Effect of hydrogen peroxide on radiofrequency-oxidation of dairy manure

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A novel technology involving a combination of radiofrequency (RF) heating and hydrogen peroxide (H₂O₂) addition was used to treat dairy manure as a part of a manure management and resource recovery scheme; the process was to release nutrients and to disintegrate dairy manure for subsequent struvite crystallisation process and/or anaerobic digestion. The factors affecting the process, namely, H₂O₂ dosage, heating time and radiofrequency temperature, were studied using a surface response design methodology. The results indicated that solids disintegration efficiency in terms of soluble chemical oxidation demand concentration in the treated solution was in a range of 15–18% of total chemical oxygen demand. Very high volatile fatty acid concentrations were also produced. Orthophosphate (ortho-P) concentrations were in the range of 36–52% of total phosphorus in the treated solution. The optimal operating conditions for both solids disintegration and ortho-P release were predicted to be RF temperature of 83°C, holding time of 55–60 min and H₂O₂ dose of 1.7–1.8%.

Introduction

Dielectric heating is generated by the interaction of dielectric materials with electromagnetic radiation: radiofrequency (RF) heating is operated at frequencies 13–56, 27–12 and 40–68 MHz and microwave (MW) heating is carried out at 915 and 2450 MHz in North America (Laughton and Warne, 2003). Dielectric heating provides uniform and faster heating rates than conventional heating processes. The longer wavelength of RF allows for a greater depth of penetration, compared to MW. RF technology has applications in drying of food products in the food processing industry, soil remediation, off-gas and natural gas treatments and disinfection of wastewaters (Lagunas-Solar *et al.*, 2005; Ramaswamy and Tang, 2008).

The RF heating process was utilised as a pretreatment process for nutrients release and solids disintegration from dairy manure; the purpose of this process was to increase yields of phosphorus recovery and/or bioenergy production in the subsequent processes. The treatment efficiency of the RF process was found to be comparable to that of the MW process (Nkansah-Boadu *et al.*, 2015). The RF-oxidation (RF/hydrogen peroxide (H₂O₂)) process, which uses a combination of RF heating with H₂O₂, had higher treatment efficiency than RF heating alone. The factors affecting treatment efficiency of the RF/H₂O₂ process are H₂O₂ dosage, power intensity, temperature and reaction time. In the previous RF/H₂O₂ studies on the separated solids fraction from dairy manure, phosphorous release was 29–76% of total phosphate (TP), whereas soluble chemical oxygen demand (SCOD) was in a range

of 6–30% of total chemical oxygen demand (TCOD) (Nkansah-Boadu *et al.*, 2015). Very low yields of solids disintegration were due to constituents of dairy manure itself, which were very difficult to hydrolyse, and low dosages of H₂O₂ (0.1, 0.2 and 0.3% H₂O₂ per %total solids (TS)) were used. Dairy manure contains fats, proteins, lignin, carbohydrates and inorganic residue, as well as nutrients and metals. The solids fraction of dairy manure after liquid-solids separation resulted in higher lingo-cellulosic and phosphorus content than that of unseparated manure, making the separated fractions a better substrate for nutrient and energy recovery (Barnett, 1994; Hjorth *et al.*, 2010; Rico *et al.*, 2007). Nkansah-Boadu *et al.* (2015) concluded that in order to obtain the most nutrients and soluble materials from separated solids manure, lower power intensity and holding times between 20 and 60 min should be used, and higher H₂O₂ dosages are needed.

This study was designed to use higher H₂O₂ dosage (0.3–0.5% H₂O₂ per %TS) and lower holding time (20–60 min). The objective was to explore optimal operating conditions for achieving a high degree of solids disintegration and nutrient solubilisation from dairy manure.

Materials and methods

Apparatus

A 6 kW radiofrequency oven (RF) was used in this study. The RF electrodes were housed in an aluminium box suspended

on polypropylene insulators. A transmission line connected the generator output to the oven electrode. The system had a capacity of accommodating up to 9 L of sample in a single run at an operating temperature of up to 95°C. Commercially available microwave-safe plastic containers of 1.5 L total capacity were used as reaction vessels, with aluminium plates moulded to their bottom surface. The vessels were covered with an aluminium lid that was attached to another aluminium base plate with Teflon spacers in between. The temperature was measured using a Neoptix fibre optic probe inserted into the container through a hole in the lid. The aluminium lid can be removed from the container, without removing the Teflon spacers and base plate, when experiments are not performed.

