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Microwave Enhanced Advanced Oxidation in the Treatment of Dairy Manure

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1. Introduction

Microwave heating is a dielectric heating process, in which heat is generated via the interaction of dielectric materials with electromagnetic radiation. The dielectric constant is a measure of the material's capacity to retard microwave energy as it passes through, while the loss factor is a measure of the material's capacity to dissipate the energy. The materials with high loss factor are easily heated through microwave irradiation. Energy dissipation mechanism in the materials is via ionic conduction and dipolar rotation. Generally, the dielectric properties of a material are related to temperature, moisture content, density and material geometry. Microwave heating has the advantages of higher heating rates, no direct contact between the heating source and heating material, selective heating, reduced equipment size and better process control than those of conventional heating. Moreover, both DNA and bacterial cellular membranes can be damaged by microwave irradiation. Such an effect on the treatment process, besides heating, is referred to as the athermal effect (Hong et al. 2006).

Microwave heating has been applied in various processes and manufacturing industries, such as food process, wood drying and waste treatment process (Jones, et al., 2002). For the sewage wastewater treatment industry, there are many applications of microwave heating on sludge treatment for reducing volume, improving dewaterability, enhancing digestibility, enhancing nutrient release, pathogen destruction, and stabilizing heavy metal (Menendez, et al., 2002; Liao, et al., 2005; Wojciechowaska 2005; Hong et al., 2006; Eskicioglu et al., 2007; Hsieh et al., 2007; Yu, et al., 2010). It has also been reported that the overall treatment efficiency could be increased with a combination of microwave heating with chemicals (thermo-chemical) for the treatment of sludge (Chan, et al., 2007; Qiao, et al., 2008). The common chemicals used on thermo-chemical process are acid, base and oxidants. The microwave enhanced advanced oxidation process (MW/H₂O₂-AOP) uses microwave irradiation in combination with hydrogen peroxide to generate hydroxyl radicals to react with organic compounds. As a result, the structure of the solid materials is altered, and nutrients can be released into solution in the process. During this treatment, the suspended solids (SS) content of the slurries is also reduced. Its mechanism is assumed to be similar to the wet-air oxidation process wherein the first process involves the breakdown of large particulate organic matters, such as carbohydrate and proteins into smaller and more soluble organic components, and the second process involves the further oxidation or gasification of some of the resulting

organic products (Shanableh & Shimizu, 2000; Liao, et al., 2007). The factors affecting the performance of the MW/H₂O₂-AOP have been identified; they are microwave temperature, hydrogen peroxide dosage, microwave intensity, reaction time, and acid addition. The effects varied with the application, depending on the soluble materials of interest, and various waste organic slurries used in the process (Wong et al., 2007). Dairy manure contains fats, proteins, lignin, carbohydrates and inorganic residue, and is rich in a variety of nutrients including nitrogen, phosphorus, and minerals (Rico, et al., 2007) and it should be deemed as a valuable biological resource, rather than a waste product. Lignocellulosic components from dairy manure can be transformed into fermentable saccharides via enzyme, or acid hydrolysis, which can further be converted into ethanol and other valuable products (Wen, et al., 2004). Nutrients, such as phosphorus and ammonia-nitrogen can be recovered via a struvite crystallization process. Carbonaceous matters can also be subjected to anaerobic digestion for methane production, which is a valuable bioenergy source. However, most of the phosphorus in dairy manure (about 65%) is in a form that is not easily soluble, especially those in the form of structural makeup (Barnet, 1994). Besides, high suspended solids are typical of dairy manure; hence, a pre-treatment step is required to solublize the nutrients and to disintegrate solids first in order to achieve resource recovery.

The MW/H₂O₂-AOP, which can disintegrate solids and release nutrients into solution, can be a potential effective pre-treatment method for nutrient and energy recovery from dairy manure. The effectiveness of the MW/H₂O₂-AOP under both batch operation and a continuous mode of operation for solubilisation of nutrients and organic matters from dairy manure are therefore reported in this chapter.

2. Materials and methods

2.1 Apparatus

A lab-scale Milestone Ethos TC microwave oven digestion system (Milestone Inc., USA) was used for a batch mode operation. The system operates at a frequency of 2,450 MHz with a maximum power output of 1,000 W. The system has the capacity of handling up to 12 vessels in a single run: one reference and 11 sample vessels, each with a volume of 100 mL. A thermocouple is inserted into the reference vessel, providing real time temperature monitoring during the runs. The maximum operating temperature and pressure are 220 °C and 435 psig, respectively.

A household microwave oven (Panasonic Genius Prestige Countertop) was modified for use in a continuous mode operation. The system operates at a frequency of 2,450 MHz with a maximum power output of 1,000 W. A silicon tube with 6.35 mm diameter was wound into a continuous horizontal coil and held by a custom made perforated polypropylene shelf. The total length of the silicon tube inside the MW is 40 m and the volume is approximately 1.3 L. The dairy manure was pumped into the MW oven through the silicon tube and was collected from the outlet. An appropriate amount of concentrated sulfuric acid was added to the liquid manure to the desired acid concentration before the mixture was pumped into the MW oven. The desired H₂O₂ dosage in the process was controlled by the flow rate and the concentration of the prepared H₂O₂. Different exit temperatures after the MW treatment can be achieved by controlling the flow rate of both the liquid manure and H₂O₂; a higher flow rate yields a lower exit temperature. The overall heating rate of 5 °C/min was used in this study. The unit was not pressurized; the exit temperatures were therefore lower than the boiling point of water.

2.2 Substrate

Dairy manure was obtained from the UBC Dairy Education & Research Centre in Agassiz, British Columbia, Canada. The dairy manure used for the batch operation was the solid portion obtained after the solid-liquid separation. Once collected from the farm the dairy manure was stored in a closed container at 4°C. The dairy manure sample had total solids (TS) of 33%, which contained large amounts of sand, the bedding material, as well as undigested lignocellulosic materials. Distilled water was added to the dairy manure samples and subsequently decanted to remove the sand. The resulting dairy manure had a TS of 5.6% for the first part of the batch operation (Part 1), while 3.7 % TS for the second part of the study at pH 4 (Part 2).

For a continuous operation, the liquid manure after the solid-liquid separation was again passed through a U.S. Standard No. 18 sieve (1 mm openings) to remove large fibres and particles to avoid solids deposition in the silicon tube in the MW unit. It was then diluted four times with distilled water to have TS of 0.83%.

