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Ozone Treatment of Animal Manure for Odor Control

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Abstract: Problem statement: The effectiveness of ozone in reducing odor emission from liquid animal manure was evaluated under batch and continuous treatment operations. **Results:** The results indicated that the use of ozone for the treatment of animal manure proved to be effective in reducing the odor offensiveness. A minimum 3.4 level out of 10 (66% reduction) was achieved in the continuous operation; while a minimum of 3.1 (69% reduction) was achieved in the batch operation. Increasing the level of ozone (O_3) increased the level of offensiveness which was attributed to the presence of intermediate products due to the interaction between ozone and hydrogen sulfide and methylamine. **Conclusion:** The cost analysis indicated that the treatment is economical as a ton of manure could be treated at a cost of $ 0.23.

Key words: Manure, ozone, odor, chemical oxidation, batch, continuous

INTRODUCTION

For years, livestock operations such as animal feedlots and poultry have operated with little concern from the public. These operations were very small in nature and rural populations were quite accustomed to the low levels of the odor emitted from these operations. Currently, these operations are getting larger in size and hence producing large amounts of wastes which are causing air, water and soil pollution. In addition, non agricultural populations have their first or second residence in farming areas and are largely responsible for the air pollution complains[1-4].

Animal manure contains various complex organic and inorganic compounds as shown in Table 1. When handling animal manure, extremely noxious odors arise. The odorous compounds originate during the anaerobic decomposition of animal waste. Anaerobic decomposition of animal waste is a complex biochemical process (Fig. 1) that involves a consortium of microorganisms including several groups of acid producing and methane forming bacteria[5]. The acid formers are the primary producer of organic acid, while the methane formers use the acids to produce methane and carbon dioxide.

The decomposition process of organic matter involves the breakdown of protein, carbohydrates and fats into a number of end products[6]. In general, the decomposition process results in the formation of several compounds including alcohols, esters, carbonyls, sulfides, mereaptans, amines, amino acids, organic acids and different gases as shown in Table 2. The organic acids may include formic, acetic, propionic and bactric. Amino acids may also change to amines by decarboxylation. The breakdown of protein may result in sulfur related amino acids which may produce various sulfides and mercaptans[7]. The breakdown of fats is an energy releasing process that results in the formation of alcohols and fatty acids which may be broken down to acetic acid. The breakdown of carbohydrates leads to the production of alcohols, Aldehydes, ketons and organic acids[5]. Among the compound of anaerobic decomposition, hydrogen sulfide (H_2S), ammonia (NH_3) and methylamine (CH_3NH_2) are largely responsible for the animal manure odors[6].

Merkel *et al*.[6] identified amines, alcohols, carbohydrates, sulfides, disulfide and mercaptans as volatiles from animal waste and found amine and sulfides to be the most important in terms of the amount of malodorous materials. Burnett[7] noticed the formation of organic acids (including butyric, vateric, isobutyric and sovaleric) in liquid chicken manure when the pH was below 8. Table 3 shows the threshold limits for some odorous compounds identified as volatiles from animal manure. The threshold limit refers to the airborne concentration above which the reported exposure will cause adverse effects to human and animals. Concentrations of ammonia and sulfides above the threshold limits have been reported in livestock and poultry facilities as shown in Table 4.

Table 1: Compounds found in animal manure

Protein	Non-Protien-N	Fats	Carbohydrates	Minerals	Others
B-lactoglobuline	Ammonia	Triglycerides	Cellulose	Ca	Waxes
σ-lactoalbumin	Urea	Diglycerides	Hemicellulose	P	Hydrocarbons
Immunoglobuline	Creatinine	Monoglycerides	Lignin	S	Oils
Protosses	Creatine	Ketoacid glycerides	Sugars	Zn	Plastics
Peptones	Uric Acid	Ketonogenic glycerides		Fe	
Poly peptides	&-Amine	Lactonogenic glycerides		Cu	
Peptides	Phosphoethanolamine	Nevtrm plasmatorens		K	
Enzymes	ß- Phosphoglyceroethanolamine	Phospholipids		Na	
Amino acids	Phynyleacetylglutamine	Sphinolipids		Cl	
Arganine	Hippuric acid	Sterols		Mg	
Cysteine	Ortic acid	Squalene		F	
Histidine	Indican	Caretonides		I	
Isoleucine		Vitemins (A, D, E, K)		Mo	
Leucine		**Fatty acids**		Mn	
Lysine		Butric		Co	
Methionine		Caproic			
Phenylalanine		Coprylic			
Threonine		Capric			
Tryptophan		Lauric			
Tyrosine		Myristic			
Valine		Myristoleic			
		Pentadelanol			
		Pelmitic			
		Palmitoleic			
		Marganl			
		Stearic			
		Oleic			
		Linoteic			
		Linoleni			

