JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH
Part B—Pesticides, Food Contaminants, and Agricultural Wastes
Vol. B38, No. 5, pp. 631–643, 2003

Solids Separation Coupled with Batch-Aeration Treatment for Odor Control from Liquid Swine Manure

Pius M. Ndegwa*

Biosystems and Agricultural Engineering, Oklahoma State University,
Stillwater, Oklahoma, USA

ABSTRACT

Previous studies on solids/liquid (S-L) separation for odor control from swine manure indicated that the practice might not technically be feasible because of the complexity of removing the fine particles, which are usually the major source of the odor problems. This study coupled S-L separation by sedimentation with an aeration treatment to quickly break down the fine as well as dissolved solids. Results showed that S-L separation of manure prior to aeration, at the same level of aeration, took only 1.5 days compared to 3 days needed for the control, to bring down volatile fatty acids (VFAs) to the ''threshold of unacceptable level''. In addition, it took 2.3 and 5 aeration-days for VFAs to reach the ''acceptable level'' for the separated liquid manure and the control, respectively. Results also showed that within the three weeks of post-aeration storage, the VFAs in the separated liquid manure consistently stayed 13.5 folds below the acceptable level. In the unseparated manure, the VFAs gradually increased upwards from 2.2 folds below acceptable level achieved at the end of aeration treatment, to 1.38 folds below the acceptable level at the end of the third week of storage and looked poised to definitely rise above the acceptable level in a matter of days. A strong relationship (R=0.99) between pH and the VFAs in the manure suggested that; degradation of VFAs rendered manure more basic as shown by the increase in pH. After only three days of aeration, the oxidation reduction potential

*Correspondence: Pius M. Ndegwa, Biosystems and Agricultural Engineering, 120 Agricultural Hall, Oklahoma State University, Stillwater, OK 74078, USA; E-mail: ndegwa@okstate.edu.

DOI: 10.1081/PFC-120023520
0360-1234 (Print); 1532-4109 (Online)
www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

(ORP) in the separated liquid manure stabilized at a much higher level of −15 mV, while the ORP in unseparated manure stabilized at a much lower level of −200 mV. The S-L separation treatment thus significantly improves the oxygen transfer efficiency, which in turn significantly reduces the aeration power needed to maintain adequate ORP if prolonged aeration is desired.

Key Words: Batch aeration; Swine manure; Odor potential; Volatile fatty acids; Solids separation.

INTRODUCTION

Among the most challenging environmental issues facing the swine industry today is odor. In contrast to other environmental challenges, technologies for elimination of odor from swine production facilities are not readily apparent. There seems to be a general consensus, however, that most of the odor-generating organic substances are produced from manure solids and therefore separating solids from manure liquid can theoretically reduce odor emissions from the manure. Some limited work has been done on feces/urine separation at the time of excretion. Kroodsma[1] reported successful reduction of odor from a pig facility after solids were separated from the liquids, immediately after the feces and the urine were voided. While this idea of separate feces-urine may be pursuable in future designs, technologies for dealing with the odor issues in the current and most widely used system of collection and handling of manure as slurry, must continue to be developed. The major problem arising out of these slurry systems is that; once the feces, urine, and water comes together, some of the feces dissolves making solids/liquid separation a much more futile attempt thereafter.

The impact of solids/liquid separation on odor reduction is largely determined by the amount of biodegradable organic solids and nutrient elements removed from the manure. A review of previous work on this subject by Westerman and Zhang[2] concluded that finer particles in the manure decompose faster and to a greater extent than coarse particles. In addition, most of the reduced carbon compounds, protein, and nutrient elements (especially nitrogen and phosphorus) are contained in the fine particles. Since these compounds are the precursors of odor generation, it can be inferred that the fine particles would basically contribute more to the odor problems than coarse particles, during manure storage. In an earlier study,[3] fresh swine manure was separated into various fractions with size ranges of <2.0, <1.4, <1.0, <0.5, <0.25, <0.15, and <0.075 mm, before storage. Although productions of odorous compounds were observed to decrease with the degree of solids/liquid separation prior to storage, it was concluded that, solids separation did not significantly reduce the production of the odorous compounds in the liquid swine manure. It was suggested that; for effective control of production of these odorous compounds solids separation needed to go beyond the levels investigated. However, given the difficult and uneconomical processes of removing solids finer than 0.075 mm, solids/liquid separation may not be a feasible method of odor control unless coupled with another treatment process.