2.3 Experimental design

2.3.1 Batch operation

For Part 1, few variables were held constant, including the dosage of hydrogen peroxide (1.5 mL of 30% concentration, or expressed as 0.28 g H₂O₂/g TS), treatment time (20 minutes), and treatment temperature (120 °C). In an effort to isolate the effects of pH and hydrogen peroxide on the microwave process, experiments under acidic, neutral, and basic conditions, as well as in the absence and presence of hydrogen peroxide were tested. The experimental conditions included microwave treatment only (MW), microwave treatment with hydrogen peroxide (MW/H₂O₂), microwave treatment in acidic condition (MW/H⁺), microwave treatment with hydrogen peroxide in acidic condition (MW/H₂O₂/H⁺), microwave treatment in basic condition (MW/OH⁻), and microwave treatment with hydrogen peroxide in basic condition (MW/H₂O₂/OH⁻). Four replicates were conducted for each experimental condition. In adjusting to acidic conditions, dilute H₂SO₄ was dripped into the dairy manure solution to reach a pH of 4; whereas for basic conditions, dilute NaOH solution was added to reach a pH of 10.

For Part 2, the acidified dairy manure was chosen. Variables including treatment temperature, treatment time, and hydrogen peroxide dosage at pH 4 were tested for their effects on solids disintegration and nutrient solubilization. Based on a computer statistical program, the Box-Benken design for response surface plots was chosen, and a series of 15 trials was required (Sall, et al., 2005). The temperature range was between 80 and 160 °C, treatment time ranged from 10 to 20 min, while hydrogen peroxide dosage was from 0 to 0.14 g H₂O₂/g TS. The rate of temperature increase for all the experiments were set at 20 °C per minute up to the designated treatment temperature and subsequently held for the specified time period. The experimental design is listed in Table 1.

2.3.2 Continuous operation

The MW/H₂O₂-AOP experiments were operated at temperatures of 60, 70, 80 and 90 °C. The H₂O₂ dosage was fixed at 0.1% (v/v) and the acid dosages were 0.2, 0.5 and 1% (v/v) for each temperature. A set of experiments without H₂O₂ was performed to serve as control. Overall, sixteen individual experiments each with three replicates were conducted.

Set #	Temp °C	Heat time (min)	Dosage (mL)	g H ₂ O ₂ /g TS
1	120	15	0.25	0.068
2	160	20	0.25	0.068
3	120	15	0.25	0.068
4	80	10	0.25	0.068
5	80	15	0	0.000
6	160	15	0.5	0.135
7	160	15	0	0.000
8	80	20	0.25	0.068
9	160	10	0.25	0.068
10	120	10	0	0.000
11	120	15	0.25	0.068
12	80	15	0.5	0.135
13	120	20	0	0.000
14	120	20	0.5	0.135
15	120	10	0.5	0.135

Table 1. JMP design for Part 2 of batch operation

2.4 Chemical analysis

The samples were centrifuged at 3500 rpm for 10 minutes first, and then their supernatants were extracted for analysis for soluble chemical oxygen demand (SCOD), orthophosphate, soluble ammonia, volatile fatty acids (VFA) and reducing sugar. For dairy manure, the orthophosphate analysis could be affected by dilution due to interference, resulting in erroneous values; in order to obtain correct results, the initial dairy manure sample was first diluted to 0.5% TS before proceeding with the analysis (Wolf et al., 2005). It was also proven in a previous study that after microwave treatment the results obtained are reliable (Kenge, et al., 2009). The initial dairy manure samples were also analyzed for TS, total chemical oxygen demand (TCOD), total phosphate (TP) and total Kjeldahl nitrogen (TKN). All of the chemical analyses, except that of reducing sugar, followed the procedures outlined in Standard Methods (APHA, 1998). The colorimetric method was employed to determine the total reducing sugar content using anthrone reagent (Raunkjer, et al., 1994).

All chemical analyses were determined by a flow injection system, except determinations of TS and COD (Lachat Quik-Chem 8000 Automatic Ion Analyzer, Lachat Instruments, USA). A Hewlett Packard 5890 Series II gas chromatograph, equipped with a flame ionization detector (FID), was used to measure VFA. Volatile separation was accomplished with an HP FFAP (free fatty acid phase) column (0.25 m × 0.31 mm with 0.52 μm film thickness). The injection temperature was set at 175 °C and the flame ionization detector was at 250 °C. Helium gas was used as the carrier at a head pressure of 69 kPa.

3. Results and discussion

3.1 Batch operation

3.1.1 Part 1

The effects of pH and H_2O_2 on the nutrient release were evaluated in Part 1. The concentration of ortho-P and VFA increased with an addition of acid without the MW treatment, while concentration of both SCOD and reducing sugar decreased. It was suggested that the agglomeration of fine suspended particles of dairy manure occurred under the acidic condition, resulting in a decrease of the SCOD concentration. The reduction of reducing sugar concentration might be due to chemical reactions. There was no significant change of any initial concentration with the addition of NaOH (Table 3). Upon the addition of acid, the SCOD concentration decreased by about half. This may be attributed to chemical reactions between various soluble constituents in the samples. As a result, increased particle size caused the precipitation, and it was subsequently filtered out prior to this test. It appeared that acid addition aided the solubilization of ortho-P, and the VFA production. However, it was not clear the role acid played in the reaction mechanism.

Reducing sugar was produced from all treatments. Microwave heating enhanced its yield, regardless of acidic or basic conditions. A significant amount of reducing sugar was produced in either the MW or MW/OH⁻ treatment. The best yield was obtained with the MW/H⁺/H₂O₂-AOP. The addition of hydrogen peroxide did not significantly help in producing more reducing sugar (Table 2). For the microwave pretreatment of dairy manure for anaerobic digestion, sugar (glucan/xylan) production was also reported (Jin et al., 2009). In their study, sugar yield was not affected by the different types of acid applied, sulfuric acid or hydrochloric acid, but was rather affected by the concentration of acid. The best yield in their study was produced either in 0.5% (v/v) of sulfuric acid or in 0.185% (v/v) of hydrochloric acid, but the yield did not increase further with a higher acid concentration. Sugar production was the worst in the given conditions with 2% H₂SO₄ addition. The comparison between the study by Jin et al. (2009) and this study should be made with the note that higher concentrations of acid, or base, and a lower hydrogen peroxide dosage were used in their study.

The low yield of reducing sugar was due to a diluted acid used in this study. Concentrated acid used for sugar production was more effective than diluted acid hydrolysis (Sun and Cheng, 2002). As high as 75% concentrated acid was used for treating dairy manure to produce more than 84% of glucose (g/100g cellulose) at 120 °C and 30 min of reaction time. The yield of glucose decreased with an increase of reaction time (Liao et al., 2006). Their results pointed out that the reaction period was also critical for the sugar yield.