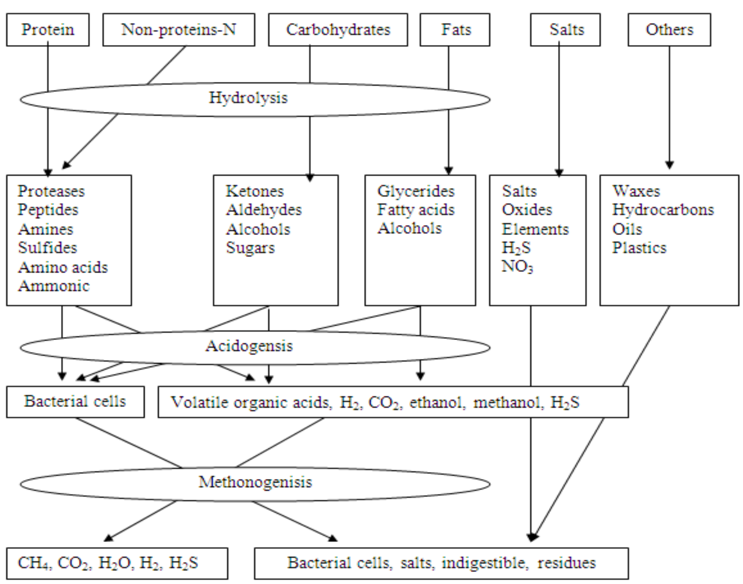


Fig. 1: Anaerobic decomposition of animal waste

Chemical and biological treatments of animal wastes are used to control odors during the storage and handling. There are wide variety of products being sold to treat and/or prevent odors which include: (a) masking agents or counter actants, (b) digestive deodorants, (c) absorbents, (d) feed additives and (e) chemical deodorants[6]. The masking agents have achieved a limited success in controlling odors in livestock and poultry facilities as they are broken down by bacteria.

Table 2: By products of anaerobic decomposition[13]

Group	Examples
Alcohols	Methanol
	Ethanol
	2-propanol
	n-propanal
	n-butanol
	iso-butanol
	iso-pentanol
Acids	Butyric
	Acetic
	Propionic
	Iso-butyric
	Iso-valeric
Amines	Methylamine
	Ethylamine
	Trimethylamine
	Triethylamine
Carbonyls	Acetaldehydes
	Proponaldehyde
	Butryoldhyde
	Iso-butyraldehyde
	Hexanol
	Acetone
	3-pentanon
	Formaldehyde
	Heptaldehyde
	Valeraldehyde
	Octaldehyde
	Decaldehyde
	Diacetyl (2,3-Diketo-butane)
Esters	Methyl formate
	Methyl acetate
	Iso-propyl acetate
	Iso-butyl acetate
	Iso-propyl propionate
	Propyl acetate
	n-butyl acetate
Gases	Carbon dioxide
	Methan
	Ammonia
	Hydrogen sulfide
Sulfides	Dimethyl sulfide
	Diethyl sulfide
	Di sulfides
Heterocycles	Idole
	Skatole
	Pyrazines
Others	Methyl mereaptans

Table 3: Threshold limits for various compounds

Substrate	Concentration in air (10^{-9} g L^{-1})
Acetaldehyde	360
Acetic acid	25
Ammonia	35
n-butyl acetate	710
Butyl mercaptan	35
Diethylamine	75
Dimethylamine	18
Ethylamine	25
Ethylmercaptan	12
Iso-propylamine	12
Methlmercaptan	20
Triethylamine	100

*: Threshold limit refers to the airborne concentration under which the reported exposure will cause no adverse effect

Table 4: Concentration of odorous compounds measured in the vicinity of livestock production facility

Source	NH_3 (mg m^{-3})	Sulfides (mg L^{-3})	Reference
Broiler house	2.38	1.0-15.0	Koelliker *et al*.[8]
Beef feedlot	0.12	5-27	Burnett[9]
Swine building	7.4-24.0	100	Cai *et al*.[10]

They have been used to control odor in chemical manufacturing, petroleum refining and textile facilities.