To reduce odors in stored swine manure, biodegradable organic materials are commonly oxidized to stable inorganic end products by aerobic bacteria.[2,4] Under

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

aerobic conditions, nitrogen compounds are converted to ammonium by ammonifying bacteria and then oxidized to non-odorous nitrites and nitrates by nitrifiers. Sulfur compounds are likewise converted to non-odorous sulfates instead of the odor causing sulfides and other mercaptan compounds.[5] In addition, aerobic treatment of manure does not allow accumulation of volatile fatty acids and various other intermediate odorous compounds during treatment and this reduces odor problems during treatment processes. Once manure stabilization has occurred, the manure can invariably be stored for longer periods without odor problems.[2] It is well established that during aeration treatments, the oxygen transfer rate and efficiency is affected by factors such as: the surface area in contact with air, mixing/turbulence, temperature, and the amount of solids or other constituents in the manure. In general, the less and the finer the solids, the better the aeration efficiency.

It is hypothesized that, a solids/liquid separation treatment prior to an aeration treatment would effectively and economically reduce the potential of odor generation in stored liquid swine manure. Solids separation will not only remove the coarse particles that degrade slowly and over a longer time, but will also improve the oxygen transfer efficiency, therefore, effecting stabilization of the liquid manure in a much shorter time. This is both economical and environmentally friendly since odors will only be a problem within a short period of time and moreover, not only will lower aeration rates be used, but also for shorter period of time.

Subjectivity in the measurement and quantification of odor has always been a big hindrance in the development of strategies toward odor solutions. The olfactometry methods that uses the human nose are not only limited in their use by this subjectivity but also by the cost and difficulty of collecting representative samples.[6] A more recent technique of odor measurement known as an electronic nose that uses electronic sensors to measure individual chemical odorants is in development and has so far shown tremendous potential.[7,8] Other remarkable studies that are helpful in standardizing manure odor studies have been conducted in the past and relate chemical characteristics to odor intensities and offensiveness of excreta. Bell[9] found a close relationship between volatile fatty acids (VFAs) and odor offensiveness of anaerobically and aerobically stored poultry manure. Barth et al.[10] correlated concentrations of total organic acids (TOAs), hydrogen sulphide, and ammonia in dairy cattle manure, stored aerobically and anaerobically, with odor intensity and found that TOAs concentrations correlated best with odor intensity. A review paper by Spoelstra's[11] indicates that for manure slurry stored anaerobically, VFAs, indoles and phenols are suitable indicators of odors. Another study by Williams[12] found good correlations between odor offensiveness and both VFAs and the five-day biochemical oxygen demand (BOD_5). Williams[12] further established that not only were better correlations obtained with supernatant's VFAs and BOD_5 contents of the manure, but also that supernatant BOD_5 appeared to be a better indicator of odor offensiveness. Other more recent studies have also confirmed a strong linear relationship between VFAs and BOD_5 in the supernatant of swine manure.[3,13] From the above studies, it is quite apparent that the VFAs and BOD_5 contents in manure supernatant can be used not only as valid indicators of odor and their respective concentrations as valid quantifiers of odor intensities, but also the two parameters can be used interchangeably. Therefore, in this study, VFAs contents were used as indices to quantify odor intensities during aeration of the swine manure.

The objectives of this study were to investigate the effect of solids/liquid separation on potential of odor generation reduction in aerated liquid swine manure and the concurrent effect of solids removal on the aeration efficiency. The VFAs of the supernatants were used as odor indicators and their concentrations were used to determine odor strengths during the aeration process based on past indices developed using an odor panel.[14]

MATERIALS AND METHODS

Equipment and Instrumentation

A schematic diagram of a unit of the equipment and instrumentation used in this study is shown in Figure 1. The reactors, made of clear Plexiglas columns (91-cm tall and 15-cm diameter) had an operating volume of 14 L of liquid manure, leaving approximately 15-cm head-space to facilitate mixing and to provide room for any frothing created by aeration. To aerate the manure, a positive pressure air pump (Model DOA-P104-AA, Gast MFG Corp.) was used to introduce air into the manure through a flexible rubber air diffuser (Catalogue # W107A, Won Brothers Inc.) placed at the bottom of each reactor. A variable area flow meter (Model P-32461-64, Cole-Parmer Instrument Company) was used to regulate and maintain the flow of aeration air in each unit. An airflow rate of 0.067-L[air]$\cdot$L^{-1}[manure]$\cdot$min^{-1} was maintained throughout