When treated with MW alone, SCOD values increased due to the disintegration of organic particles. However, for the MW/H⁺ and MW/H⁺/H₂O₂ treatment, the SCOD value fell to below that of the MW treatment alone. On the other hand, it appeared that the disintegration of organic matters was enhanced in basic conditions. The high concentrations of SCOD were obtained for both MW/OH⁻/H₂O₂ and MW/OH⁻. These results were not quite similar to those of Jin et al. (2009). In their study, the high acid concentration (2% of acid) yielded the highest SCOD, about 35% of TCOD whereas the low acid concentration (0.5%) produced less SCOD than that of either NaOH or calcium oxide addition. In this study, high SCOD was obtained with the basic treatment. Despite the high SCOD yield with NaOH treatment, ortho-P, ammonia, and VFA release appeared to be lacking.

VFA was produced in a few of the trials. One common variable in the VFA production trials was the H_2SO_4 addition. It was clear that when acid was added, VFA was produced with or without MW. As hydrogen peroxide was added, VFA was reduced slightly. At the same time, TCOD was reduced for the acid trials with hydrogen peroxide, which indicated that instead of retaining carbon to form products such as VFA, carbon left the system as CO_2 as an end oxidation product. The presence of acid was also stabilizing the hydroxyl radicals to be more potent in oxidizing organics.

Phosphates have been known to be soluble in solution after treatment with the MW/ H_2O_2 -AOP. Orthophosphate was released in large amounts upon the addition of acid, at almost half the total phosphorus in solution. With the MW/ H_2O_2 -AOP treatment on top of acid addition, the release was even greater, at 62% of total phosphorus from the initial substrate. Soluble phosphate release was not significant for the basic treatment, with or without hydrogen peroxide addition. Dairy manure contained various ions, such as carbonate, ammonia, magnesium, calcium, sodium and sulfate, as well as phosphate. At a high pH (basic) condition, various phosphate precipitates can be formed in the sample, such as struvite, and many forms of calcium phosphate (Wang and Nancollas, 2008; Jin, et al., 2009); therefore, orthophosphate release after the MW treatment would be easily precipitated out of solution again. Basic condition would not be suitable for dairy manure treatment in terms of orthophosphate release. As mentioned earlier, basic conditions would be suitable for the purpose of solid disintegration, as a very high SCOD concentration was obtained in base treatment. The results indicated that in order to release considerable amounts of orthophosphate into solution, acid addition is required for the MW treatment. Hydrogen peroxide would also help an increase of phosphate release, but is not necessarily required in the process.

Ammonia was not produced in large quantities after the MW/ H_2O_2 -AOP treatment (Table 2). The initial ammonia concentration in solution barely increased after treatment with any chemical addition.

The results indicated that reducing sugar can be obtained from dairy manure with the MW treatment, regardless of treatment conditions. In order to solubilize phosphorus, dairy manure should be treated in acidic condition with an addition of hydrogen peroxide to maximize its yield. If the main goal is to disintegrate manure solids, the basic condition shall be chosen, which would yield the highest SCOD concentration.

	o- PO_4 (mg P/L)	NH_4^+ (mg N/L)	SCOD (g/L)	Reducing sugar (mg/L)
initial concentration	6.3 ± 0.2	600 ± 25	15 ± 0.6	672 ± 16
initial acid addition	130 ± 1.4	600 ± 28	6.0 ± 0.1	216 ± 31
initial base addition	4.6 ± 0.1	480 ± 0	17 ± 1.5	869 ± 69
MW	8.0 ± 0.8	830 ± 88	22 ± 1.9	1190 ± 95
MW/ H_2O_2	7.0 ± 0.3	830 ± 33	19 ± 2.0	1130 ± 91
MW/ H^+	240 ± 16	740 ± 220	14 ± 2.3	788 ± 133
MW/ H^+/H_2O_2	240 ± 4.5	790 ± 180	14 ± 2.3	1460 ± 62
MW/ OH^-	30 ± 1.9	670 ± 200	27 ± 1.5	1360 ± 126
MW/ OH^-/H_2O_2	13 ± 3.5	610 ± 110	25 ± 3.8	1180 ± 217

Table 2. Results from Part 1 of batch operation

3.1.2 Part 2

Based on the results from Part 1, an acidic condition was chosen for Part 2 of the study. The design was modeled after a study by Kenge et al. (2010), where a control without the addition of hydrogen peroxide was included. In that study, hydrogen peroxide (0.30-0.59 g H₂O₂/g TS) was in excess; its incremental effects on the solubilization of nutrients could not be fully evaluated. Large amounts of hydrogen peroxide were also not helpful in producing reducing sugar from dairy manure (Jin et al., 2009; Kenge et al., 2010). Therefore, lower dosages of hydrogen peroxide, ranging from 0 to 0.14 g H₂O₂/g TS were used in Part 2, instead of 0.28 g H₂O₂/g TS of hydrogen peroxide used in Part 1.

3.1.2.1 Reducing sugar

The surface plot depicting the trend of reducing sugar production is showed in Figure 1. With the addition of hydrogen peroxide, reducing sugar release increased. It can be expected that with the addition of hydrogen peroxide, reducing sugar release increases due to its aid in the breakdown of lignocellulosic materials in dairy manure.

