nm filter. The slowly hydrolyzable COD, X_{S2} fraction was decreased to 53.7% for the filtrate collected from 2-nm filter due to the removal of particulate COD fraction.

The kinetic parameters estimated by OUR modeling are also depicted in Table 3. The maximum specific growth rate, μ_H , was defined as 3.5/d, which is compatible with the reported values of 3.5–6.5/d for domestic wastewater [29,30]. The half-saturation coefficient, K_{S1} , was 5 mg COD/L, in the range of 0.3–20 mg COD/L reported for domestic wastewater [30]. The maximum hydrolysis rate for X_{S1} was estimated as 5.2/d for the disintegrated samples, which is higher than the reported values for domestic sewage [31]. This result clearly showed that ultrasonic disintegration increased the hydrolysis rate of the domestic WAS. The maximum hydrolysis rate for X_{S2} was estimated as 2.9/d for the disintegrated samples, which is in accordance with the reported studies for the domestic sewage. The hydrolysis half-saturation constant for X_{S2}

Table 3

Model calibration results of kinetic and stoichiometric coefficients and COD fractionation for the disintegrated WAS samples

Model parameter	Unit	Disintegrated sludge		
		Total	AP40	1 kDa
Maximum heterotrophic growth rate, $\hat{\mu}_{H1}$	1/d	3.5	3.5	3.5
Half-saturation constant for growth, K_{S1}	mg COD/L	5	5	5
Maximum hydrolysis rate for X_{S1} , k_{h1}	1/d	5.2	5.2	5.2
Hydrolysis half-saturation constant for X_{S1} , K_{X1}	g COD/g COD	0.10	0.10	0.10
Maximum hydrolysis rate for X_{S2} , k_{h2}	1/d	2.9	2.9	2.9
Hydrolysis half-saturation constant for X_{S2} , K_{X2}	g COD/g COD	0.26	0.10	0.10
Endogenous decay rate, b_H	1/d	0.24	0.24	0.24
Heterotrophic yield coefficient, Y_H	g COD/g COD	0.58	0.58	0.58
Soluble microbial product ratio, f_{ES}	–	0.05	0.05	0.05
Particulate microbial product ratio, f_{EX}	–	0.15	0.15	0.15
State variables		Unit		
Total biomass	mg VSS/L	2,350	1,725	1,870
X_{H1}	mg COD/L	1,100	900	850
Activity	%	33	38	32
Total COD, C_{T1}	mg COD/L	9,650	3,340	1,495
Soluble COD, S_{T1}	mg COD/L	2,800*	2,800*	1,495**
Particulate COD, X_{T1}	mg COD/L	6,850	540	–
Biodegradable COD, C_{S1}	mg COD/L	3,210	3,210	1,470
Readily biodegradable COD, S_{S1}	mg COD/L	100	100	100
Rapidly hydrolysable COD, X_{S1}	mg COD/L	580	580	580
Slowly hydrolysable COD, X_{S2}	mg COD/L	2,530	2,530	790

*Filtered through 450 nm.

**Filtered through 2 nm.

was decreased from 0.26 to 0.10 g COD/g COD when the disintegrated WAS sample was filtered through 1,600- and 2-nm filters. The nonbiodegradable fraction in the total disintegrated WAS affects the hydrolysis rate and removal of almost whole nonbiodegradable COD fraction as a result of filtering through 1,600-nm filter enhanced the hydrolysis process of the slowly hydrolyzable fraction in the remaining filtrate. A similar result was reported by Dimock and Morgenroth [32] as they observed that smaller particles, which have a higher specific surface area than larger particles, are hydrolyzed faster than larger particles. The results of the respirometric analyses clearly showed the biodegradation characteristics of the ultrasonic disintegrated sludge and indicated that ultrasonic disintegration increased the maximum hydrolysis rate of the domestic WAS compared with domestic wastewater.