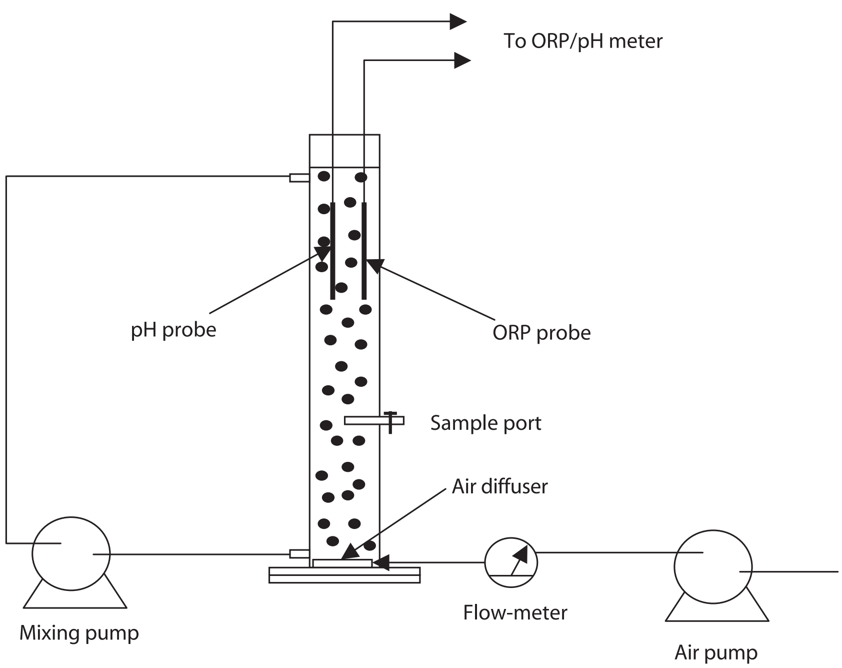

Figure 1. A unit of equipment and instrumentation used in this study.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

the study period. The oxidation-reduction potential (ORP) of the liquid manure was determined using a platinum band ORP probe and a voltmeter (Accumet 1003, Fisher Scientific). A handheld pH meter (Accumet 1003, Fisher Scientific) equipped with an ATC probe was used to monitor the pH and the temperature in each reactor on a daily basis just prior to daily sampling of manure.

Manure Collection, Loading, and Sampling

Swine manure from a nursery barn located at the Oklahoma State University Swine Research Facility was collected in plastic containers. The manure collection system in this Research Facility is a pull-plug system operated either once or twice a week implying that the manure slurry was fairly fresh. The piglets in this barn were fed a regular corn-soybean meal and were two weeks away from weaning. Pertinent characteristics of the manure collected and used in this study are given in Table 1.

Prior to filling the reactors, the manure slurry was thoroughly stirred to ensure uniformity of the feed in all the reactors. Each reactor was then filled with 14 L of this well mixed manure. To facilitate solids/liquid separation in two of the reactors for the solids separation treatment, the manure was allowed to quiescently settle for five hours. The liquid portion in two of the reactors was then decanted out into separate containers. The two reactors were cleaned thoroughly of the solids before pouring back the separated liquid manure.

Before starting the aeration in each case, the manure in each reactor was again thoroughly stirred using a re-circulation pump (Little Giant Model 2E-38N) for about 10 minutes and a sample was drawn from approximately 30 cm from the bottom of each reactor for further laboratory analyses. For the rest of the duration of the study, samples were taken every day. Analyses were done immediately after the sampling whenever possible and if not, all the samples were kept in a deep freezer until the time of analyses. The frozen samples were then thawed and allowed to reach the room temperature prior to analyses.

Laboratory Analyses

The following parameters were determined using standard laboratory methods:[15] total solids (TS), total volatile solids (TVS), soluble ortho-P, total phosphorus (TP), and Total Kjeldahl nitrogen (TKN). To determine the soluble ortho-P, a well-mixed sample

Table 1. Some pertinent characteristics of the manure used in this study.

Parameter	Quantity
Total solids (TS), mg/L	15.59±0.81
Total volatile solids (TVS), mg/L	10.28±0.64
Total phosphorus (TP), mg/L	493.17±9.94
Soluble orthophosphate, mg/L	424.97±16.16
pH	5.5±0.0
Oxidation–reduction potential, mV	−264±8

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

was diluted and vigorously shaken for 5 minutes. The diluted sample was then filtered using GF/A Whatman filter papers. The soluble ortho-P in the filtrate was determined colorimetrically as the phosphomolybdate complex after reaction with ascorbic acid.[15] The TP was determined using the Persulfate Digestion Method, by which all the species of P in a sample are first converted to soluble ortho-P. The samples are then filtered and the TP measured calorimetrically using the ascorbic acid method. The volatile fatty acids (VFAs) in the filtrates were determined using an esterification method. This method is based on esterification of the carboxylic acids present in the sample followed by colorimetric determination of the esters produced by the ferric hydroxamate reaction. All VFAs are reported as their equivalent mg/L acetic acid.[16]