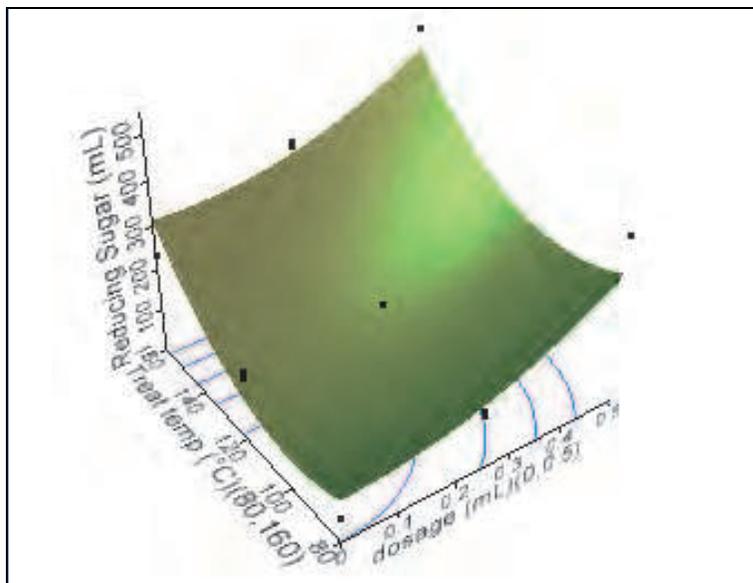


Fig. 1. Surface plot for Part 2 – reducing sugars

Reducing sugar concentration also increased with an increase of temperature. In the study by Kenge et al., (2010), temperature was the most significant factor affecting reducing sugar production; an increase of microwave temperature increased reducing sugar production. An increase in hydrogen peroxide dosage also increased reducing sugar yield at lower temperatures; however, its yield remained relatively constant at higher microwave temperatures. A much higher dosage of hydrogen peroxide was applied in the earlier study, causing solubilized reducing sugars to be further oxidized to form other oxidation products. Due to a balance between reducing sugars being solubilized and oxidized at the same time, reducing sugar concentration in solution remained relatively constant. The rates of reducing sugar production and sugar oxidation to form other compounds have not been measured, but it appeared that equilibrium between the two rates was reached in this case. However, results of this study showed that reducing sugar increased slightly with an increase of hydrogen peroxide at high operating temperatures. This might be due to the fact that there was no excess hydrogen peroxide in solution to engage and aid in further oxidation reactions.

The results obtained from this study and previously indicated that temperature and hydrogen peroxide dosage are factors affecting reducing sugar production (Kenge et al., 2010). The process could be operated with or without H₂O₂ for reducing sugar production; the substantial amounts of reducing sugar could also be obtained at a higher temperature and a longer heating period without H₂O₂.

3.1.2.2 Solids disintegration and nutrient release

SCOD release in Part 2 can be seen in Table 3. In general, higher SCOD concentrations were obtained at higher operating temperatures. Temperature was the most important factor for solids disintegration. At the same operating temperature, it could be operated either at a longer heating period without the addition of H₂O₂, or at a shorter heating period with an addition of H₂O₂ to yield the similar SCOD concentration. Hydrogen peroxide had some impact on the disintegration of solids, but it was not very significant in such low dosages. Microwave temperature was also a key factor for release of phosphates. Orthophosphate increased with an increase of microwave temperature (Figure 2).

Set #	Reducin g sugar (mg/L)	o-PO ₄ (mg P/L)	NH ₄ ⁺ (mg N/L)	SCOD (g/L)	TCOD (g/L)	VFA (mg/L)
1	106 ± 19	109 ± 4.8	43 ± 0.5	2.9 ± 0.2	20 ± 3.7	127 ± 6
2	344 ± 58	367 ± 4.0	71 ± 2.6	4.6 ± 0.2	35 ± 3.6	252 ± 7
3	126 ± 169	167 ± 3.9	57 ± 1.0	3.0 ± 0.4	33 ± 2.1	203 ± 5
4	65 ± 95	113 ± 4.0	40 ± 3.4	4.1 ± 0.3	19 ± 4.9	133 ± 14
5	60 ± 69	333 ± 5.0	50 ± 1.7	3.9 ± 0.1	37 ± 5.3	236 ± 26
6	517 ± 53	356 ± 4.3	73 ± 1.4	5.0 ± 0.1	36 ± 0.2	238 ± 9
7	230 ± 79	121 ± 0.5	51 ± 0.6	3.7 ± 0.4	19 ± 2.3	153 ± 20
8	104 ± 50	162 ± 8.4	51 ± 3.3	2.8 ± 0.6	38 ± 6.6	188 ± 14
9	296 ± 47	172 ± 3.4	66 ± 0.6	4.0 ± 0.2	37 ± 3.3	248 ± 12
10	110 ± 40	16 ± 6.7	54 ± 1.3	3.4 ± 0	31 ± 0.9	213 ± 19
11	172 ± 29	331 ± 6.0	56 ± 1.8	3.2 ± 0.1	34 ± 3.0	254 ± 10
12	387 ± 47	106 ± 3.8	42 ± 1.0	3.6 ± 0	20 ± 1.3	140 ± 5
13	111 ± 35	334 ± 10.8	55 ± 1.6	3.7 ± 0.5	37 ± 1.4	220 ± 22
14	183 ± 32	159 ± 6.5	56 ± 0.7	3.2 ± 0	32 ± 2.6	188 ± 16
15	149 ± 94	163 ± 3.6	55 ± 3.0	3.3 ± 0.3	28 ± 2.5	194 ± 17
Initial	322 ± 48	60 ± 3.2	16 ± 0.4	5.9 ± 0.1	36 ± 4.1	188 ± 19

Table 3. Results for Part 2 of batch operation

The polyphosphates contained in dairy manure could be broken down to form ortho-P at elevated temperature; the rate and extent of polyphosphates were dependent on the heating temperature (Kuroda, et al., 2002). Acid also help solublize organic phosphorus and polyphosphate (Chan, et al., 2007). A trend can be seen from Figure 2, where Treatment time highly favours the release of ortho-P, with a slight increase of hydrogen peroxide. Irrespective of hydrogen peroxide dosage and treatment temperature, ortho-P increased with treatment time (Figure 2). It can be seen from both parts of this study that acid addition

is crucial to the release of ortho-P from dairy manure into solution. The ortho-P results obtained in this study were consistent with results from previous studies (Kenge, et al., 2010; Yu, et al., 2010). It was reported by Jin, et al. (2010) that the optimal condition for orthophosphate release was at 135 °C and 26 min in microwave treatment of dairy manure. It seemed that the MW/H₂O₂-AOP was operated near the optimal condition for the release of orthophosphate and other soluble components in this study. In view of the results, the process should be operated at a high temperature region (120-160 °C), a long reaction time (15-20 min) and dosage of 0.07-0.14 g H₂O₂/g TS for maximizing soluble components from dairy manure.

Ammonia is one of the soluble products from the MW/H₂O₂-AOP, and it is a constituent of a potent fertilizer, struvite. No dramatic increases in ammonia production were found.