Substrate

Separated dairy manure was obtained from the Dairy Education & Research Centre, University of British Columbia in Agassiz, British Columbia, Canada, and it was stored in the Department of Civil Engineering Laboratory at 4°C. Separated dairy manure contained large amounts of sand, bedding material, as well as undigested lingo-cellulosic materials. For the separated dairy manure, distilled water was added to the samples and subsequently decanted to remove the sand. The resulting separated dairy manure had 5.5% TS.

Experimental design

The manure samples, acidified using sulphuric acid to pH 4.0, were subjected to the RF heating process. The study was carried out in three 1.5 L vessels, and a sample volume of 600 mL in each vessel was used. Using a statistical program, MINITAB, version

16.0, an experimental design consisting of 15 trials was selected (Minitab, 2007). The Box-Behnken design for response surface plots was chosen for the experiments. The three factor levels chosen were temperature of 75°C, 85°C and 95°C, holding time of 20, 40 and 60 min and H₂O₂ dosage of 1.5, 2.0 and 2.5% (v/v) (Table 1). H₂O₂ dosages were equivalent to 0.1, 0.3 and 0.5% H₂O₂ per %TS. Initially, the RF power was set at 35% (approximately 1.2 kW/L manure treated) until the manure samples reached the desired temperature, after which they were held at that temperature for the desired holding time.

Chemical and statistical analysis

The initial and treated dairy manure samples were centrifuged at 4500 rpm for 10 min first, and then their supernatants were extracted for analysing SCOD, orthophosphate (ortho-P), ammonia, volatile fatty acids (VFA) and metals in the soluble portion. All of the chemical analyses were carried out following the procedures outlined in Standard Methods (APHA, 1998). For ortho-P analysis, the initial dairy manure sample was determined at 0.5% TS to ensure correct measurement (Wolf *et al.*, 2005). Treated and initial dairy manure were also analysed for TS, TCOD, TP and total Kjeldahl nitrogen (TKN). Ortho-P, ammonia, TP and TKN were determined by a flow injection system (Lachat Quik-Chem 8000 Automatic Ion Analyzer, Lachat Instruments, USA). A Hewlett-Packard 6890 Series II gas chromatograph, equipped with a flame ionisation detector, was used to measure VFA. Volatile separation was accomplished with an HP free fatty acid phase column. Calcium (Ca) and magnesium (Mg) were determined using a Varian Spectra 220 Fast Sequential Atomic Absorption Spectrometer.

Trial	T: °C	t: min	D: %, v/v	TS: %	Ortho-P: mg/L	Ammonia: mg/L	SCOD: g/L	TCOD: g/L	VFA: g/L
Raw				5.5 ± 0.3	14 ± 7	626 ± 30	7.1 ± 0.7	50 ± 11	0.9 ± 0
Acid				5.4 ± 0.3	135 ± 8	885 ± 15	8.5 ± 0.4	54 ± 4	0.6 ± 0
1	95	40	2.5	5.3 ± 0.4	93 ± 8	778 ± 12	9.4 ± 0.4	52 ± 6	5.5 ± 0.1
2	85	20	1.5	5.3 ± 0.2	117 ± 13	790 ± 26	8.8 ± 0.3	55 ± 0.4	5.3 ± 0.5
3	95	60	2	5.1 ± 0.0	94 ± 3	832 ± 25	8.8 ± 0.5	54 ± 5	5.1 ± 0.3
4	85	20	2.5	5.1 ± 0.3	109 ± 6	800 ± 18	8.9 ± 0.5	47 ± 15	5.1 ± 0.2
5	85	60	2.5	5.5 ± 0.0	105 ± 46	835 ± 33	8.3 ± 0.2	49 ± 16	5.1 ± 0
6	85	60	1.5	5.8 ± 0.1	100 ± 6	840 ± 22	8.1 ± 0.3	53 ± 24	4.9 ± 0.1
7	85	40	2	5.5 ± 0.0	100 ± 4	803 ± 25	8.4 ± 0.4	50 ± 10	5.1 ± 0.2
8	75	40	1.5	5.3 ± 0.1	99 ± 2	838 ± 33	8.8 ± 0.1	47 ± 1	5.0 ± 0.2
9	75	40	2.5	4.7 ± 0.1	111 ± 4	815 ± 30	8.4 ± 0.3	49 ± 6	4.9 ± 0
10	85	40	2	5.6 ± 0.2	105 ± 4	798 ± 34	8.4 ± 0.7	55 ± 3	4.6 ± 0.3
11	85	40	2	5.7 ± 0.0	89 ± 6	807 ± 60	8.1 ± 0.7	53 ± 1.3	4.4 ± 0.1
12	75	60	2	5.6 ± 0.0	95 ± 3	803 ± 41	8.7 ± 0.7	54 ± 2	4.3 ± 0.1
13	75	20	2	5.6 ± 0.3	104 ± 6	760 ± 31	10 ± 0.3	52 ± 17	4.3 ± 0.1
14	95	40	1.5	6.1 ± 0.1	90 ± 11	830 ± 13	8.8 ± 1.1	50 ± 0	4.4 ± 0.1
15	95	20	2	5.1 ± 0.2	91 ± 3	815 ± 18	8.3 ± 0.3	49 ± 1	4.9 ± 0.2