4. Conclusions

Ultrasonic disintegration solubilized the WAS, and the denitrification rates of the disintegrated WAS were compatible with the results obtained for the readily biodegradable fraction of the domestic wastewater. Respirometric evaluation involving PSD-based COD fractionation offered an insight into the biodegradation characteristics of the disintegrated domestic WAS. The PSD-based COD fractionation indicated the remarkable effect of ultrasonic disintegration on the domestic WAS as 54% of the solubilized COD was accumulated at the <2 nm size range. Respirometric evaluation combined with PSD-based COD fractionation demonstrated that the disintegrated filtrate collected after 1,600-nm filter was completely biodegradable. Model evaluation of the experimental data clearly proved that the ultrasonic disintegration increased the maximum hydrolysis rate of the domestic WAS compared with domestic wastewater and removal of nonbiodegradable COD fraction by filtering through 1,600-nm filter enhanced the hydrolysis process of the slowly hydrolyzable fraction. Overall, the results suggest that ultrasonic disintegration of the WAS is a promising pretreatment for the enhancement of denitrification potential.

References

- [1] S. Koroglu, G.E. Zengin, N. Yagci, N. Artan, COD fractionation and denitrification potential of sonicated waste activated sludge liquids, *Environ. Technol.* 33 (13) (2012) 1505–1510.
- [2] D. Bilanovic, P. Battistoni, F. Cecchi, P. Pavan, J. Mata-Alvarez, Denitrification under high nitrate concentration and alternating anoxic conditions, *Water Res.* 33(15) (1999) 3311–3320.
- [3] J. Charlton, Biological nutrient removal applied to weak sewage, *Water Sci. Technol.* 29(12) (1994) 41–48.
- [4] T. McCue, R. Shah, I. Vassiliev, Y.H. Liu, F.G. Eremektar, Y. Chen, A.A. Randall, Evaluation of influent pre-fermentation as a unit process upon biological nutrient removal, *Water Sci. Technol.* 47(11) (2003) 9–15.
- [5] X. Wang, Z. Qiu, S. Lu, W. Ying, Characteristics of organic, nitrogen and phosphorus species released from ultrasonic treatment of waste activated sludge, *J. Hazard. Mater.* 176 (2010) 35–40.
- [6] P. Kampas, S.A. Parsons, P. Pearce, S. Ledoux, P. Vale, J. Churchley, E. Cartmell, Mechanical sludge disintegration for the production of carbon source for biological nutrient removal, *Water Res.* 41(8) (2007) 1734–1742.
- [7] S. Pilli, P. Bhunia, S. Yan, R.J. LeBlanc, R.D. Tyagi, R.Y. Surampalli, Ultrasonic pretreatment of sludge: A review, *Ultrason. Sonochem.* 18 (2011) 1–18.
- [8] D. Hrustak, M. Zavacky, P. Ditl, Energetical comparison of substrate disintegration methods used for increasing biogas production, *J. Chem. Chem. Eng.* 5 (2011) 514–520.
- [9] J. Müller, Disintegration as a key step in sewage sludge treatment, *Water Sci. Technol.* 41(8) (2000) 123–130.
- [10] C.W. Randall, J.L. Barnard, H.D. Stensel, Design and retrofit of waste water treatment plants for biological nutrient removal, in: W.W. Eckenfelder, J.F. Malina, J.W. Patterson (Eds.), *Water Quality Management Library*, vol. 5, Technomic Publications Co. Inc., Lancaster, PA, 1992, pp. 1–420.
- [11] K. Kujawa, B. Klapwijk, A method to estimate denitrification potential for predenitrification systems using NUR batch test, *Water Res.* 33 (1999) 2291–2300.
- [12] I. Pala-Ozkok, G. Kor-Bicakci, A. Ural, T. Katipoglu-Yazan, N. Yagci, E. Ubay-Cokgor, D. Orhon, Modeling acute impact of sulfamethoxazole on the utilization of simple and complex substrates by fast growing microbial culture, *J. Chem. Technol. Biotechnol.* (2013), doi: 10.1002/jctb.4165.
- [13] S. Doğruel, Biodegradation characteristics of high strength municipal wastewater supported by particle size distribution, *Desalin. Water Treat.* 45 (2012) 11–20.
- [14] E. Dulekgurgen, S. Doğruel, Ö. Karahan, D. Orhon, Size distribution of wastewater COD fractions as an index for biodegradability, *Water Res.* 40 (2006) 273–282.
- [15] M. Henze, C.P.L. Grady, W. Gujer, G.V.R. Marais, T. Matsuo, *Activated Sludge Model No. 1*, IAWPRC Science and Technical Report No. 1., IAWPRC, London, 1987.
- [16] G. Insel, D. Orhon, P.A. Vanrolleghem, Identification and modelling of aerobic hydrolysis—Application of optimal experimental design, *J. Chem. Technol. Biotechnol.* 78 (2003) 437–445.
- [17] D. Dochain, P.A. Vanrolleghem, M. Van Daele, Structural identifiability of biokinetic models of activated sludge respiration, *Water Res.* 29 (1995) 2571–2578.
- [18] P. Reichert, J. Ruchti, W. Simon, *Aquasim 2.0*, Swiss Federal Institute for Environmental Science and Technology (EAWAG), Duebendorf, Switzerland, 1998.
- [19] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater*, twenty-first ed., American Public Health Association, Washington, DC, 2005.
- [20] *Water Quality—Determination of the Chemical Oxygen Demand*, Ref No ISO 6060-1986, first ed., International Standards Organization, Switzerland, 1986.

