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# Ultrasonication of wastewater sludge—Consequences on biodegradability and flowability

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ABSTRACT

The present study deals with pre-treatment of wastewater sludge by ultrasonic waves at frequency of 20 kHz using fully automated lab-scale ultrasonication equipment. Different wastewater sludge solids concentrations, ultrasonication intensities, and exposure times of pre-treatment were investigated for the optimization of ultrasonication treatment process. The parameters of pre-treatment process were optimized by using response surface methodology. A $2^3$ central composite design was performed for optimization. The screening experiment step comprised steepest ascent methodology to determine optimal domain. The effect of ultrasonication treatment was assessed in terms of increase in soluble solids and the biodegradability of the wastewater sludge. In addition, rheological parameter of wastewater sludge, namely, viscosity was also measured to ascertain the suitability of wastewater sludge for conventional treatment processes as well as submerged fermentation, a major step for the production of value-added products from sludge. It was observed that the ultrasonication intensity and pre-treatment exposure time significantly affected the efficiency of the ultrasonication process followed by the solids concentration. The optimal conditions of ultrasonic pre-treatment were 0.75 W/cm$^2$ ultrasonication intensity, 60 min, and 23 g/L total solids concentration. The increases in soluble chemical oxygen demand and biodegradability, by aerobic sludge digestion process, in terms of total solids consumption increased by 45.5% and 56%, respectively. The flowability of ultrasonicated sludge in terms of viscosity showed exponential behaviour at different total solids concentrations, and pseudoplastic and thixotropic behaviour similar to raw sludge. Nevertheless, the magnitude of viscosity values of ultrasonicated sludge was always lower than the raw sludge.

## 1. Introduction

The increasing stringent regulations on disposal of wastewater sludge (WWS) have lead to efforts towards reuse of sludge as biosolids for agricultural application. Value addition of WWS by utilizing it as a raw material for commercially viable products such as, biopesticides, biofertilizers, bioplastic and enzymes is a novel sustainable approach of sludge management [1,2]. In fact, the bioconversion is more advantageous than conventional sludge disposal techniques such as, land filling and incineration, due to its positive impact on environment and economy. However, the limiting factor for reuse of WWS as alternative material in the bioconversion process is that WWS is insoluble, possesses low homogeneity and comprises recalcitrants. Additionally, WWS includes, cell wall and the membrane of prokaryotes composed of complex organic materials such as, peptidoglycan, teichoic acids, and complex polysaccharides, which are not readily biodegradable [3]. In this context, several pre-treatment methods such as, thermal and thermo-alkaline hydrolysis and partial oxidation have been effectively applied to enhance biodegradability of WWS with encouraging results in particular for *Bacillus thuringiensis* biopesticides and *Bacillus licheniformis* proteases production [4–6]. The exposure of insoluble, non-biodegradable (recalcitrant organic matter), and the microbial cells to pre-treatment process rupture the cell wall, and membrane followed by release of the intracellular organics in the bulk solution, which in turn enhances the overall digestibility. Likewise, the high viscosity of sludge which affects mass transfer (oxygen and nutrient) could be modified for improving the efficacy of value addition of WWS using pre-treatment strategies.

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*Abbreviations:* CCD, central composite design; EPS, extracellular polymeric substances; FFD, fractional factorial deign; RS, raw sludge; SCOD, soluble chemical oxygen demand (g/L); TCOD, total chemical oxygen demand (g/L); TS, total solids (g/L); ULS, ultrasonicated sludge.

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Ultrasonic disintegration was actually applied for the disruption of microbial cells in order to extract intracellular material. Subsequently, several authors have reported the successful application of ultrasonication as pre-treatment process for sludge stabilization [3,7]. Ultrasonic wave is a pressure wave that propagates through a medium, resulting in vast amount of energy dissipation, and violent collapse of gas and vapour bubbles (termed "acoustic cavitation"), which possibly induces many physico-chemical effects [8]. The hydromechanical shear forces produced by ultrasonic cavitation disrupt the cells in sludge, leading to release of organic substances of sludge into the liquid phase [9]. The sludge disintegration was also enhanced by the increase of temperature in the bulk liquid during ultrasonication [10]. In fact, ultrasonication would be a prospective method in augmenting sludge biodegradability for value addition by solubilization of organic matter, decrease in sludge viscosity and increase in its homogeneity. However, until date, none of the studies discussed the enhancement of biodegradability for sludge value addition, i.e. production of biopesticides, bioplastics, enzymes, bioflocculants, among others using ultrasonication as pre-treatment. Most of the literature pertains to the augmentation of rate of anaerobic digestion for increased biogas production, stability and dewaterability [11,12].

The objective of the present work is to study the optimization of ultrasonication process to improve the solubilization and the biodegradability of wastewater sludge using response surface methodology. Furthermore, the effect of ultrasonication process and solids concentration on rheology of wastewater sludge in terms of viscosity was studied to ascertain its actual suitability as a raw material for sludge value addition via fermentation.

## 2. Materials and methods

### 2.1. Sludge

Secondary sludge (cyclic backwash of installed BIODROF® biofilter to remove excess biofilm and/or, biomass chunks) used in the study was obtained from CUQ (Communauté urbaine de Québec, Canada) aerobic wastewater treatment facility. The sludge total solids (TS) was concentrated from 1.5% (w/v) to higher TS concentrations by gravity settling and centrifugation of the settled sludge at 1600 × *g* for 3 min in a Sorvall RC 5C plus Macrocentrifuge (rotor SA-600). The supernatant was discarded; the particulates were diluted with demineralized water to obtain three concentrations (20, 30 and 40 TS g/L) and was homogenized in a Waring™ blender for 30 s. Maximum storage period of sludge was 1 week at 4 ± 1 °C to minimize microbial degradation.