T, temperature; t is holding time; and D is H₂O₂ dosage.

Table 1. Experimental results

Results and discussion

Nutrient release

The dairy manure used in this study had ortho-P of 14 mg/L and TP of approximately 240 mg/L (Table 1). At pH 4, the ortho-P concentration increased to 135 mg/L, which represented almost 60% of TP, an increase of almost nine times from that of the initial manure. For releasing phosphorus from dairy manure, acid addition was essential (Kenge *et al.*, 2009; Lo and Liao, 2011). Dairy manure contains a lot of undigested animal feed such as straw along with organic matter and lipids; phosphorus in dairy manure is constituted in many forms, such as inorganic P, residual P (nucleic acid-type), acid-soluble organic P and lipid P. These are neither very soluble nor easily hydrolysed (Barnett, 1994). Therefore, phosphorus in dairy manure could not be solubilised without addition of acid. With RF/H₂O₂ treatment, ortho-P did not increase more than that of acidified manure.

The regression equation obtained from the statistical analysis of ortho-P data is as follows

$$\text{Ortho-P (mg/L)} = 98 - 5.2T - 3.5t + 1.6D + 2.9Tt - 2.1TD$$

$$1. + 3.4tD - 5.8T^2 + 3.6t^2 + 6.1D^2$$

where T is temperature in °C, t is holding time in minutes, and D is H₂O₂ dosage in %v/v. A correlation coefficient of 78% was observed. The surface response profile of three factors on ortho-P release is shown in Figure 1. Statistical analysis of results from the experiment's matrix revealed that temperature was the most important factor affecting the ortho-P release. The effect of each factor on ortho-P release in ascending order of significance was temperature > holding time > H₂O₂ dosage.

Similar studies on microwave-enhanced advanced oxidation process (MW/H₂O₂-AOP) treatment of dairy manure have shown a strong relationship between heating temperature and soluble phosphorus release; an increase of soluble phosphate in the solution was observed as the microwave temperature increased from 60°C to 90°C for dairy manure (Pan *et al.*, 2006). However, between the range studied (75°C, 85°C and 95°C) in RF/H₂O₂, temperature had a negative effect on ortho-P release, indicating lower RF temperature would result in higher ortho-P release. A maximum ortho-P release of 117 mg/L was obtained at 85°C, 20 min holding time and 1.5% H₂O₂ dosage. The samples treated at 95°C resulted in some of the trials with low ortho-P content. One possible explanation for this low release could be that at 95°C, the resulting solution contained more polyphosphates instead of ortho-P; ortho-P to soluble TP ratios of as low as 78% were observed at 95°C. The results also indicated that among the three different holding times tested (20, 40 and 60 min), 20 min was sufficient to release most of the soluble TP as ortho-P.

It can be seen from the prediction model that the optimal operating condition for ortho-P release was at temperature of 83°C, holding time

Figure 1. Surface plots for ortho-P release

55 min and H₂O₂ dose of 1.8%. H₂O₂ dosage had a positive effect on ortho-P release; however, its effect was less compared to RF temperature and reaction time. In the current study, a higher dosage of H₂O₂ (1.5%, 2% and 2.5%) was used as opposed to less than 1.5% used in the earlier studies (Nkansah-Boadu *et al.*, 2015). It was evident from the present study's results that with an increased addition of H₂O₂, the RF/H₂O₂ could be operated at lower RF temperature or holding time and yet achieve comparable TP to ortho-P conversion.