RESULTS AND DISCUSSION

Status of VFAs Compared to Critical Odor Levels

The status of the VFAs in both the separated liquid manure and in the unseparated manure (control), during the aeration treatment are detailed in Figure 2. It is evident that solids separation from manure resulted in more rapid degradation of VFAs during the aeration treatment compared to the control treatment. According to past research work,[2,14] at the level of 230 mg/L VFAs in the pig slurry, the odor level was found acceptable by an odor panel, while a threshold of unequivocal unacceptability was reached at 520 mg/L VFAs. In other words, manure slurries stored until the VFAs concentration reaches 230 mg/L should not cause any problems, while those containing VFAs levels above 520 mg/L should release offensive odors. In this study, it took only 1.5 days compared to 3 days during the aeration treatment to bring down VFAs levels to the 'threshold of unacceptable level' in the separated liquid manure, and in the

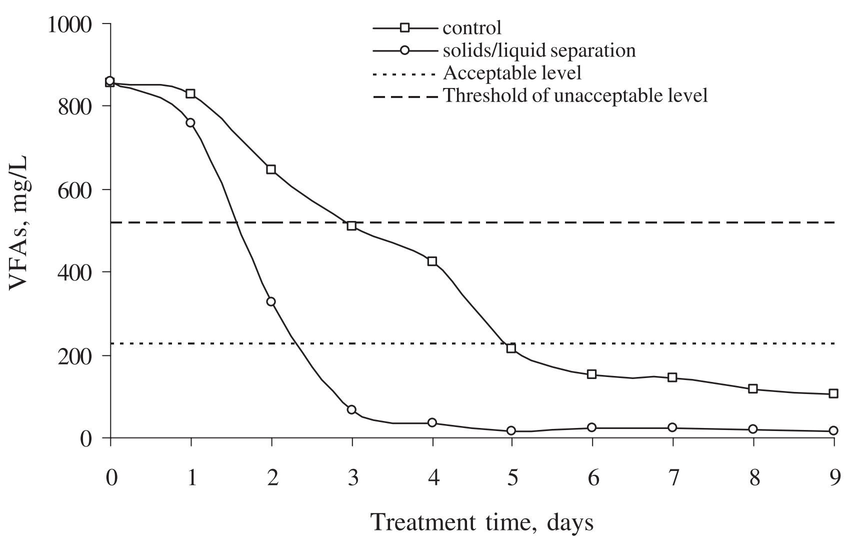

Figure 2. Variations of volatile fatty acids (VFAs) during the aeration treatment in swine manure.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

control, respectively. In addition, it took less than another day (0.8 days) extra to reduce the VFAs levels to the 'acceptable level' in the separated liquid manure compared to another 2 days needed for the control treatment to reach this same level, i.e. 2.3 days, and 5 days from start of aeration for the separated liquid manure and the control, respectively, to reach the acceptable level.

The status of VFAs during approximately three weeks of post-aeration storage in both the separated liquid manure and the control are shown in Figure 3. It is quite apparent that within the three weeks of post-aeration storage, the VFAs in the separated liquid manure consistently stayed significantly below the acceptable level (13.5 folds lower). In the unseparated manure, however, the VFAs gradually increased upwards from 2.2 folds below acceptable level achieved at the end of aeration treatment, to 1.38 folds below the acceptable level at the end of the third week of storage and looked poised to definitely rise above the acceptable level in a matter of days. It is not hard to explain these observations. A review paper[2] explicitly noted that finer particles in the manure decompose faster and to a greater extent than coarse particles. Solids/liquid separation by sedimentation is limited to the separation of the coarse particles implying that only fine particles remained after the solids/liquid separation. The subsequent aeration treatment was, therefore, able to degrade these fine materials not only faster, but also to more stable final products. On the other hand, the coarse particles in the unseparated manure not having been completely degraded continue to slowly degrade during the post-aeration storage producing more odorous compounds. In a study by Sneath,[14] in which the solids were separated from the liquid after aeration to improve sedimentation, similar observations were reported during the post-aeration storage. However, although solids/liquid separation after aeration may improve the settling of the solids, this practice may not achieve the low VFAs levels obtainable from the aeration of separated liquid manure. In addition, solids/liquid separation after aeration, as can be deduced from the results of this study will take much longer to achieve