### 2.2. Ultrasonication pre-treatment

The ultrasonication was carried out using ultrasonic homogenizer Autotune 750 W (Cole-Parmer Instruments, Vernon Hills, IL, US). The ultrasonication equipment was operated at frequency of 20 kHz, using platinum probe with tip diameter of 25 mm. Four hundred milliliters of wastewater sludge sample at ambient temperature was placed in a 1 L beaker. The ultrasonic probe was dipped in such a way that it was immersed 2 cm into the sludge. The process efficiency was evaluated by measuring the improvement of solubilization of sludge organic matter in terms of the ratio of change in soluble chemical oxygen demand (SCOD) after ultrasonication to total chemical oxygen demand (TCOD) (Eq. (1)) and biodegradability in terms of TS reduction during aerobic degradation process (Eq. (2))

$$\text{SCOD increment} = \frac{\text{SCOD after ultrasonication} - \text{SCOD before ultrasonication}}{\text{TCOD}} \times 100\% \tag{1}$$

$$\text{Biodegradability} = \left(1 - \frac{\text{TS concentration after biodegradation}}{\text{TS concentration before biodegradation}}\right) \times 100\%. \tag{2}$$

### 2.3. Response surface methodology

Application of response surface methodology for the optimization of ultrasonication will help in overcoming the limitations of time consuming conventional optimization method of 'one-factor-at-a-time' (at each step, a single factor is changed while other factors remain constant). Moreover, the statistical optimization method can evaluate the effective factors and help in building models to study interaction and select optimum conditions of variables for a desirable response. Various stages of the optimization scheme are presented in Fig. 1. In the response surface method, the factors of pre-treatment processes, namely, ultrasonication intensity, ultrasonication time and TS concentration were considered as independent variables, and SCOD increment and biodegradability of pre-treated sludge as dependent variables. To begin with, the screening experiments were carried out to determine the direction of optimal domain of each process. Two-level fractional factorial design (FFD) was employed in the screening step. Once the provisional optimal values were determined, a central composite design (CCD) was used to verify the significance of impact of each factor on the response of SCOD increment and biodegradability. The optimization step required 14 experiments and 6 replicates in all. The levels of each factor along with their codes and values of two experimental designs are listed in Table 1. After running the CCD experiments, a second-order polynomial regression equation was fitted to the data (Eq. (3)). Analysis of data by analysis of variance (ANOVA), regression analysis and the response surface methodology were performed with the statistical software of STATISTICA (version 6, Statsoft Inc., US)

$$Y = \beta_0 + \sum_{i=1} \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} X_i X_j \tag{3}$$

where $Y$ = predicted response of the dependent variable; $X_i$ and $X_j$ = independent variables influencing the response of $Y$; $\beta_0$ = constant of the second-order equation; $\beta_i$ = linear regression coefficient of each independent variable; $\beta_{ii}$ = quadratic regression coefficient of each independent variable; $\beta_{ij}$ = regression coefficient of interactions between two independent variables.

The SCOD increment and biodegradability of raw (as control) and ultrasonicated sludge at TS concentrations as listed in Table 1 were measured in both screening and optimization experiments.

### 2.4. Aerobic biodegradability test

Examination of biodegradability was carried out by inoculating the ultrasonically pre-treated and raw sludges with microbial consortia of 2% (v/v) of fresh activated wastewater sludge (1.5 mL) at solids concentration of 25 g/L followed by incubation at 25 ± 1 °C at 150 rpm on a rotary shaker for 20 days. Oxygen corresponded to the oxygen entrained from the atmosphere into the shaking flasks on a rotary shaker. The biodegradability was assessed by the decrease in TS consumed by the microorganisms after incubation (20 days). At the end of incubation, the volume loss due to evaporation was readjusted to 75 mL with Milli-Q water.