The ammonia concentrations are presented in Table 1. Dairy manure had an initial ammonia concentration of 626 mg/L and a TKN value of 1588 mg/L. As indicated in Table 1, 1.5% of H₂O₂ dosage resulted in some of the trials with highest ammonia concentration (trials 6, 8 and 14). The lowest ammonia concentration was obtained at 75°C, 2% H₂O₂ and heating time of 20 min (trial 13). Overall, ammonia did not increase in large quantities after the RF/H₂O₂

treatment. A possible reason could be that the majority of the nitrogen was degraded into intermediate products, such as amino acids or peptides, while only small amounts of ammonia were formed in the process. Similarly, the ammonia concentration in solution was observed to barely increase after MW/H₂O₂-AOP treatment (Lo and Liao, 2011). There was no significant release of ammonia over the range of 60–80°C, regardless of the operating conditions (Chan *et al.*, 2010).

The regression equation obtained from the statistical analysis of data is as follows

$$\begin{aligned} \text{Ammonia (mg/L)} &= 803 + 55T + 18t - 8.8D \\ &\quad - 6.7Tt - 7.1TD - 3.8tD \\ 2. \quad &\quad - 0.6T^2 + 0.3t^2 + 13D^2 \end{aligned}$$

A correlation coefficient of 60% was observed. Temperature was the most significant factor affecting ammonia release. The combined effects of temperature and time, as well as second order of H₂O₂ dosage also resulted in more ammonia being released. The yield of ammonia from this study was comparable to microwave studies to treat dairy manure (Jin *et al.*, 2009; Pan *et al.*, 2006). From the prediction model, the optimal operating condition for releasing ammonia into solution was at a temperature of 107°C, holding time of 29 min and H₂O₂ dose of 2.4%. The critical value of temperature was outside the parameter range studied, implying that more ammonia can be produced with an increase in temperature near 107°C.

The dairy manure contained Mg concentration of 279 ± 17 mg/L and Ca of 697 ± 53 mg/L. It was found that initially, only 189 ± 19 and 158 ± 15 mg/L of Mg and Ca, respectively, had solubilised. As noted, most of the potassium contained in the dairy manure was soluble. When the manure was acidified to pH 4, almost all of Mg and Ca solubilised. RF heating and H₂O₂ had very little effect on the release of Mg and Ca; the amounts of released metals were dictated by pH.

Solids disintegration

The soluble COD concentrations are summarised in Table 1. The dairy manure samples had an initial SCOD and TCOD concentration of 7.1 and 50 g/L, respectively. SCOD in the treated solutions were in a range of 15–19% of TCOD. High SCOD concentrations were observed in trials 1 and 4, where 2.5% H₂O₂ dosage was used. The TCOD of the RF/H₂O₂ treated dairy manure trials, with 2.5% H₂O₂ (trials 1, 4, 5 and 9), were found to decrease; a similar decreasing trend in TS was also observed among these trials. Highest SCOD concentration was observed at 75°C, 20 min holding time and 2% H₂O₂ dosage. Its concentration increased to 10 g/L, representing an increase of about 41%. It should be noted that for this treatment trial, the manure was acidified to pH 3.5, which was slightly lower than all other trials (pH 4.0). Settling property of this treatment trial was also observed to be better than other RF/H₂O₂ trials. Similar results

were reported in the previous MW/H₂O₂-AOP studies; a higher SCOD in the treated solution, as well as a better settling property, was obtained at a higher H₂O₂, a higher microwave temperature and a lower pH (Lo and Liao, 2011; Zhang *et al.*, 2015).