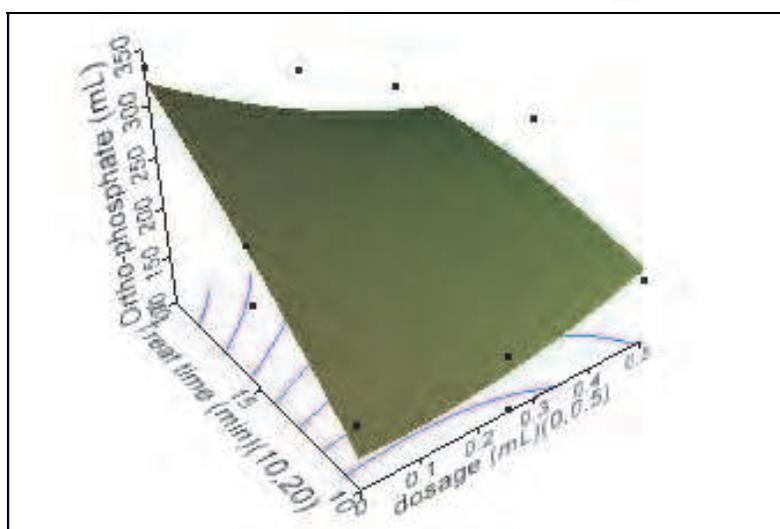


Fig. 2. Surface plot for Part 2 - orthophosphate

3.2 Continuous operation

The disadvantages of a batch operation are: (1) the materials must be transported twice from the reaction vessel, and (2) the amount of sample that can be treated at one time is limited by the batch reaction time and the sample vessel volume. Besides these shortcomings, hydrogen peroxide was also introduced prior to microwave irradiation, limiting the synergistic effects between H₂O₂ and microwave irradiation. The alternative to batch operation is a continuous process, which is more suitable for an industrial application.

The results are presented in Figures 3 to 7. The most pronounced effect on the solubilization of solids was due to microwave heating temperature (Fig. 3).

The SCOD solubilization remained relatively steady at a range of 60 to 70 °C, regardless of the acid concentration. Acid concentration aids the process to maintain or even increase the hydroxyl radical concentration by stabilizing them and thereby inhibiting their degradation. The narrow range of treatment temperature involved may mask the synergetic effects of adding acid to the process as the continuous mode of operation is not pressurized to exceed boiling point. The SCOD increased with an increase of microwave temperature to a higher range of 80 to 90 °C. This was due to the fact that heating would also increase the decomposition of H₂O₂ into hydroxyl radicals and therefore enhance the oxidation process when H₂O₂ was applied simultaneously with microwave heating (Eskicioglu, et al., 2008).

Heating alone can also add to the degradation of the substrate's structural integrity. The results showed that SCOD solubilization from dairy manure was most affected by MW temperature. To a lesser extent, it was also affected by acid concentration, especially at the higher temperature levels of 80 to 90 °C.

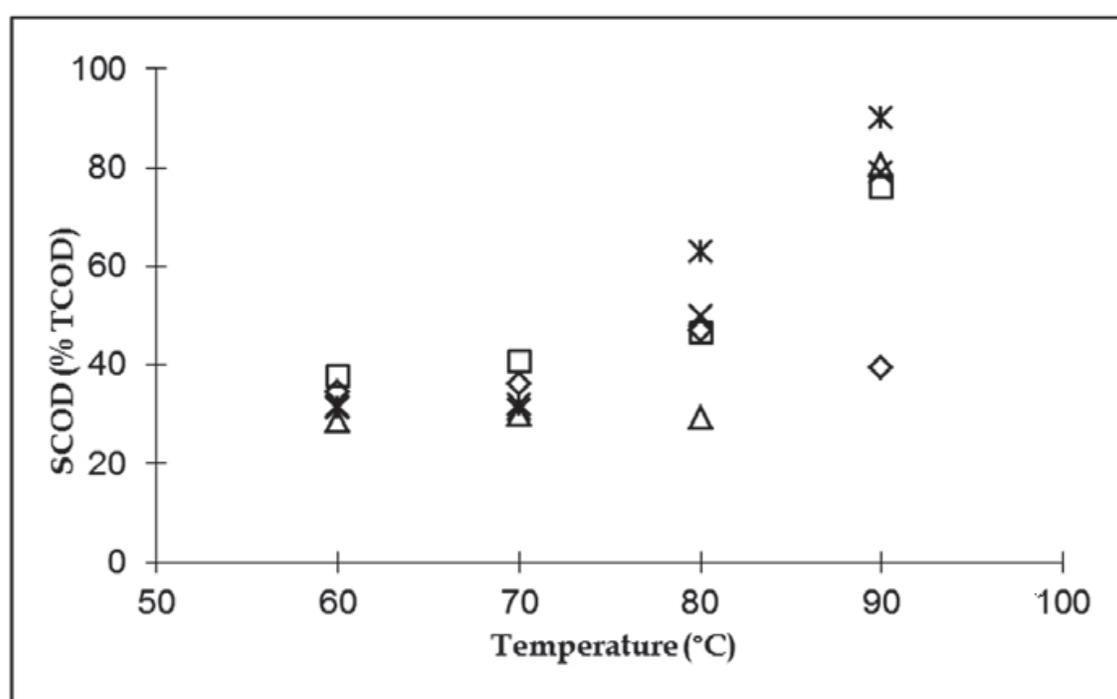


Fig. 3. Soluble COD as a per cent of TCOD (◇ influent; □ MW only; △ MW/H₂O₂-AOP with 0.2% acid; × MW/H₂O₂-AOP with 0.5% acid; ✱ MW/H₂O₂-AOP with 1.0% acid)

It was evident that an acidic condition was critical for phosphorus solubilization from dairy manure (Fig. 4). Without the acid addition, as microwave temperature increased from 60 to 90 °C, the ortho-P decreased from 34% to 11% of TP, which was lower than in the untreated substrate. Phosphorus solubilization was greatly improved with an addition of acid. However, acid dosages did not display significant effects on the solubilization of phosphorus; an acid addition of 0.5% appeared to be sufficient.

There was no significant release of ammonia over the range of 60 to 80 °C, regardless of the acid dosages (Fig. 5). However, up to 70% of TKN was solubilised at 90 °C. The effect of acid dosage on NH₄-N solubilization was similar to that of phosphorus solubilization; the MW/H₂O₂-AOP needed to be operated in an acidic condition; 0.5% of acid concentration was sufficient.

The VFA comprised of various organic acids, such as acetic, propionic, i-butyric, i-valeric, valeric, hexanoic, and heptanoic acids. However, acetic acid is the major component of the VFA, ranged from 46 to 53%. A considerable amount of VFA was released from the dairy manure after the MW/H₂O₂-AOP treatment. The component of acetic acid increased in the treated solutions, ranging from 53 to 84% of total VFA. Overall, the best VFA production of approximately 330 to 420 mg/L was solubilized with an acid dosage of 0.5%. Acid in combination with the MW/H₂O₂-AOP produced more VFA with increasing temperature, except for the highest acid dosage of 1%, where a slight decrease was found at the higher temperatures. This trend may not be conclusive to say higher acid dosage is detrimental to

VFA production, but it indicates that higher acid concentrations may have an effect in reducing VFA in dairy manure (Fig. 6).