- [21] F. Wang, S. Lu, M. Ji, Components of released liquid from ultrasonic waste activated sludge disintegration, *Ultrason. Sonochem.* 13 (2006) 334–338.
- [22] S.K. Khanal, D. Grewell, S. Sung, J. Van Leeuwen, Ultrasound applications in wastewater sludge pre-treatment: A review, *Crit. Rev. Environ. Sci. Technol.* 37 (2007) 277–313.
- [23] B. Akin, S.K. Khanal, S. Sung, D. Grewell, J. Van Leeuwen, Ultrasound pre-treatment of waste activated sludge, *Water Sci. Technol.* 6 (2006) 35–42.
- [24] C. Bougrier, H. Carrère, J.P. Delgenès, Solubilisation of waste-activated sludge by ultrasonic treatment, *Chem. Eng. J.* 106 (2005) 163–169.
- [25] S. Sözen, D. Orhon, The effect of nitrite correction on the evaluation of the rate of nitrate utilization under anoxic conditions, *J. Chem. Technol. Biotechnol.* 74 (1999) 790–800.
- [26] A. Soares, P. Kampas, S. Maillard, E. Wood, J. Brigg, M. Tillotson, S.A. Parsons, E. Cartmell, Comparison between disintegrated and fermented sewage sludge for production of a carbon source suitable for biological nutrient removal, *J. Hazard. Mater.* 175 (2010) 733–739.
- [27] Y. Peng, Y. Ma, S. Wang, Denitrification potential enhancement by addition of external carbon sources in a pre-denitrification process, *J. Environ. Sci.* 19 (2007) 284–289.
- [28] A. De Lucas, L. Rodríguez, J. Villaseñor, F.J. Fernández, Denitrification potential of industrial wastewaters, *Water Res.* 39 (2005) 3715–3726.
- [29] M. Henze, W. Gujer, T. Mino, M.C.M. van Loosdrecht, Activated Sludge Models ASM1, ASM2, ASM2d and ASM3. IWA Scientific and Technical Report No. 9, IWA Publishing, London, 2000.
- [30] E. Ubay Çokgör, S. Sözen, D. Orhon, M. Henze, Respirometric analysis of activated sludge behaviour—I. Assessment of the readily biodegradable substrate, *Water Res.* 32 (1998) 461–475.
- [31] G. Insel, B. Güder, G. Güneş, E.U. Ubay Cokgor, Are standard wastewater treatment plant design methods suitable for any municipal wastewater? *Water Sci. Technol.* 66(2) (2012) 328–335.
- [32] R. Dimock, E. Morgenroth, The influence of particle size on microbial hydrolysis of protein particles in activated sludge, *Water Res.* 40 (2006) 2064–2074.