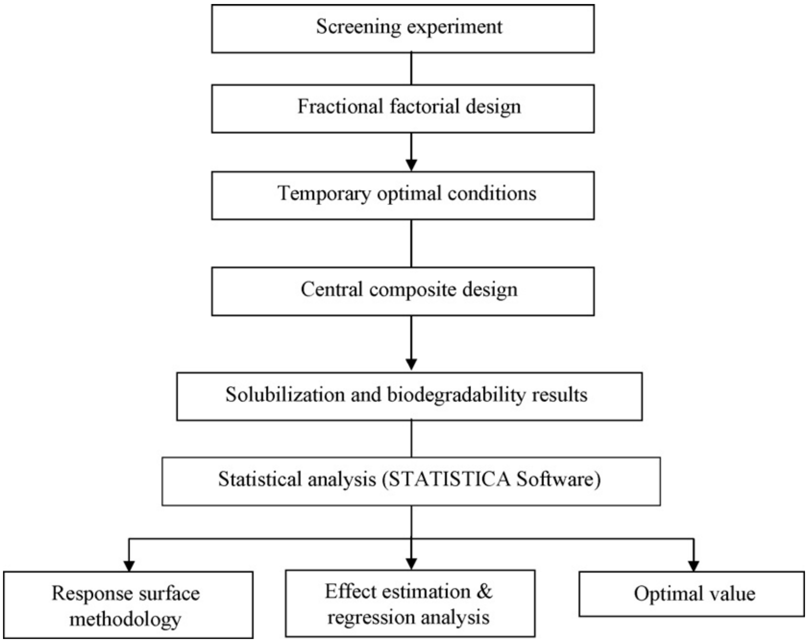

**Fig. 1.** Schematic of optimization of ultrasonication process.

Our previous studies have demonstrated that pre-treatment of sludge (thermal-chemical hydrolysis) resulted in increase in biodegradability and concomitantly increased the yield of value-added products, namely, *Trichoderma* ssp. and *B. thuringiensis*-based biopesticides [2]. Conidia concentration increased from $10^5$ to $10^7$ colony forming units/ml for *Trichoderma* ssp. and the entomotoxicity increased from 12 to 16 billion spruce budworm units/liter for *B. thuringiensis* on pre-treatment. Hence, pre-treatment increased the yield of value-added products brought about by the increase in biodegradability of wastewater sludge.

Therefore, in this research biodegradability was used as a parameter to assess the effectiveness of the ultrasonication sludge pre-treatment process of WWS to increase the concentration yield of value added products required to make the process economical.

## 2.5. Parameter analysis

### 2.5.1. General

Total solids (TS), volatile solids (VS), suspended solids (SS), dissolved solids (DS), volatile suspended solids (VSS), and chemical oxygen demand (COD) were determined as per Standard Methods [13]. Chemical oxygen demand was measured in total sludge (TCOD) and in supernatant (SCOD) by centrifuging at 7650 × *g* in 15 min at 4 °C, followed by filtration of the sludge supernatant. Changes in general parameters in raw and ultrasonicated sludge are presented in Table 2.

### 2.5.2. Viscosity

Rheological properties in terms of viscosity of raw and ultrasonicated sludges were determined by using a rotational viscometer Brookefield DVII PRO+ (Brookfield Engineering Laboratories, Inc., Stoughton, MA, USA) equipped with Rheocalc32 software. Two different spindles, namely, SC-34 (small sample adaptor), and ultra-low centipoise adapter were used with a sample cup volume of 18 mL/50 mL (spindle dependent). The gaps between spindle and respective sample chamber were 1.235 and 4.830 mm respectively, for ultralow (viscosity range, 1.0–30 mPa s), and small sample (viscosity range, ≥30 mPa s) adapter spindle to accommodate sludge flocs. The calibration and viscosity testing procedure for each spindle was carried out as per instrument manual. Time-dependent profile was studied at low shear rate (3.67 $s^{-1}$) and viscosity of sludge sample at different TS concentrations was measured at 36.69 $s^{-1}$. The shear rate behaviour was determined from 1.4 to 56 $s^{-1}$. All measurements were done at 25 ± 1 °C and viscosity was referred to as “apparent viscosity”. The viscosity data acquisition and analysis was carried out using software, Rheocalc V2.6 (comprising commands, B.E.A.V.I.S. – Brookfield Engineering Advanced Viscometer Instruction Set, allowed the creation of programs to control connected instrumentation and manipulate data acquisition).

**Table 1**
Codes and values of independent variables of experimental designs for screening using response surface methodology

| Factor, symbol | Experimental design | Level | | | | |
|---|---|---|---|---|---|---|
| | | −2 | −1 | 0 | +1 | +2 |
| Ultrasonication intensity (W/cm$^2$), $X_1$ | FFD | | 0.27 | 0.51 | 0.75 | |
| | CCD | 0.56 | 0.62 | 0.75 | 0.86 | 0.92 |
| Time (min), $X_2$ | FFD | | 20 | 40 | 60 | |
| | CCD | 43 | 50 | 60 | 70 | 77 |
| Total solids (g/L), $X_3$ | FFD | | 23 | 33 | 44 | |
| | CCD | 10 | 15 | 23 | 31 | 36 |

**Table 2**
Changes in analytical parameters after ultrasonication (at optimal conditions: ultrasonication intensity, 0.75 W/cm$^2$; time, 60 min; TS = 23 g/L)

| Parameters | Raw sludge | Ultrasonicated sludge |
|---|---|---|
| Total solids (TS) (g/L) | 23 ± 0.25 | 23 ± 0.19 |
| Volatile solids (VS) (g/L) | 13.9 ± 0.34 | 9.8 ± 0.23 |
| Suspended solids (SS) (g/L) | 21.4 ± 0.17 | 17.9 ± 0.13 |
| Volatile suspended solids (VSS) (g/L) | 13 ± 0.13 | 9 ± 0.11 |
| pH | 5.7 | 5.7 |
| Total chemical oxygen demand (TCOD) (g/L) | 102 080 ± 243.8 | 102 080 ± 151.0 |
| Soluble chemical oxygen demand (SCOD) (g/L) | 39 100 ± 146.0 | 80 500 ± 146.0 |