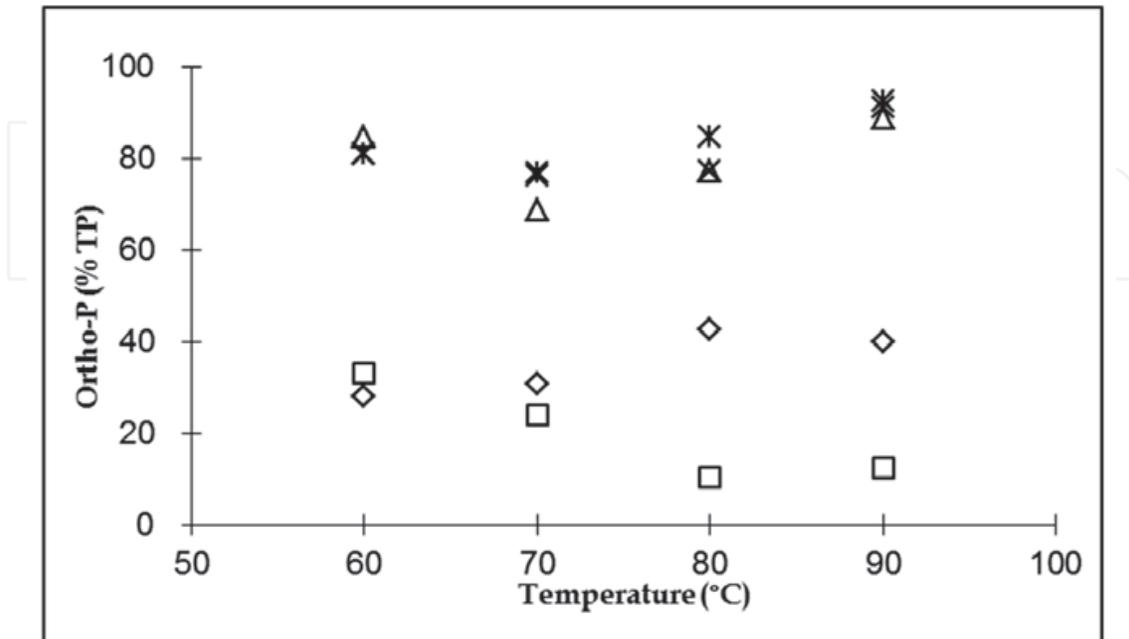


Fig. 4. Orthophosphate release as a per cent of TP (◇ influent; □ MW only; △ MW/H₂O₂-AOP with 0.2% acid; × MW/H₂O₂-AOP with 0.5% acid; ✱ MW/H₂O₂-AOP with 1.0% acid)

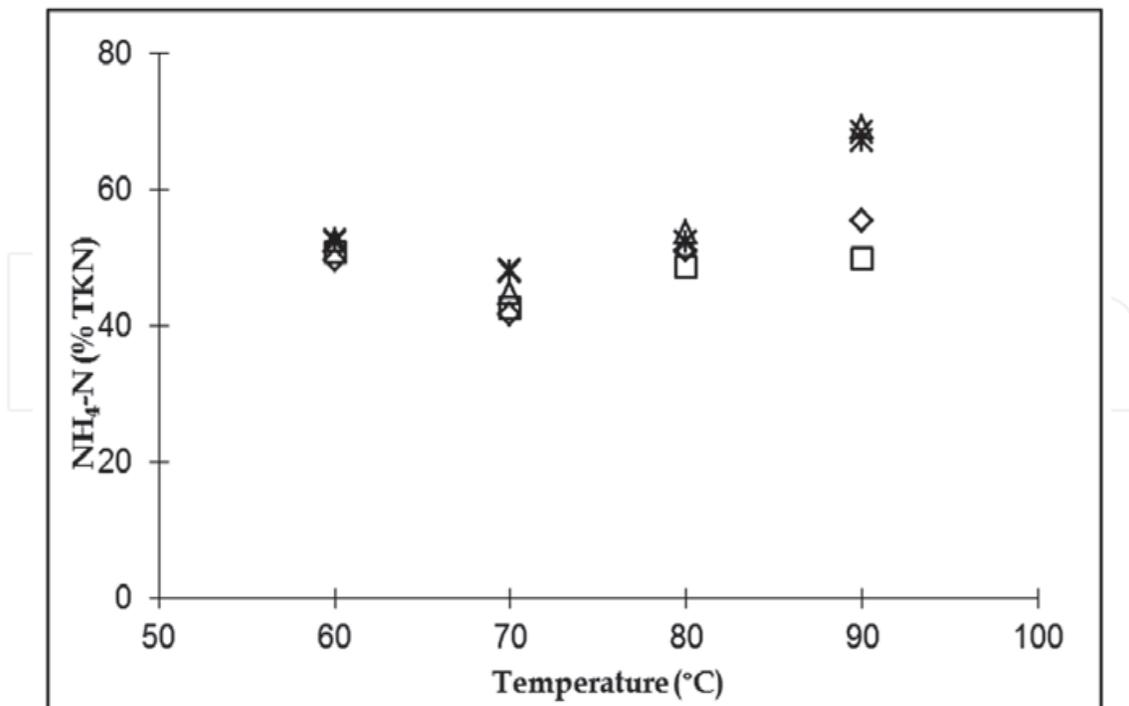


Fig. 5. Ammonia release as a per cent of TKN (◇ influent; □ MW only; △ MW/H₂O₂-AOP with 0.2% acid; × MW/H₂O₂-AOP with 0.5% acid; ✱ MW/H₂O₂-AOP with 1.0% acid)