The regression equation obtained from the statistical analysis of SCOD data is as follows

$$\begin{aligned} \text{SCOD (mg/L)} &= 8281 - 130T - 293t + 78D \\ &\quad + 547Tt + 206TD + 19tD \\ 3. \quad &\quad + 529T^2 + 223t^2 + 29D^2 \end{aligned}$$

A correlation coefficient of 75% was observed. RF temperature and holding time were found to have a negative effect on SCOD release. This may be due to the fact that the SCOD could be further oxidised and/or decomposed into carbon dioxide (CO₂) at a higher temperature and a longer reaction time, therefore, the concentrations for trials 4 and 8 did not increase as much as that of trial 13. The combined effect of temperature and time and temperature and dosage were also found to be an important factor for SCOD release. H₂O₂ dosage had a positive effect on SCOD release, indicating an increase in dosage would result in higher SCOD concentration in the treated solution. Similarly, the interaction effect of temperature and dosage had relatively larger positive effect on SCOD release. When lower dosage of H₂O₂, which was not sufficient to react with manure particles, was used, second order of H₂O₂ dosage as well as second order of power intensity had positive effects on SCOD release, and the effect of H₂O₂ dosage itself became negative on solids disintegration (Nkansah-Boadu *et al.*, 2015). The results from these two studies demonstrated that the degree of solids disintegration was determined by a combination of H₂O₂, temperature and reaction time in RF/H₂O₂; however, each factor had a different impact on SCOD release. The surface response profile of three factors on SCOD release in this study is shown in Figure 2. The optimal operating condition for releasing SCOD was at a temperature of 83°C, holding time of 60 min and H₂O₂ dose of 1.7%.

VFA concentration of the raw manure was 0.9 g/L and increased to 5.5 g/L after RF/H₂O₂ treatment, a remarkable increase from the initial value. The VFA was present mainly in the form of acetic acid; however, other VFAs such as propionic, butyric and valeric were also found along with acetic acid after the RF treatment. The regression equation obtained from the statistical analysis of VFA data is as follows

$$\begin{aligned} \text{VFA (g/L)} &= 5 + 0.18T - 0.03t + 0.13D \\ &\quad + 0.05Tt + 0.3TD + 0.1tD - 0.1T^2 \\ 4. \quad &\quad + 0.05t^2 + 0.35D^2 \end{aligned}$$

A correlation coefficient of 66% was observed. The optimised operating conditions for releasing VFA into solution were a

Figure 2. Surface plots for SCOD release

temperature of 89°C, holding time of 49 min and H₂O₂ dose of 1.8%. VFA concentrations were found to increase with increasing temperatures and dosage. Lowest VFA concentrations were obtained at 75°C (trials 9, 12 and 13). In RF/H₂O₂ treatment of dairy manure, organic matters could be transformed to VFA at high temperatures via thermal decomposition and oxidation: H₂O₂ would also facilitate oxidation in RF/H₂O₂. A higher dosage favours a higher VFA production. The VFA concentration was almost twice as high as those observed by Nkansah-Boadu *et al.* (2015). Higher levels of VFA would help in subsequent anaerobic digestion of RF/H₂O₂-treated manure. However, an increase in holding time was found to result in lower VFAs. The decrease in VFAs with a longer reaction time could be due to either vaporisation of VFAs or oxidation to CO₂ generation as the end product.

Energy estimation and potential benefits

The energy required for the RF/H₂O₂ process was estimated using the method of Danesh *et al.* (2008). The energy required by the RF/H₂O₂ batch system for separated manure was in a range of

191–291 kJ/L. The energy required for RF/H₂O₂ heating of manure was comparable to that of previous RF/H₂O₂ and MW/H₂O₂-AOP processes (Nkansah-Boadu *et al.*, 2015).

The RF/H₂O₂ process would result in reducing solids content and improving settleability, as well as releasing phosphorus and magnesium into solution. Phosphorus removal and recovery by struvite crystallisation (magnesium ammonium phosphate) from dairy wastewater would also improve the effluent quality. The high SCOD concentration in the RF/H₂O₂-treated solution would help in an anaerobic digestion process. Overall, the RF/H₂O₂ treatment of dairy manure may improve nutrient management efficiency, environmental performance and potential for new revenue streams resulting from biogas production and struvite sales for the dairy industry.

Conclusions

The results indicated that the optimal operations for both SCOD and ortho-P yield were predicted to be RF temperature of 83°C, holding time of 55–60 min and H₂O₂ dose of 1.7–1.8%. The RF/H₂O₂ process was as effective as MW/H₂O₂-AOP for the treatment of dairy manure; both processes provided similar treatment efficiency in terms of solids disintegration, release of nutrient and metals.

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