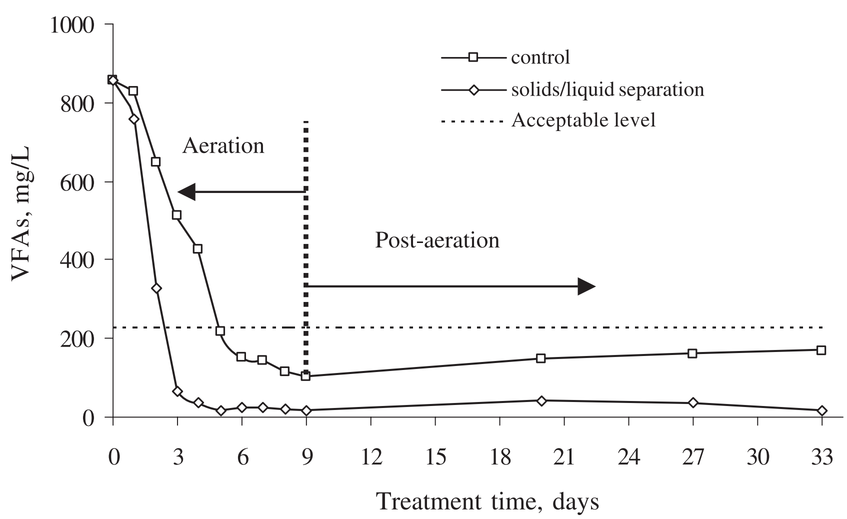

Figure 3. Effect of storage on VFAs after the batch aeration treatment of swine manure.

similar level of acceptable odor level, which translates into more energy use for this treatment option.

The pH Change versus Status of VFAs

The changes in VFAs and the pH in the manure during the aeration process in both the separated liquid manure and in the control are both presented in Figure 4. It is quite obvious that either one is dependent on the other, or both are dependent on another factor whose effect has opposite effects to each of these two variables. When the pH of the manure is plotted against the VFAs content in the manure, two observation can be made from the plot presented in Figure 5: 1) there is a very strong relationship between the two parameters, with a correlation coefficient of 0.99, and 2) the plot shown in Figure 5 is a typical weak acid titration-curve if the VFAs-axis is replaced by molar equivalent of a strong base. In the former case, it can be inferred that, degradation of VFAs reduces the acidic level that manifests as an increase in pH of the manure. The observed weak acid-titration-curve greatly strengths the previous inference because only degradation of the VFAs in the manure will most probably produce this kind of a profile.

In this study, the degradation of the VFAs may be equated to the neutralization of VFAs with a strong base to explain the curve shown in Figure 5. During titration of a weak acid using a strong base, the point of inflection on titration curve occurs when one-half of the weak acid has been titrated to its conjugal base. At this point, the pH equals the pK_a of the weak acid. In Figure 5, the slope of the plot is zero at a pH of 7.52 and this gives the point of inflection. This would be the pK_a of the weak acid in question if the titration was being conducted in aqueous environment. Since our swine manure media is not aqueous per se, this value is hard to interpret although it is most probably a combined pK_a of many weak acids grouped together as VFAs in this study.

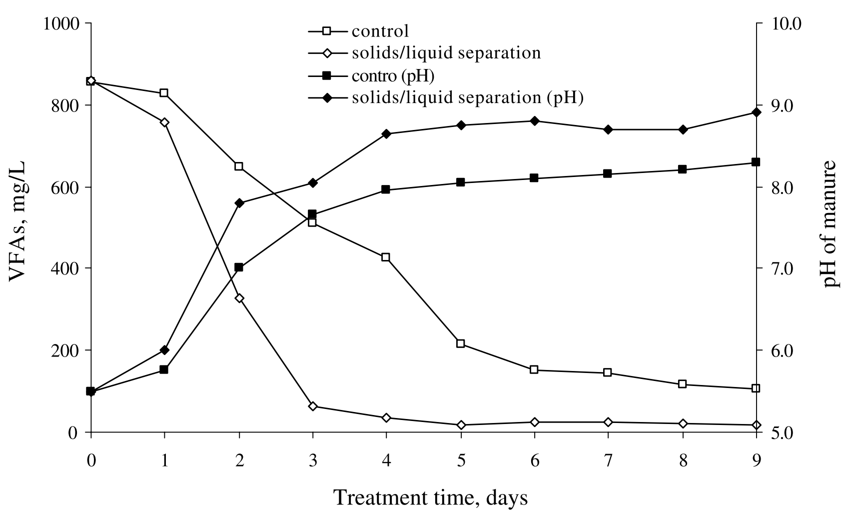

Figure 4. Changes in volatile fatty acids (VFAs) and pH during batch aeration treatment of swine manure.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