The digestive deodorants are mostly enzymes and have been found to work in some cases. The anaerobic decomposition of manure gives several offensive odors and some deodorants may only eliminate certain odors. Adsorptive materials are products with large surface areas such as activated carbon, silica gel and active aluminum. They are associated with airborne particles and adsorb odors before it is released to the environment. The feed additives are compounds added to feed to reduce odor as there is a correlation between feed ingredients and odor quality. Yeast, dry lacto and wet lacto have shown limited success. Chemical deodorants are strong oxidizing agents or germicider that alter or eliminate bacterial actions responsible for odor production. Also, oxidizing agents transform odorous compounds into less offensive ones by chemical oxidation.

Chemical oxidation of animal manure has been reported by several authors[7,11,12]. The common denominator among the proven effective chemical compounds such as sodium hypochloride (NaOCl), potassium permanganate ($KMnO_4$) and hydrogen proxide (H_2O_2) is their high cost. Ozone has been reported to be the most powerful oxidant after F_2O and O_2[12]. Ozone is a bluish, unstable gas with a pungent odor. It liquefies at -112°C and has an odor detection level of 0.02-0.05 ppm. Ozone decomposes spontaneously. Some specifications of ozone are shown in Table 5. Table 6 shows some chemical reactions between ozone and selected odorous compounds.

Objectives: Ozone is well known for its oxidizing properties and can be used to reduce the bacterial population responsible for production of offensive products from animal manure. The aim of this study was to evaluate the effectiveness of ozone in reducing odor emission from animal manure. The specific objectives were:

- To evaluate the effectiveness of ozone in a batch operation for treating animal manure
- To evaluate the effectiveness of ozone in a continuous flow operation for treating animal manure

Table 5: Ozone specifications

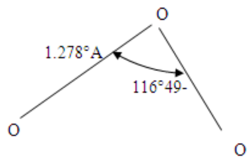
Characteristic	Description
Atomic weight	48 g $mole^{-1}$
Color	Bluish
Odor	Pungent
Oxydo-reduction potential	+2.07 V
Odor detection limit	0.02-0.05 ppm
Stability	Unstable gas, decompose spontaneously in atmospheric or aquatic medium into O_2 and O
Production	Through the action of ultraviot light or light voltage electric discharge
Atomic structure	

Table 6: Some ozone chemical reactions

Compound	Reaction
Amine (R_3N)	$R_3N + O_3 \rightarrow R_3NO + O_2$
Methane (CH_4)	$2CH_4 + 2O_3 \rightarrow CO_2 + CO + 4H_2O$
Hydrogen sulfide (H_2S)	$H_2S + O_3 \xrightarrow{\text{MajorPath}} S + H_2O + O_2$
	$H_2S + O_3 \xrightarrow{\text{MinorPath}} SO_2 + H_2O$
Methyl Mercaptan (CH_3SH)	$CH_3SH + O_3 \rightarrow CH_3 - SO_3H$
Dimethyl sulfide (CH_3SCH_3)	$CH_3SCH_3 + O_3 \rightarrow CH_3SOCH_3 + O_2$
Dimethyl disulfide ($CH_3S_2CH_3$)	$CH_3S_2CH_3 + 2O_3 \rightarrow 2CH_3SO_3$

- To evaluate the possibility of injecting ozone into animal manure during the strong period

MATERIALS AND METHODS

Experimental setup: The experimental setup shown in Fig. 2 consisted of the ozone generator, manure treatment colum, pumping system and the manure pit. The ozone generator used in this study was OZOLab T25 (Degremont, Monteral, Quebec, Canada). The generator is capable of producing up to 16 g ozone/h from air. Ozonated air flow can be varied from 150-1500 L h^{-1}. It can, also, produce ozone from oxygen up to 26 g ozone h^{-1}. The flow of cooling water varies from 25-250 L h^{-1}. Air (or O_2) is injected into a desiccator at a pressure of 6-8 atmosphere. After desiccation, the pressure is reduced to 0.5 atmosphere and the air (or O_2) is introduced into the ozone producing cell (long glass tube). The ozone production is monitored by a tension variation in the glass tube which can be as high as 20,000 volts.

A 550 L column was used for both batch and continuous treatment operation of liquid animal manure Ozonated air (or O_2) was injected through a diffusion plate at the bottom of the column.