## 3. Results and discussion

### 3.1. Screening experiments

The results of screening experiments, including eight combined runs and three runs of replication are shown in Table 3. The highest response of both solubilization and biodegradability was recorded in run no. 4 at ultrasonication intensity of 0.75 W/cm$^2$, with time duration of 60 min at a TS concentration 23 g/L. The SCOD increment and solids degradation were highest at 45.5% and 56%, respectively. It was observed that the ultrasonication intensity and ultrasonication time had substantial impact on the solubilization as well as biodegradation of sludge. The values of SCOD increment were higher than those obtained by Bougrier et al. [14], in which the ratio of SCOD/TCOD after ultrasonication treatment at 20 kHz frequency in 10 min was 32% at a specific energy of 14 550 kJ/kg. These values were drawn from the graphs and also re-calculated using the Equation, $E = Pt/vTS$; where, $P$ = ultrasonic power (W) calculated from ultrasonication intensity, $t$ = ultrasonication time (s), $v$ = sample volume (L) and TS concentration (g/L). The lower ratio of SCOD/TCOD reported by these authors was due to the shorter duration of ultrasonication. In fact, it has been reported that the sonication of biological sludge is a multi-stage process [15]. In the first stage (0–20 min), mechanical forces break down the porous flocs into small particles; in the second stage (20–60 min) ultrasonication solubilizes extracellular polymers and causes cell lysis releasing intracellular materials (inactivating the biomass). The transformation of solid-state bound organic compounds into a soluble form could be induced continuously by the elevated bulk temperature during sonication. Therefore, the required ultrasonication time was 60 min for sludge disintegration resulting in decrease in volatile suspended solids further aided by the hydromechanical shear forces and the increase of bulk temperature. The effective impact of the lower solids concentration (23 g/L) on solubilization and biodegradation of sludge was also in agreement with the results of Verma et al. [2] who reported the optimal TS concentration as 20 g/L for the biodegradability of alkaline thermal hydrolyzed sludge to produce *T. viride*-based biopesticides. At higher solids concentration, the microorganisms could be inhibited by higher amount of substrates and some unknown compounds (produced during pre-treatment process) in sludge [4]. Moreover, high solids concentration leads to mass and oxygen transfer limitation during biodegradation.

Furthermore, the specific supplied energy calculated using Equation, $E = Pt/vTS$ is also given in Table 3. Taking into account the supply of energy, the run no. 2 in which 0.75 W/cm$^2$ of ultrasonication intensity, 20 min of ultrasonication time and 23 g/L of total solids with a specific energy of 3456.5 kJ/kg was chosen as optimal condition which gives 37.56% of SCOD increment and 32.6% of biodegradability. However, based on percent SCOD increment (run no. 4), 45.5% solubilization and 56% biodegradability gave the best results for solids concentration of 23 g/L. Thus, run no.4 was preferred to set the provisional optimum conditions for the optimization experiments.

### 3.2. Optimization studies

#### 3.2.1. Effect of ultrasonication on biodegradability of sludge

The results of 2$^3$ CCD experiments are presented in Table 4 showing the highest TS reduction obtained from the first experiment of 36% at ultrasonication intensity of 0.62 W/cm$^2$, in 50 min and 15 g/L TS concentration. Under these conditions, the biodegradability increase was observed from 26.3% to 36%, at TS concentration of 15 g/L for raw and ultrasonicated sludges, respectively. The biodegradability enhancement by ultrasonication is lower compared to alkaline thermal hydrolysis (26.5–44.5%) as reported in the studies of Verma et al. [2]. The disparity could be explained by the combined effect of alkaline hydrolysis at high temperature (121 °C) as a physicochemical process on biodegradability enhancement. Meanwhile, the effect of ultrasonication as a physical process on biodegradability is only mechanical. In the light of the results obtained in this study, it is possible that the biodegradability can be improved if ultrasonication was combined with chemical process.

The statistical significance of the second-order polynomial model was verified by ANOVA. The analysis indicated that the second-order polynomial model resulted in a determination coefficient $R^2$ of 0.87, which ensured a satisfactory adjustment of the quadratic model to the experimental data. Table 5 presents the estimation of effects of each factor and their interactions on the biodegradability along with the regression coefficients of each component determined by regression analysis. The evaluation of statistical significance of the three factors and their interaction was based on probability ($p$) values. The quadratic effects of the ultrasonication intensity ($X_1^2$) is highly significant ($p < 0.001$), followed by the quadratic effects of exposure time and solids concentration ($p < 0.01$). The linear effects of three factors and their interactive effects are of very little significance ($p$-values presented in Table 5).

The regression coefficients were then fitted in the Eq. (3) to give the following model (Eq. (4)). However, the regression coefficients which were found insignificant ($p < 0.01$) were excluded from the model

$$Y = 5.98 - 0.18X_1 + 0.002X_1^2 - 0.058 * X_2 + 0.0004\ X_2^2 + 0.0005X_3^2 \tag{4}$$

The linear coefficient of the ultrasonication intensity ($X_1$) has negative effect and it is highly significant ($p < 0.001$). The linear coefficient of the treatment time ($X_2$) having negative effect is statistically significant ($p < 0.01$). All quadratic coefficients comprising three factors have positive effects and the quadratic coefficient of ultrasonication intensity ($X_1^2$) is the most significant. The regression coefficients of interaction of each pair of the independent variables are not significant. The response surface graphs are shown in Fig. 2 as a function of two factors at a time, holding the third factor at fixed zero level and are in fact more helpful in interpreting the main effect and the interactions. In order to arrive at the choice of fixed parameters using response surface methodology, following sequential procedure was employed: (a) fix one independent variable at