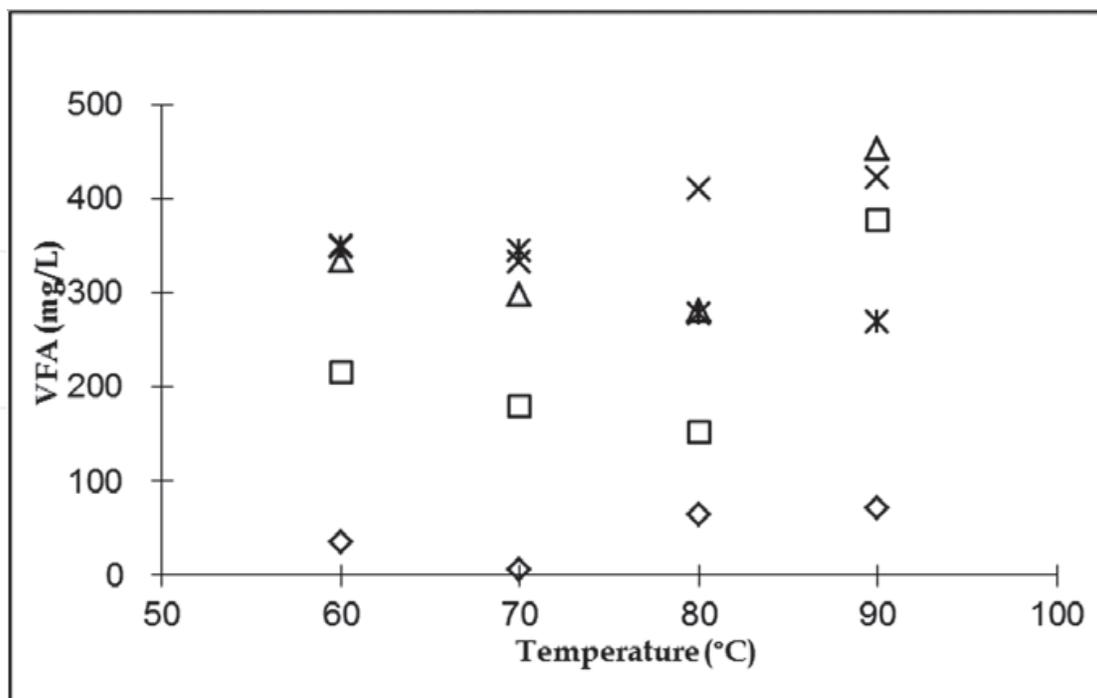


Fig. 6. Productions of volatile fatty acids (◇ influent; □ MW only; △ MW/H₂O₂-AOP with 0.2% acid; × MW/H₂O₂-AOP with 0.5% acid; ✱ MW/H₂O₂-AOP with 1.0%

For the MW only treatment, the reducing sugar concentrations remained similar to those in the influents; however, reducing sugar concentrations decreased after treatment with the MW/H₂O₂-AOP. For the MW/H₂O₂-AOP, the reducing sugar concentrations increased gradually with an increase of microwave temperature. With an increase in acid concentrations for every treatment temperature, reducing sugar concentrations were further decreased (Figure 7). The reducing sugars produced from dairy manure are from the hydrolysis of hemicellulose and cellulose, the resulting solution most likely contains a mixture of pentose and hexose. Indeed, reducing sugars of arabinose, xylose, galactose and glucose have been identified from the hydrolysis of dairy manure using an ion chromatograph (Wen, et al., 2004).

The decrease in reducing sugars could be explained as the further oxidation of soluble reducing sugars into VFA and CO₂ during the MW/H₂O₂-AOP. The oxidation process is more favourable at a lower pH, in other words, a higher acid dosage. Very low concentrations (less than 90 mg/L of reducing sugars) were obtained from different treatments at low microwave temperatures.

This was due to the manure being sieved and diluted; therefore, the lignocellulosic materials, a precursor to sugar production, were low in the manure used in this study. The other reason was that temperatures and acid concentration applied were much lower than that of optimal conditions. As indicated in conventional acid hydrolysis of lignocellulosic materials in dairy manure for the production of simple sugars, samples required pre-treatment with 75% acid concentration and 30 min of reaction time for the de-crystallization of fibre, and then were further hydrolyzed in 12.5% of acid at 135 °C for 10 minutes (Liao, et al., 2006). For the MW/H₂O₂-AOP treatment of dairy manure, a higher reducing sugar production was obtained at above 120 °C (Kenge, et al., 2010). The results show that the important factors affecting reducing sugar yield were temperature and acid concentration.

The presence of small amounts of hydrogen peroxide during the treatment process would decrease the degrees of polymerization and cellulose crystallinity, at the same time, it would increase the accessible surface area and pore size of lignocellulosics. However, too much of hydrogen peroxide would decrease reducing sugar yield. It would favor the further oxidative reaction to form VFA or CO_2 (Kenge, et al., 2010).

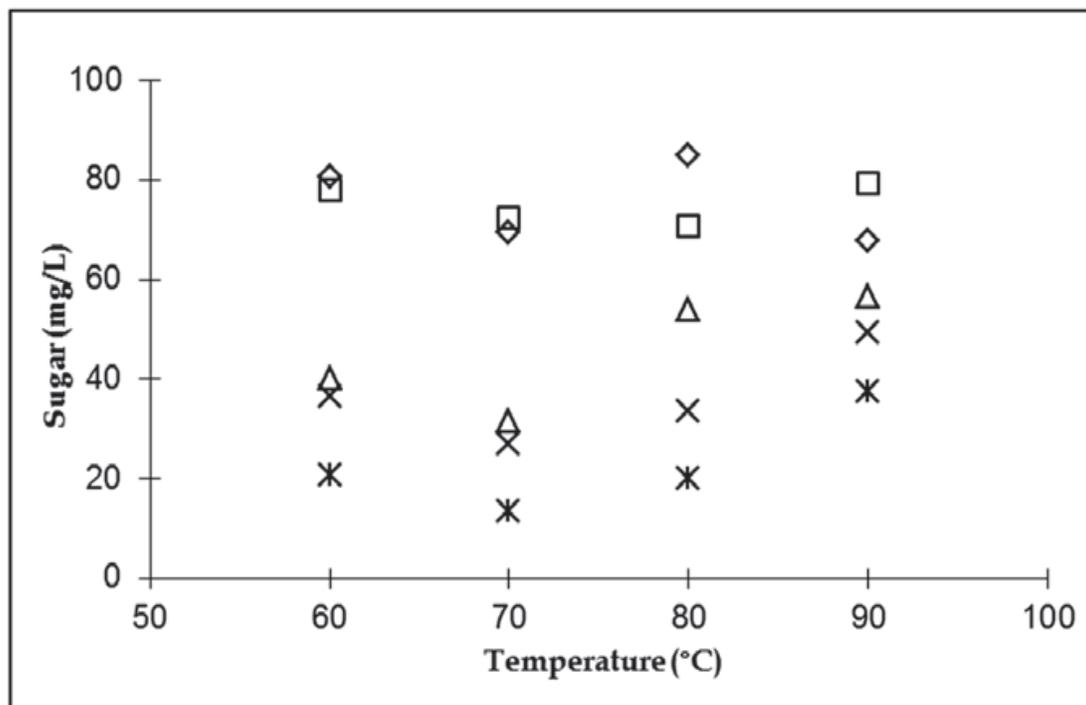


Fig. 7. Production of reducing sugars (◇ influent; □ MW only; △ MW/H₂O₂-AOP with 0.2% acid; × MW/H₂O₂-AOP with 0.5% acid; ✱ MW/H₂O₂-AOP with 1.0% acid)

3.2.1 Comparison of batch and continuous operations

Four experimental sets using a batch microwave unit were also conducted for the purpose of comparison to the continuous process. Three replicates were used at two testing temperatures of 60 and 90 °C. The rate of temperature increase was set at 5 °C/minute to attain the target temperature, at which time, the reaction was terminated. Two sets of experiments at each temperature were operated: one with both acid (0.2% v/v) and H₂O₂ (0.1% v/v), the other without.