Table 7: Ozone application rate during continuous operation

Ozonated air flow		O_3 application rate (O_3 L^{-1} manure)	
mg O_3 L^{-1}	LO_3 h^{-1}	425 L h^{-1}	850 L h^{-1}
11475	0170	27.0	13.6
13005	0510	30.6	15.3
14450	0850	34.1	17.0
15980	1190	37.6	18.8

The Nova Scotia Agriculture College dairy barn was selected as site of the experiment. The barn has a slotted floor and an underground manure collection pit. It housed 200 milking cows. The study was carried out during the month of July when the manure decomposition was particularly high and the odor was noticeable. The pit confined approximately 175 m^3 of manure with an average moisture content of 79%.

Experimental procedure: For the batch operation, the column was filled with 550 L of raw manure. Ozone was then injected at the base of the column at a rate 25 mg O_3 L^{-1} of manure (about 540 L of ozonated air h^{-1}). A total of 5 samples were collected every hour. The experiment was repeated 5 times.

For the continuous flow operation, the column was filled with 550 L raw manure. Two manure flow rates were selected: 425 and 850 L h^{-1}. Manure was pumped to the bottom of the column so that the application of ozonated air and manure were in the concurrent flow mod. This gave manure/ozonated air contact times of 38.8 and 79.6 min for the manure flow rates of 850 and 425 L h^{-1}, respectively. The ozone application rate was varied from 11475-15980 mg O_3 h^{-1} as shown in Table 7.

Odor evaluation: Suprathreshold analysis of odor offensiveness used by Sobel[15] was preferred to the dilution threshold methods designed for odor strength evaluation. The experimentation standards and odor analyses were as follow: (a) each treatment (batch or continuous) was repeated 5 times. (b) The samples collected in each treatment were judged by a 10 person panel, thus resulting in 50 values (5×10). And (c) for each set of 50 values corresponding to a particular treatment (batch or continuous), the mean and standard deviation were calculated.

The panel of the participants first evaluated two control samples 0 and M. the sample marked 0 contained distilled water while the sample marked M. contained untreated anaerobically decomposed animal manure. The panel members then evaluated the treated manure samples according to the construction given in the evaluation sheet (Fig. 3). Each sample was rated on scale of 0-10 (0 for no offensive odor and 10 for very strong offensive odor). Two minutes intervals between each sample evaluation was observed. Additional comments were left to the discretion of the panelists.

Table 8: Example of odor evaluation of a batch treatment

	Panelists odor score (1-10)												
Replicate	1	2	3	4	5	6	7	8	9	10	Mean	SD	CV (%)
1	5	7	6	6	5	6	7	8	6	7	6.3	1.0	15.5
2	6	5	6	7	6	7	7	6	5	7	6.2	0.9	14.1
3	7	6	7	6	5	7	7	5	6	7	6.3	0.8	13.1
4	6	5	7	6	6	6	7	7	6	7	6.4	0.9	14.1
5	7	6	6	6	7	6	5	6	7	7	6.0	1.0	16.2
Average of 5 replicates											6.2		

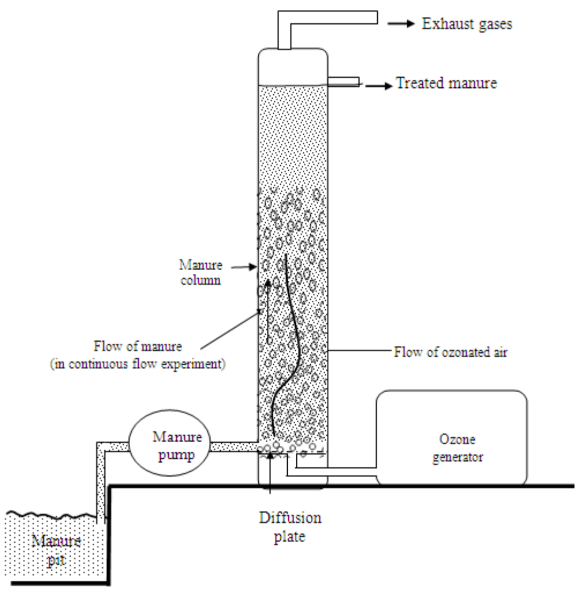


Fig. 2: Experiment set up

RESULTS

The calculations of the evaluation results were performed according to those suggested by Ghaly[16]. Table 8 shows a sample calculation for the 50 values (5 replicates × 10 panel members) of each treatment. The effect of treatment time (ozonation rate) on the odor offensiveness of batch treated animal manure is shown in Fig. 4. The effect of ozone application rate on the odor offensiveness of manure treated under continuous flow operation with different manure flow rates are shown in Fig. 5.