**Table 3**
Results of screening experiments of the $2^{3-1}$ FFD

| Run | Ultrasonication parameters | | | | Ultrasonicated sludge characteristics | |
|---|---|---|---|---|---|---|
| | Ultrasonication intensity (W/cm$^2$) | Time (min) | TS (g/L) | Specific energy (kJ/kg) | SCOD increment (%) | TS reduction (%) |
| 1 | 0.27 | 20 | 23 | 1 226.1 | 36.0 | 31.3 |
| 2 | 0.75 | 20 | 23 | 3 456.5 | 37.6 | 32.6 |
| 3 | 0.27 | 60 | 23 | 3 678.3 | 38.4 | 32.6 |
| 4 | 0.75 | 60 | 23 | 10 369.6 | 45.5 | 56(12.88)[a] |
| 5 | 0.27 | 20 | 44 | 640.9 | 30.9 | 34.8 (15.31)[a] |
| 6 | 0.75 | 20 | 44 | 1 806.8 | 34.7 | 33.2 |
| 7 | 0.27 | 60 | 44 | 1 922.7 | 33.9 | 32.5 |
| 8 | 0.75 | 60 | 44 | 5 420.5 | 39.2 | 33.4 |
| 9 | 0.51 | 40 | 33 | 3 234.5 | 35.8 | 35.8 (11.81)[a] |
| 10 | 0.51 | 40 | 33 | 3 234.5 | 35.9 | 34.8 |
| 11 | 0.51 | 40 | 33 | 3 234.5 | 35.7 | 33.3 |
| Control-1s[b] | – | – | 23 | – | | 27.4 (6.3)[a] |
| Control-2s[b] | – | – | 33 | – | | 27.9 (9.21)[a] |
| Control-3s[b] | – | – | 44 | – | | 26.1 (11.48)[a] |

[a] Values in parentheses correspond to the TS reduction calculated as g/L.

[b] Controls 1s, 2s, 3s refer to raw sludges at TS concentrations of 23, 33, and 44 g/L. "s" refers to screening experiments.

**Table 4**
Results of SCOD increment and biodegradability of optimization experiments of CCD

| Run | Factors in coded units | | | SCOD increment (%) | Biodegradability (%) |
|---|---|---|---|---|---|
| | $X_1$ | $X_2$ | $X_3$ | | |
| 1 | −1 | −1 | −1 | 28.6 | 36.00 |
| 2 | 1 | −1 | −1 | 25.5 | 33.33 |
| 3 | −1 | 1 | −1 | 22.1 | 30.00 |
| 4 | 1 | 1 | −1 | 23.4 | 28.00 |
| 5 | −1 | −1 | 1 | −2.3 | 35.65 |
| 6 | 1 | −1 | 1 | 3.4 | 25.65 |
| 7 | −1 | 1 | 1 | −0.8 | 35.32 |
| 8 | 1 | 1 | 1 | −0.4 | 29.03 |
| 9 | −2 | 0 | 0 | 9.6 | 30.87 |
| 10 | 2 | 0 | 0 | 11.2 | 28.70 |
| 11 | 0 | −2 | 0 | 10.8 | 30.87 |
| 12 | 0 | 2 | 0 | 12.5 | 22.61 |
| 13 | 0 | 0 | −2 | 9.0 | 21.00 |
| 14 | 0 | 0 | 2 | 17.1 | 26.39 |
| 15 | 0 | 0 | 0 | 15.0 | 16.09 |
| 16 | 0 | 0 | 0 | 14.2 | 20.00 |
| 17 | 0 | 0 | 0 | 15.2 | 13.48 |
| 18 | 0 | 0 | 0 | 14.8 | 21.30 |
| 19 | 0 | 0 | 0 | 14.8 | 18.70 |
| 20 | 0 | 0 | 0 | 14.6 | 16.09 |
| Control-1 op | – | – | 10 | | 27.00 |
| Control-2 op | – | – | 15 | | 26.30 |
| Control-3 op | – | – | 23 | | 25.9 |
| Control-4 op | – | – | 31 | | 25.6 |
| Control-5 op | – | – | 36 | | 19.9 |

Controls from 1 op to 5 op refer to raw sludge at TS concentrations of 10, 15, 23, 31, and 36 g/L. "op" refers to optimization experiment.

**Table 5**
Effect of estimation and regression coefficient of the components of the model fitted to the data of CCD

| Component | Effect estimation | | | | Regression coefficient | | | |
|---|---|---|---|---|---|---|---|---|
| | SCOD increment | | Biodegradability | | SCOD increment | | Biodegradability | |
| | Effect | $p$ | Effect | $p$ | Regression coefficient | $P$ | Regression coefficient | $p$ |
| Constant | 0.7454 | 0.000 | 0.1739 | 0.0000 | −0.2345 | 0.9163 | 5.9673 | 0.0001 |
| $X_1$ | 0.0107 | 0.8001 | −0.0372 | 0.0755 | 0.0573 | 0.4727 | −0.1844 | 0.0004 |
| $X_1^2$ | −0.0378 | 0.3950 | 0.1140 | 0.0001 | −0.0008 | 0.395 | 0.0022 | 0.0002 |
| $X_2$ | −0.0115 | 0.7805 | −0.0323 | 0.1077 | 0.013 | 0.6972 | −0.0581 | 0.0027 |
| $X_2^2$ | −0.0247 | 0.5372 | 0.0782 | 0.0012 | −0.0001 | 0.5372 | 0.0003 | 0.001 |
| $X_3$ | −0.2534 | 0.0001 | 0.0106 | 0.5812 | −0.0327 | 0.3899 | −0.0212 | 0.2269 |
| $X_3^2$ | 0.0034 | 0.9364 | 0.0639 | 0.0069 | 0.00003 | 0.9364 | 0.0005 | 0.0069 |
| $X_1X_2$ | −0.0023 | 0.9659 | 0.0109 | 0.6590 | −0.00002 | 0.9659 | 0.0001 | 0.659 |
| $X_1X_3$ | 0.0198 | 0.7161 | −0.0290 | 0.2549 | 0.0002 | 0.7162 | −0.0003 | 0.2549 |
| $X_2X_3$ | 0.0153 | 0.7784 | 0.0359 | 0.1655 | 0.0001 | 0.7785 | 0.0002 | 0.1655 |

temporary optimum value obtained from the screening experiments as discussed earlier; (b) choose two independent variables to construct 3-D graphs; (c) finally obtain the surface response graphs.