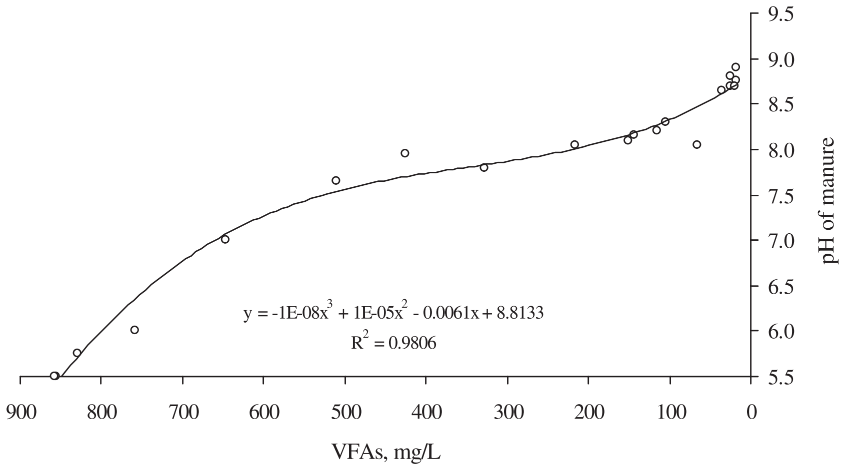

Figure 5. Relationship between volatile fatty acids (VFAs) and pH during batch aeration treatment of swine manure.

One may also be tempted to think that perhaps the VFAs are not being degraded but are merely changing into their salts because of the creation of an alkaline environment as portrayed by increasing pH in the manure. But since there is no addition of a strong base, it is more probable that, the oxidation of the fatty acids is actually part of the reason the pH rises during the aeration process. If indeed, the VFAs are just changing into their salts, this could change the treatment approach of swine manure for odor control because it essentially means that, pH adjustment alone could alleviate some of the odor problems. Further research work is recommended along this line of thought.

Effect of Solids Removal on Aeration and VFAs

The variations of ORP during aeration in both the separated liquid manure and the control are presented in Figure 6. During the first three days of aeration, the oxidation level remained higher in the control than in the separated liquid manure. A possible explanation for the preceding observation is that, microbial action was enhanced more in the separated manure than in the unseparated manure because of the improved contact between the microbial mass, the fine, and the dissolved substrate. The kinetic rates of degradation of the fine and dissolved solids are also of course higher than of the coarse particles and this increased substrate degradation kinetics require more oxidation power. These postulations are confirmed by examining Figures 7 and 8. These two figures indirectly quantify microbial activities because the change in volatile solids closely follows microbial biomass growth, while temperatures of the reactor contents indicate microbial activity level from metabolic respiration. The temperatures in the control reactors remained lower than the temperatures in the reactors with separated liquid manure from the first day till the fourth day of aeration treatment. On the other hand, only a little change in microbial biomass was recorded during this time in the control, while a significant growth of microbial biomass was observed in the separated liquid manure in the same time. Both temperature and microbial biomass

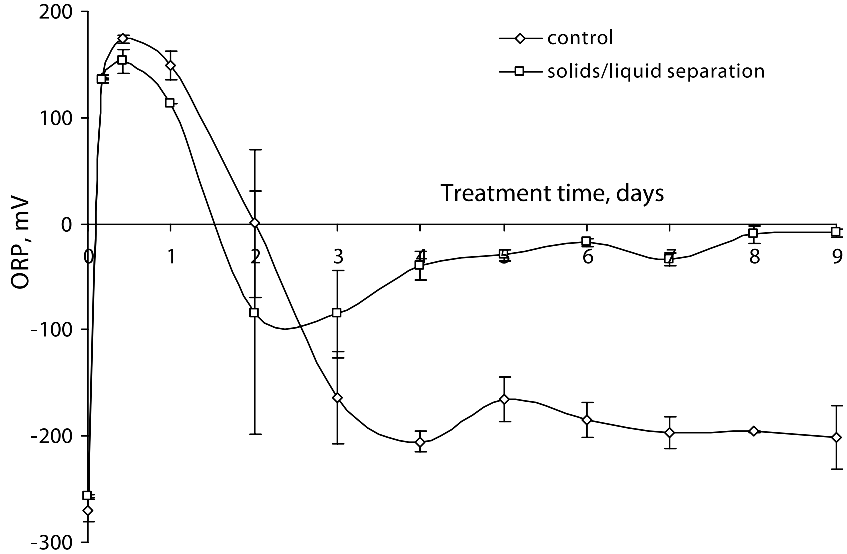

Figure 6. Variations of oxidation-reduction potential during batch aeration treatment of swine manure.

growth gradually declined after this point in the separated liquid manure. In the control treatment, both temperature and microbial growth continued to rise marginally indicating late degradation of the coarse particles.

Prolonged aeration treatments, however, seemed to be in favor of separated liquid manure in terms of maintaining higher oxidation status at the same level of aeration.