DISCUSSION

The odor evaluation date obtained from the panelists indicated that the test can be used with high confidence. A panel of 10 member and 5 replicates of the sample seemed very reasonable when using this type of order evaluation. The standard deviation varied from 0.8-1.0 and the coefficient of variation was in the range of 13.1-16.2%.

The batch experiment results (Fig. 4) indicated that 1 h treatment duration can reduce the offensive nature of the odor from 10-4.6 (56% reduction). Increasing the treatment duration slightly decreased the offensive nature of the odor to 4.0, 3.6, 3.3 and 3.1 for the 2-5 h treatment, respectively. This means increasing the duration time by 100, 200, 300 and 400% slightly reduced the offensive nature of the odor by 6, 9, 13 and 15%, respectively (or 13, 22, 28 and 33% over that of 1 h treatment, respectively).

The results obtained from the manure continuous flow experiment (Fig. 5) indicated that the faster the flow of the manure, the lower the reduction in the offensive nature of the odor. At the lowest ozonation rate, when the flow of the manure was 850 L h^{-1}, the offensiveness of the treated manure was reduced from 10 to only 5.5, while that of 425 L h^{-1} resulted in the reduction in the offensiveness of the treated manure from 10-3.7. The results also indicated that increasing the ozone application rate did not reduce the odor offensiveness but resulted in slight increases of the offensiveness of the treated manure. This phenomena of olfactory synergisms on both hydrogen sulfide (H_2S) and methylamine (CH_3 NH_2) interaction with ozone (O_3) was first reported by Gills[14]. The release of these chemical intermediate compounds into the manure resulted in an increase in the offensiveness of the treated manure.

The results indicated that the continuous flow experiment (425 L manure h^{-1}) is more effective than the batch experiments when compared on the basis of quantity of ozone (O_3) supplied. This may be due to the mixing action of the flowing manure and ozone which brought the manure in close contact throughout the column with each other while in the batch system, the mixing was less and the manure at the top of the column came in contact with the residual O_3. It appears that a proper design of the O_3 diffuser and mixing can further improve the ozone treatment of animal manure.

Name:………………………………

Date.………………………………..

A- Rating: Please rate the samples as to presence and offensiveness of the odor according to the following scale. Describe the odor of each sample using one of the description below. If the odor bring to mind a different descriptive term, please feel free to comment. Thank you for your assistance in this matter.

Presence	Rating	Offensiveness
No odor	0 1	Not offensive
Very faint	2 3	Very faint offensiveness
Faint	4 5	Faint offensiveness
Definite	6 7	Definite offensiveness
Strong	8 9	Strong offensiveness
Very strong	10	Very strong offensiveness

B- Suggested odor description:

Mold (musty)	Earth
Fish	Yeast
Stagnant water	Ammonia
Sulfides (rotten eggs)	Grain
Petroleum	Sour (fermented)
Alcohol	Rotten cabbage (mercaptans)

C- Evaluation results:

Sample	Presence	Offensiveness	Comments
1			
2			
3			
4			
5			

Fig. 3: Odor evaluation sheet

Table 9: Cost analysis

Item	Unit	Value
Number of animals		200.00
Amount of manure produced	t day^{-1}	92.00
	t year^{-1}	33580.00
	L year^{-1}	33580000.00
Amount of ozone required	(kg year^{-1})[1]	3962.00
	(kg day^{-1})[2]	22.00
Total equipment cost[3]		88000.00
	\$/t[4]	0.13
	\$/t[5]	0.18
Total cost of treatment[6]	\$/t	0.23

[1]: Estimated at 0.000118 kg O_3 L^{-1} manure; [2]: Estimated at 180 treatments per year; [3]: Estimated at 4000 \$/ kg O_3; [4]: Estimated over 20 years amortization period; [5]: Estimated on the basis of 12% interest over 20 years using the formula $\left(\frac{0.12}{1-(1+0.12)^{-20}}\right)$; [6]: Including the capital cost and the operation cost of the equipment

These results give a quantitative insight into the affect of ozone treatment on the level of offensiveness of animal manure and can be used in the design of a mobile apparatus for the treatment of manure before pumping for land application (Fig. 6).

The cost of ozone generator equipment can be calculated in \$ kg^{-1} O_3 produced. An installation producing 10 kg O_3 day^{-1} costs \$ 40000 or 4000 \$/kg O_3. the electricity consumption of the equipment was measured during the operation and found to be 1.5 kWh per ton of manure which represent a cost of ¢ 5/ton of manure. An estimate of the cost of buying and running ozone treatment for 200 cows is shown in Table 9.