Fig. 2a shows the response for the interactive factors, ultrasonication intensity ($X_1$) and exposure time ($X_2$), when the TS concentration was 23 g/L. Higher biodegradability was observed at low ultrasonication intensity and in short duration of exposure time. The highest percentage of solids reduction was obtained in the shortest time duration of 40 min and lowest ultrasonication intensity of 0.51 W/cm$^2$. Maximum biodegradability under these conditions was predicted to be 65%. Furthermore, the response also increased when the ultrasonication intensity was increased and the time was shortened, and vice versa. The interaction between ultrasonication intensity and solids concentration presented in Fig. 2b also suggested that low ultrasonication intensity was more efficient, but it must be associated with high solids concentration. The predicted maximum biodegradability was 58% at 36 g/L TS, 0.51 W/cm$^2$ ultrasonication intensity in 60 min. Fig. 2c revealed that increase in TS concentration and exposure time did not have any effect on biodegradability when the ultrasonication intensity was kept at 0.75 W/cm$^2$. Maximum solids reduction (53%) was obtained at the lowest TS concentration of 8 g/L and the shortest time duration of 40 min.

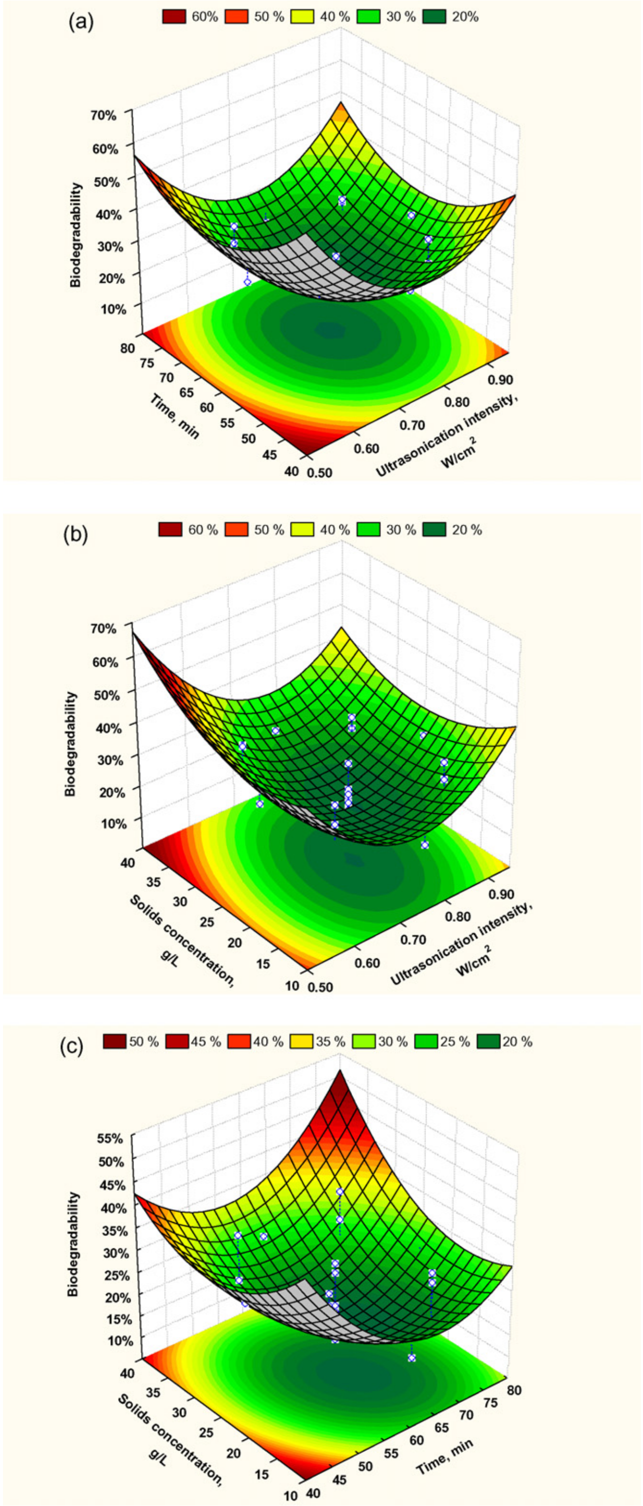

**Fig. 2.** Response surface plots of biodegradability as a function of: (a) ultrasonication intensity and time (TS is constant); (b) ultrasonication intensity and solids concentration (time is constant); time and solids concentration (ultrasonication intensity is constant). Legends represent the biodegradability measured as percentage.

The detailed analysis of significance of the factor on response of biodegradability showed that the ultrasonication intensity exhibited major effect on improving the biodegradability. This parameter relates to ultrasonic power, so that increase in ultrasonication intensity leads to increase in power input. However, in terms of improving biodegradability, it did not seem interesting to have ultrasonication intensity higher than 0.75 W/cm$^2$. Lower solids concentration would be more efficient for biodegradability. This could be explained by the absorption of the ultrasound wave by the particles, and the interruption of propagation of ultrasound energy in the slurry phase, leading to reduced cavitation effect [3,12]. From the model based on response surface methodology, the optimal conditions of ultrasonic pre-treatment of secondary sludge at 20 kHz were identified as follows: 0.75 W/cm$^2$ ultrasonication intensity, 60 min with 23 g/L TS concentration. Taking into account specific supplied energy, the optimal conditions gave energy input of 10 356 kJ/kg TS at biodegradability of 36.5%. It was reported that biogas production of ultrasonicated sludge increased for specific energy input of 7000 kJ/kg TS and then remained constant for 7000–15 000 kJ/kg TS [14]. There was a possible link between biodegradability and solubilization, as the increase in solubilization by energy input had the same evolution tendency as biodegradability (discussed below).