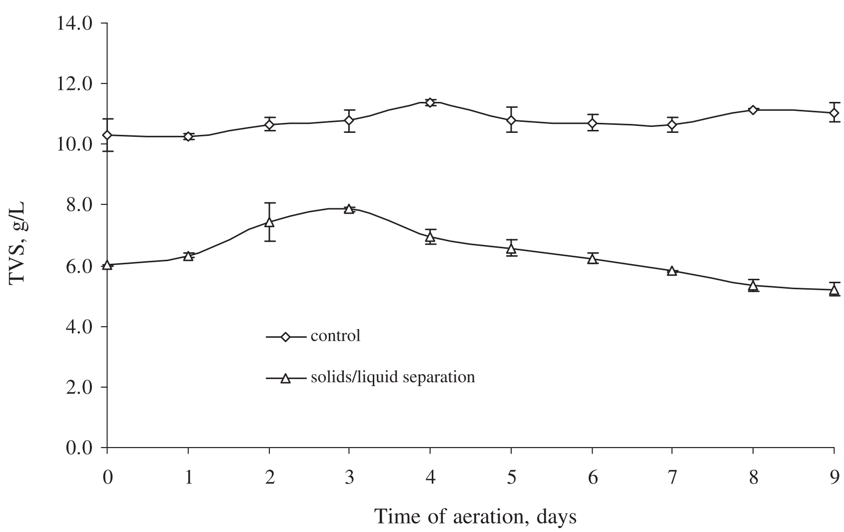

Figure 7. Changes in total volatile solids (TVS) during batch aeration treatment of swine manure.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

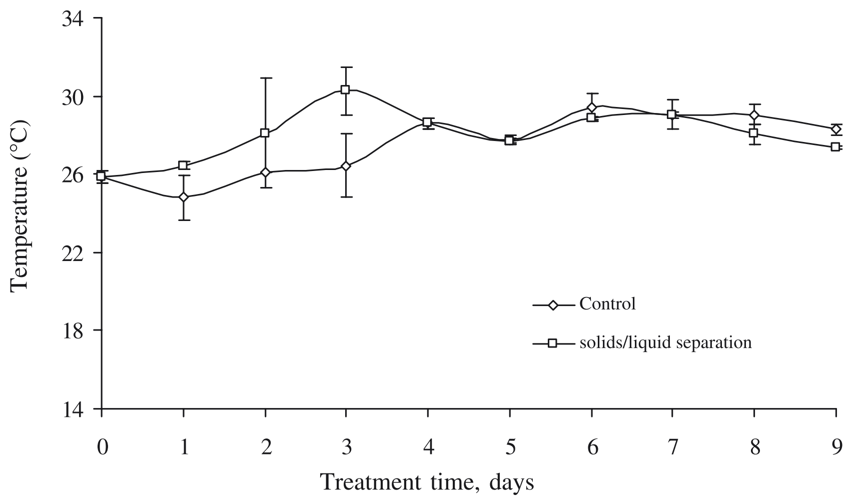

Figure 8. Temperature profiles of the treatment and the control during batch aeration treatment of swine manure.

This is quite evident in Figure 6 after the third day of aeration where, ORP in the separated liquid manure stabilized at a much higher level (-15 mV) than in the unseparated manure (-200 mV). These observations suggest that the oxygen transfer efficiency is significantly improved by the solids/liquid separation treatment prior to aeration. The consequence of this postulation is that it is possible to use lower aeration rates (or less energy) to maintain adequate ORP level especially in the latter period of the treatment. This gives solids/liquid separation an economic edge over unseparated manure in aeration treatments for control of odor generation when prolonged aeration treatments are desired.

SUMMARY AND CONCLUSIONS

Solids/liquid separation of manure prior to aeration resulted in more rapid degradation of VFAs compared to the unseparated manure during the aeration treatment. At the same level of aeration, it took only 1.5 days compared to 3 days during the aeration treatment to bring down VFAs levels to the ‘threshold of unacceptable level’ in the separated liquid manure, and in the control, respectively. In addition, it took approximately 2.3 days, and 5 days from start of aeration for the treatment and the control, respectively, to reach the acceptable level. Solids/liquid separation, therefore, significantly improves the removal of the odorous compounds from manure during aeration treatments.

Results also showed that, within the three weeks of post-aeration storage, the VFAs in the separated liquid manure consistently stayed 13.5 folds below the acceptable level. In the unseparated manure, the VFAs gradually increased upwards from 2.2 folds below acceptable level achieved at the end of aeration treatment, to 1.38 folds below the acceptable level at the end of the third week of storage and looked poised to definitely rise above the acceptable level in a matter of days. Solids/liquid separation, therefore, not only maintains odor at significantly lower levels, but also reduces chances of odor regeneration during post-storage of treated manure.