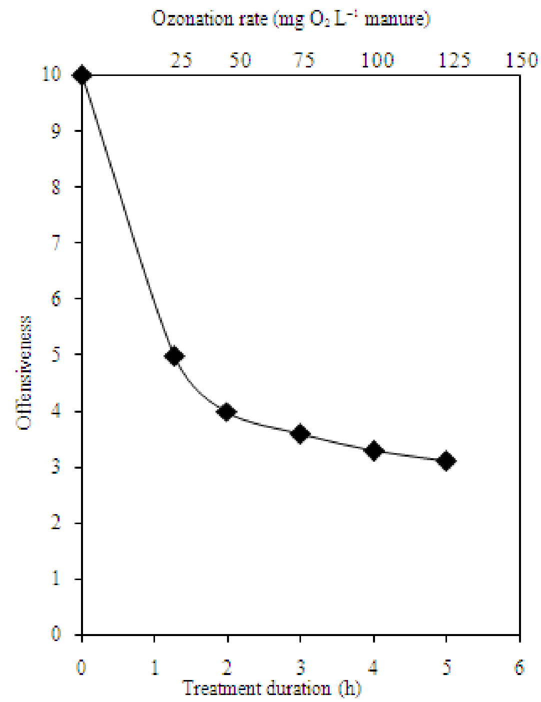


Fig. 4: Effect of treatment time on odor offensiveness during batch operation

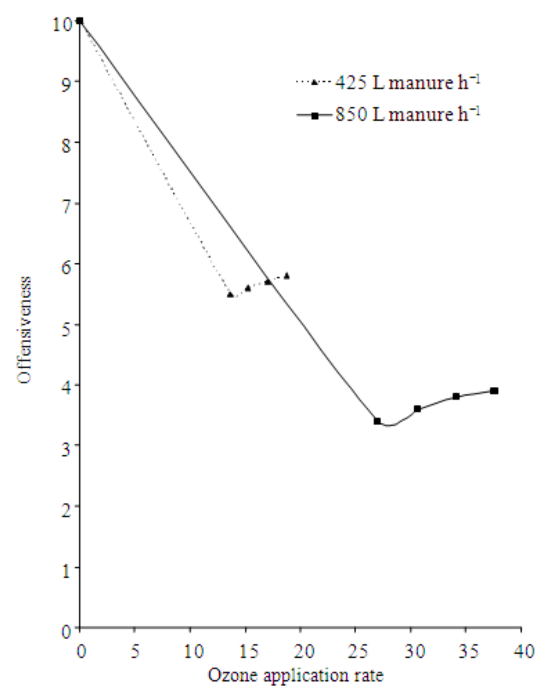


Fig. 5: Effect of ozone application rate on odor offensiveness during continuous operation at various manure flow rates

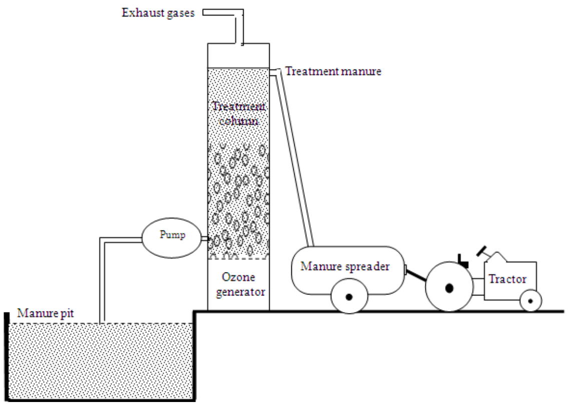


Fig. 6: Proposed mobile O_3 manure treatment during pumping for land application

CONCLUSION

The use of ozone for the treatment of animal manure proved to be effective in reducing the odor offensiveness. A minimum 3.4 level out of 10 (66% reduction) was achieved in the continuous operation, while a minimum of 3.1 (69% reduction) was achieved in the batch operation. The results indicated that mixing is very important. Increasing the amount of O_3 increased the level of offensiveness which was attributed to the presence of intermediate products due to the interaction of ozone with some chemicals, especially hydrogen sulfide (H_2S) and methylamine (CH_3 NH_2). The cost analysis indicated that the treatment is economical as a ton of manure could be treated at a cost of $0.23.

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