### 3.2.2. *Effect of ultrasonication on solubilization of sludge*

SCOD increment (solubilization) has been adopted as a measure of ultrasonic disintegration efficiency, and supposed to improve biodegradability. In fact, under powerful hydro-mechanical shear forces generated from sudden and violent collapse of microbubbles, extracellular polymeric substances (EPS) considered as matrix that embedded cell sludge were degraded [16]. Consequently, the organic matter contained in EPS and cells were solubilized, coming under perpetual attack of collapsing cavitation bubbles, increasing the tendency to augment biodegradability. According to the estimation of effects of different parameters represented in Table 5, no remarkable effects of each factor and their interaction on solubilization were observed, except that the linear effect of solids concentration was highly significant ($p < 0.001$). Nevertheless, the response surface graph of solubilization affected by the ultrasonication intensity and time at constant TS concentration of 23 g/L (Fig. 3) showed that highest solubilization occurred at 0.75 W/cm$^2$ ultrasonication intensity in 60 min. In terms of ultrasonic energy, the highest SCOD increment (45.5%) and biodegradability (56%) was obtained at specific energy input of 10 356 kJ/kg TS. These results are similar to earlier studies reported on ultrasonicated waste-activated sludge [3,14]. These studies reported that maximum solubilization (35%) in terms of SCOD was obtained for

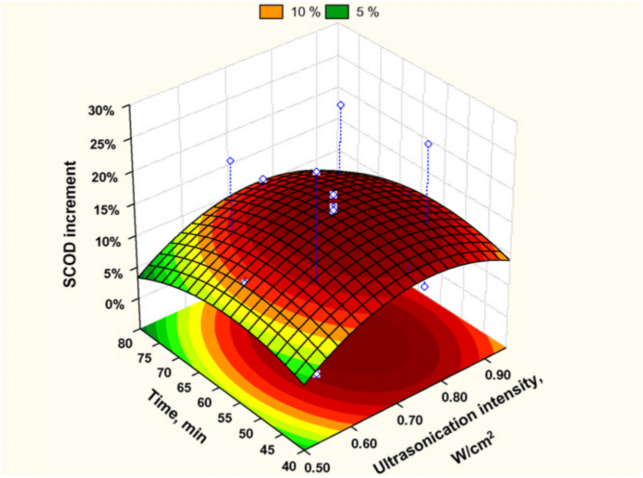

**Fig. 3.** Response surface plot of solubilization as a function of ultrasonication intensity and time. Legends represent the SCOD increment measured as percentage.

supplied energy of 10 000 kJ/kg TS. However, the biodegradability measurements were not direct and instead were reported in terms of biogas production which was found to be 1.4 times higher than untreated sludge. The results suggested that there was a correlation between improvement of solubilization and biodegradability by ultrasonication. Moreover, the floc structure of sludge volatile suspended solids was broken down during ultrasonication resulting in decrease in VSS and hence solubilization (Table 2). However, solubilization does not necessarily change the total carbon content of the sludge, but will result in an increase in biodegradability, thus correlating the two parameters.

### 3.3. *Flowability of sludge (viscosity)*

#### 3.3.1. *Effect of solids concentration*

The flowability of raw and ultrasonicated sludges was studied in terms of the correlations of viscosity with TS concentration and shear rate. The curves presenting the relation between viscosity and TS concentration of raw and ultrasonicated sludges fitted well into the exponential equations ($\text{Viscosity}_{RS} = 1.136e^{1.2008TS}$; $R^2 = 0.9549$; $\text{Viscosity}_{ULS} = 1.1985e^{1.0953TS}$; $R^2 = 0.9282$) as shown in Fig. 4. The exponential increase of viscosity with TS concentration was in agreement with earlier viscosity studies on raw, anaerobic and aerobic digested, and thermal hydrolyzed wastewater sludges [1]. Moreover, particle concentration increase, prompt formation of flocs due to high amount of EPS in sludge possessing higher solids concentration could lead to high viscosity [17,18]. The constant values of two exponential equations can be used as control parameter for mixing and pumping in sludge treatment processes [19]. As shown in Fig. 4, there was not much change in the apparent viscosity by ultrasonication process at 10 g/L TS. The decrease of viscosity by ultrasonication was observed from 20 g/L of TS. The apparent viscosity ranged from 2.89–359.7 and 2.51–199.2 mPa s, respectively, for raw and ultrasonicated sludges at 10–40 g/L solids concentration. Disintegration of sludge flocs, cell lysis, and cleavage of interactions due to hydroshear forces from acoustic cavitation and the partial hydrolysis of EPS caused by increase in bulk temperature during ultrasonication could be the reasons for the decrease in viscosity of ultrasonicated sludge [9–11]. The decline of viscosity played an important role in the increase in the biodegradability of sludge, as this strongly influenced the mass transfer in aerobic degradation. After aerobic digestion, the apparent viscosity decreased from 76.6 to 41 and 72.9 to 11 mPa s, respectively, for raw and ultrasonicated sludges at 25 g/L TS concentration. The trend in decrease in viscosity after the digestion of ultrasonicated sludge was in agreement with the data observed for 20-days digested thermal alkaline hydrolyzed sludge [2]. Under aerobic condition, microorganisms consumed sludge solids as substrate and released carbon dioxide and water. As a result, viscosity of digested sludge decreased due to the reduction of sludge solids. Moreover, EPS will also undergo biodegradation during aerobic digestion resulting in free floating sludge flocs [20].