The plot of the relationship between pH of the manure and the VFAs content in the manure indicated: 1) a very strong relationship (correlation coefficient of 0.99), suggesting that degradation of VFAs reduce acidic level in the manure revealed by the increase in pH, and 2) a typical weak acid titration-curve confirming that, degradation of the VFAs was significantly responsible for the observed increase in pH during the aeration treatment. Although, the former observation could also be interpreted to mean that the VFAs are not being degraded but merely changing into their salts as the environment becomes more basic. Since there was no addition of a strong base in this study, it is less likely that, the VFAs were just changing into their salts.

From the data obtained in this study, it is more economical in prolonged aeration treatment to treat separated liquid manure than the unseparated manure. After only three days of aeration, separated liquid manure stabilized at a much higher ORP level of −15 mV, while the unseparated manure stabilized at a much lower ORP level of −200 mV. These observations suggest that the oxygen transfer efficiency is significantly improved by a solids/liquid separation treatment. The consequence of this postulation is that, it is possible to use less energy to maintain adequate ORP level in separated liquid manure than in unseparated manure, when prolonged aeration is desired; significantly improving the economic feasibility of such treatments.

ACKNOWLEDGMENTS

This research was supported with funds from Oklahoma State Agricultural Experiment Station. The author wishes to thank the Experiment Station for this support.

REFERENCES

1. Kroodsma, W. Separation as a method of manure handling and odors reduction in pig buildings. In *Odor Prevention and Control of Organic Sludge and Livestock Farming*; Nielson, V.C., Voorburg, J.J., L'Hermite, P., Eds.; Elsevier Applied Science Publishers: London, 1985; 213–221.
2. Westerman, P.W.; Zhang, R.H. Aeration of livestock manure slurry and lagoon liquid for odor control: a review. Appl. Eng. Agric. **1997**, *13* (2), 245–249.
3. Ndegwa, P.M.; Zhu, J.; Luo, A. Effects of solids separation and time on the production of odorous compounds in stored pig slurry. Biosyst. Eng. **2002**, *81* (1), 127–133.
4. Burton, C.H.; Farrent, J.W. Continuous aerobic treatment of pig slurry: evaluation of options based on long-treatment and two-stage processing. J. Agric. Eng. Res. **1998**, *69*, 159–167.
5. Zhang, R.H.; Dugba, P.N.; Bundy, D.S. Laboratory studies of surface aeration of anaerobic lagoons for odor control of swine manure. T. ASAE **1997**, *40* (1), 185–190.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

6. Hamilton, D.W.; Arogo, J. Measuring farmstead odors. In *OSU Extension Facts, F-1740*; Oklahoma Cooperative Extension Service, Division of Agricultural Sciences and Natural Resources: Oklahoma State University, USA, 1999.
7. Nimmermark, S. Use of electronic noses for detection of odour from animal production facilities: a review. Water Sci. Technol. **2001**, *44*, 33–41.
8. Brose, G.; Gallmann, E.; Hartung, E.; Jungbluth, T. Detection of the dynamics of odour emissions from pig farms using dynamic olfactometry and an electronic odour sensor. Water Sci. Technol. **2001**, *44*, 59–64.
9. Bell, R.G. Fatty acid content as a measure of the odor potential of stored liquid poultry manure. Poultry Sci. **1970**, *49*, 1126–1129.
10. Barth, C.L.; Hill, D.T.; Polkowski, L.B. Correlating odor intensity index and odorous components in stored dairy manure. T. ASAE **1974**, *17* (4), 742–4747.
11. Spoelstra, S.F. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odor development. Agric. Environ. **1980**, *5* (3), 241–260.
12. Williams, A.G. Indicators of piggery slurry odor offensiveness. Agric. Wastes **1984**, *10*, 15–36.
13. Zhu, J.; Ndegwa, P.M.; Luo, A. Effects of solid-liquid separation on BOD and VFAs in swine manure. Environ. Technol. **2001**, *22* (10), 1237–1243.
14. Sneath, R.W.; Burton, C.H.; Williams, A.G. Continuous aerobic treatment of piggery slurry for odor control scaled up to a farm-size unit. J. Agric. Eng. Res. **1992**, *53*, 81–92.
15. APHA; AWWA; WEF. *Standard Methods for the Examination of Water and Wastewater*, 19th Ed.; Franson, M.A.H., Eaton, A.D., Clesceri, L.S., Greenberg, A.E., Eds.; American Public Health Association: Washington DC, U.S.A., 1998; 4–146.
16. Hach Company Inc. Method 8196, esterification method. In *Procedure Manual*; Hach Company Inc.: PO Box 389, Loveland, CO, 1993.

Received November 11, 2002