The results of SCOD and ortho-P for both batch and continuous systems are presented in Table 4. Without the additions of H₂O₂ and acid, a simple decomposition process occurred under thermal treatment. As a result, there was little solids disintegration and little release for both nutrients. For the MW/H₂O₂-AOP, it was the thermal oxidation process that involved not only the breakdown of large particulate organic matters, but also, the further oxidation or gasification of some of the resulting organic products. Both SCOD and ortho-P concentrations for the MW/H₂O₂-AOP were higher than those of the MW treatment only (Table 4). A higher microwave temperature also increased phosphorus solubilization and solids disintegration. Higher ortho-P and SCOD concentrations were obtained from the continuous mode operation than from a batch system. The superior performance of a continuous system could be attributed to the synergistic effects of MW irradiation and H₂O₂. Since H₂O₂ was injected into

the influent stream immediately prior to MW irradiation in a continuous mode unit, the synergistic effects between H₂O₂ and MW irradiation became manifested.

Temperature (°C)	H ₂ O ₂ and H ₂ SO ₄	Ortho-P Increase (%)		SCOD Increase (%)	
		Batch	Continuous	Batch	Continuous
60	No	-3.2	5.3	-0.6	1.8
	Yes	26	57	12	37
90	No	-7.1	-14	0.1	-6.6
	Yes	28	71	12	34

Table 4. Comparison of batch and continuous operation

This study also demonstrates the feasibility to produce reducing sugar from dairy manure for the subsequent processes, such as ethanol production, and useful fermentation products. To obtain a large quantity of reducing sugars from dairy manure, the MW process should be operated at a small amount of H₂O₂ or without H₂O₂. Nutrient is also released in the MW/H₂O₂-AOP, which can also be used for energy production, or struvite as a fertilizer. However, the process has not been fully optimized yet, it was expected that under pressurized conditions, the continuous mode operation may be even more effective. More investigations should also be conducted to include a wider range of treatment temperatures. Based on the findings, a pilot-scale continuous mode MW/H₂O₂-AOP system is being conducted to further verify the feasibility of the technology for solids reduction and solubilisation of nutrients. The economic feasibility will also be conducted.

3.3 Economic implication

Applying the MW/H₂O₂-AOP to treat dairy manure, there will be significant increases of VFA and nutrients (N & P), and a decrease of solids content in the liquid filtrate. This will be very beneficial in that 1) with reduced solids content in the dairy manure, the more advanced anaerobic reactor, such as the fixe-film reactor, can be adopted for anaerobic digestion of the treated filtrate at much shorter HRTs, resulting in more methane production; and 2) with more VFA and other readily biodegradable substances in the treated dairy manure filtrate, the methane conversion efficiency will be much greater; the methane production rate from the manure filtrate can be as much as five to six times of that of the untreated manure filtrate (Lo, et al., 1985). The soluble phosphorus in the filtrate can be increased substantially by using the MW/H₂O₂-AOP. As a result, struvite production would also increase substantially. In addition, the MW/H₂O₂-AOP can destroy fecal coliforms in wastewater, making it possible for the final effluent available for barn cleaning and other purposes (Yu, et al., 2010). This not only reduces the water usage on farm, but also helps by reducing the pollution of fresh water resources.

4. Conclusion

The MW/H₂O₂-AOP could be an effective pre-treatment method to release nutrient, and disintegrate solids from dairy manure. It is recommended that the process shall be operated at high microwave temperatures (120-160 °C), a low hydrogen peroxide dosage (0.07-0.14 g H₂O₂/g TS) and a long treatment period (15-20 min).

Microwave temperature and acid concentration are factors affecting reducing sugars production. Hydrogen peroxide also plays a role in a less extent. Higher microwave temperatures favor the production of reducing sugars. The process could be operated with or without H₂O₂ for reducing sugar production; the substantial amounts of reducing sugars could be obtained at a higher temperature and a longer heating period without H₂O₂.

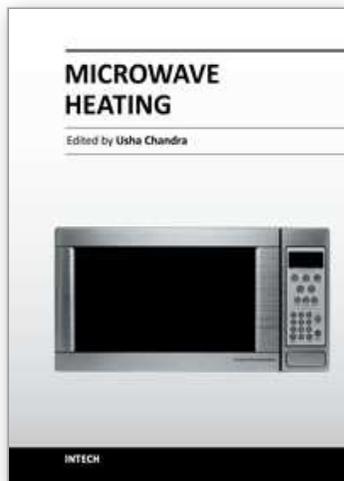
Temperature was the dominant factor for solids disintegration., At the same operating temperature, the process could be operated either at a longer heating period without addition of H₂O₂, or at a shorter heating period with an addition of H₂O₂ to yield the similar SCOD concentration. Heating time also affected orthophosphate release. Heating time and temperature were significant factors for ammonia release and VFA.

The MW/H₂O₂-AOP can be operated in a continuous operation, with equal or better results than a batch process. When the MW/H₂O₂-AOP is operated in a continuous mode, it maximizes the synergistic effects between H₂O₂ and MW irradiation, thereby promoting more nutrient solubilization and solid disintegration.

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The Microwave heating has not only revolutionized the food industry but also has extended its wings widely towards its multidimensional applications. Thus it has opened new vistas of potential research in science and technology. The book is compiled into Seventeen Chapters highlighting different aspects varying from epistemological discussion to applicability of conceptual constructs. The inclusion of discussion on the avenues in the field of Chemistry, Health & Environment, Medical Sciences and Technology makes it an exquisite work for the aspirant Researchers. As the text book for the beginners, it is designed fundamentally to be a reference monograph to the experts providing a passage for future research. The plethora of literatures are available on Microwave Applications but they seldom direct their readers to concentrate on the key aspects behind the success in microwave applications in different fields. Here is the attempt to fill up the gap with this book.

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