#### 3.3.2. *Effect of shear rate and time*

The apparent viscosity evolution as a function of time and shear rate was studied at TS concentration of 25 g/L. As shown in Fig. 4, the apparent viscosity decreased from 131.97 to 13.80 mPa s with increase in shear rate from 1.4 to 56 $s^{-1}$, and hence showed shear-thinning behaviour for raw and ultrasonicated sludges. Moreover, at constant shear rate (3.67 $s^{-1}$), the apparent viscosity (0–102 min time range) decreased from 279.94 to 169.96 and 159.9 to 100 mPa s, respectively, for raw and ultrasonicated sludges, showing the thixotropic (time dependent) behaviour of the ultrasonicated sludge. These are in agreement with earlier studies on anaerobic granular and thermal alkaline hydrolyzed sludges [1,17]. Notably, the apparent viscosity of ULS reaches a constant value (before the first 30 min) faster than the RS (after 50 min). In fact, a correlation between viscosity and shear rate led to linear behaviour with viscosity of raw sludge being highly affected by the shear rate in comparison to ultrasonicated sludge (results not shown). Briefly, rheological properties in terms of viscosity of wastewater sludge were shown to improve on pre-treatment by ultrasonication process resulting in better mixing and pumping properties in wastewater treatment plants. In fact, viscosity is an important parameter which influences pumping and mixing characteristics of any fluid [21].

When these results are compared with our earlier studies performed on enhancement of biodegradability using thermal chemical hydrolysis [2], following points come to the fore: (a) thermal alkaline hydrolysis includes use of chemicals (NaOH and $H_2SO_4$), increasing the secondary pollution load, which is absent for ultrasonication; (b) thermal treatment will omit the sterilization step for thermal alkaline hydrolysis which may not be the case for

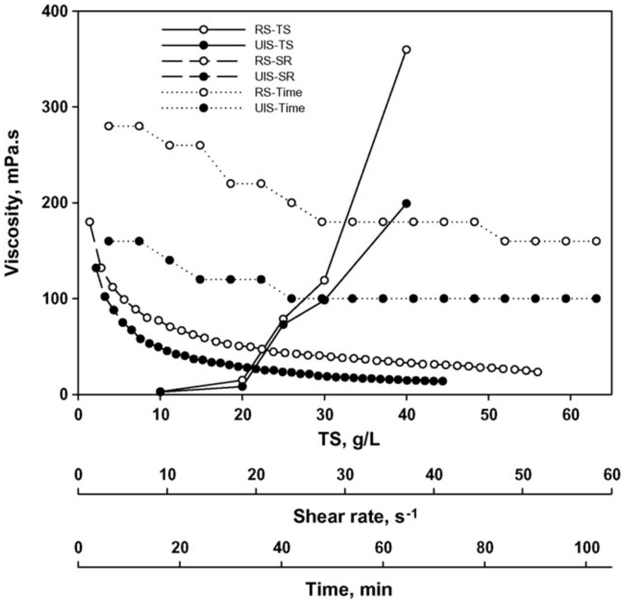

**Fig. 4.** Viscosity evolution of raw and ultrasonicated sludge as a function of TS concentration, shear rate and time.

ultrasonication necessitating an additional sterilization step due to microbial viability, if the ultrasonicated sludge is to be used for the production of value-added products; (c) thermal alkaline hydrolysis and ultrasonication might result in formation of potentially more toxic organic compounds, which will determine the efficacy of the process in terms of detoxification of waste streams. Nevertheless, ultrasonication can serve as an efficient pre-treatment tool for aerobic digestion processes and similar treatment processes in wastewater treatment plant.

Thus, future work is under progress in our laboratory on the production of *B. thuringiensis*-based biopesticides and thermoalkaline proteases for detergents using ultrasonicated sludge as a raw material (in bench scale fermenters) to evaluate effects of ultrasonication on value-addition.

## 4. Conclusions

The present research work on ultrasonication pre-treatment of secondary sludge for the enhancement of biodegradability led to following conclusions:

1. Central composite experimental design supplied enough information for optimization, while reducing the number of individual experiments. Response surface plots were extremely noteworthy in visualizing the effect and interactions of various parameters.
2. Ultrasound power defined as ultrasonication intensity plays an important role in increasing the sludge biodegradability which was determined to be 0.75 W/cm$^2$ in comparison to control.
3. The ultrasonication exposure time of 60 min must be maintained in order to obtain disruption of flocs as well as cell lysis; enhanced SCOD increment and biodegradability.
4. Total solids concentration is one of the key parameters affecting ultrasonic disintegration efficiency which was determined to be 23 g/L.
5. The biodegradability and SCOD increment of wastewater sludge was found to be 56% and 45.5%, respectively, under optimal conditions (ultrasonication intensity, 0.75 W/cm$^2$; exposure time, 60 min and TS, 23 g/L).
6. The sludge viscosity decreased on ultrasonication pre-treatment. The ultrasonicated sludge bore exponential relationship with total solids concentration, and exhibited pseudoplastic and thixotropic behaviour.

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