Removal of Carbon, Nitrogen, and Phosphorus in Pig Manure by Continuous and Intermittent Aeration at Low Redox Potentials

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A laboratory experiment was conducted to study the effect of intermittent and continuous aeration at an airflow rate of 0.0667 l.min\(^{-1}\) l\(^{-1}\) of manure on redox potential, pH, organic carbon, total Kjeldahl nitrogen (TKN), ammonium nitrogen (NH\(_4^+\)-N) and soluble orthophosphate. Results showed that aeration at this rate could not bring redox potential up to truly aerobic level. A reduction of 24 and 26% in TKN and organic carbon, respectively, was observed during the continuous aeration process. The continuous aeration at this airflow rate also reduced the initial NH\(_4^+\)-N by 32%. Intermittent aeration was approximately as half as efficient in removal of organic carbon, TKN and NH\(_4^+\)-N as the continuous aeration. However, within a 24 h aeration period, 75% of soluble orthophosphate was removed from solution for both treatments, suggesting that the phosphorus removal efficiency was independent of aeration schemes, so energy could be saved while still maintaining the removal efficiency. © 2002 Silsoe Research Institute. Published by Elsevier Science Ltd. All rights reserved

1. Introduction

Surface water pollution by agricultural wastes usually refers to the excessive discharge of the nutritive elements such as carbon, nitrogen, and phosphorus, which are the basis of metabolism of living organisms. Recently, heavy application of pig manure, a convenient way of disposal, has been found to be responsible for many environmental problems. Although the nutrients applied to soils are assimilated by microflora and plants thus retained in soil and plants, there are still considerable amounts of nutrients that are removed by water through runoff from the cropland where manure was overapplied. The organic matter content in manure is believed to be responsible for acute water pollution incidents and for odour problems (Fallowfield \textit{et al.}, 1994). Nitrate (NO\(_3^-\)) and phosphorus are culprits for polluting potable water and causing eutrophication. Although fresh pig manure contains little nitrate, organic nitrogen and ammonium (Fallowfield \textit{et al.}, 1994), the NH\(_4^+\) in manure, or derived from the mineralization of organic nitrogen as manure is applied onto soil, is readily oxidized to NO\(_3^-\) that is poorly adsorbed by soil colloids, thus making it easy to move into surface water or groundwater. Therefore, decreasing the total nitrogen in manure is critical in controlling the problem of nitrogen pollution. Phosphate may not run into water greatly by leaching because it is strongly adsorbed by soil colloids and present in the soil solution at a very low concentration. However, phosphorus pollution can result from the surface runoff and soil erosion. This process is even more serious when soil contains excessive amount of phosphate. Therefore, to ameliorate potential environmental problems, removal of organic carbon, nitrogen and phosphorus from pig manure prior to disposal should receive further research.

Aeration can be an effective way in treating animal manure for removal of nutrients and odour control without causing secondary environmental problems. This technique has been widely adopted in industrial and municipal wastewater treatment. Good results also have been reported in treating animal wastewater in removal of biochemical oxygen demand (BOD\(_5\)), chemical oxygen demand (COD), nitrogen, phosphorus and even metal ions (Osada \textit{et al.}, 1991; Bicudo & Svoboda, 1995). However, the high cost of the equipment and energy consumption has hampered its wide application in treatment of manure from animal production. Some efforts have been made to enhance the efficiency, including prolonging the pre-anaerobic...
process (Gerrish et al., 1975), intermittent aeration (Osada et al., 1991; Bicudo & Svoboda, 1995) and use of
proper aerators (Fallowfield et al., 1994). Past researchers claimed that high redox potential or dissolved oxygen (DO) level in the liquid was required to achieve high nutrient removal efficiency. Charpentier et al. (1987) stated that complete oxidation of organic carbon and trapping of phosphorus in sludge were observed only when redox potential was above 0 mV. For nitrogen removal, it is believed that two processes are involved, i.e. volatilization of NH$_3$ under high pH and denitrification of NO$_3^-$/CO$_2$ formed by nitrification during aeration process, which occurs only as redox potential is above +100 mV (Charpentier et al., 1987) or DO concentration exceeds 1% saturation (Fallowfield et al., 1994). Bicudo and Svoboda (1995) illustrated that high nitrogen removal observed (over 95%) was related to the denitrification achieved through the intermittent operation of the aerator. Retention of phosphorus in microbes was engaged in an aerobic process accomplished by aeration that brought the redox potential above 0 mV (Charpentier et al., 1987). The above research shows that high redox potential seems to play a role in nutrient removal. However, maintenance of high redox potential means high cost in energy consumption. The work presented here is to examine the removal efficiencies of carbon, nitrogen and phosphorus by continuous and intermittent aeration at low redox potential levels. Use of intermittent aeration in the experiment is to further investigate the possibility of saving energy in removal of nutrients.

2. Materials and methods

2.1. Experimental procedure

The experiment was carried out in nine plastic columns, 91.6 cm in height and 15.3 cm in internal diameter. The aeration system is shown in Fig. 1. This system consisted of an air pump that introduced air into the manure at an airflow rate of 1.0 l/min$^{-1}$ (0.0667 l/min$^{-1}$ per litre of manure) controlled by an airflow meter. The intermittent aeration was accomplished by use of an automatic timer set at a 2 h interval (on/off). Each column was filled with 15 l of liquid manure, leaving 7.5 cm headspace to keep manure from spilling and to allow stirring during sampling.

The manure used was collected from the pit of a finishing barn in the University of Minnesota Southern Research and Outreach Centre at Waseca. The manure was rigorously agitated before sampling to ensure a uniform sample. The chemical characteristics of the raw manure are presented in Table 1. The manure sampling was performed every hour after 1.5 h aeration until 5.5 h and every 2 h thereafter until 11.5 h. In the remaining experimental period, samples were taken every 24 h for up to the first 7 days and every 48 h for the next 7 days. The experiment lasted approximately for 2 weeks. When sampling, the manure was stirred with a motorized paddle-stirrer for 5 min to reach uniformity and 100 mL of manure was collected at a depth of 40 cm from the surface. The samples, after pH measurement, were stored in a freezer at $\pm 20^\circ$C, and thawed before any subsequent laboratory analysis. Three treatments were used in this study, i.e. continuous aeration, intermittent aeration and control (columns without treatment). All measurements were made in triplicate. The test was conducted under room temperature, i.e. approximately at 22°C.

2.2. Chemical analysis

All manure samples were analysed for pH, total phosphorus, soluble orthophosphate and NH$_4^+$ Redox $\begin{array}{|c|}
\hline
\text{Table 1}
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\text{Chemical characteristics of manure} \\
\text{pH} & 6.47 \\
\text{Total Kjeldahl nitrogen (TKN), g/l} & 2.88 \\
\text{Total phosphorus, mg/l} & 710.0 \\
\text{Soluble orthophosphate, mg/l} & 116.5 \\
\text{Total solids, g/l} & 26.06 \\
\text{Total volatile solids, g/l} & 20.69 \\
\hline
\end{array}$
potential (reference: Ag/Ag/Cl) was measured during sampling directly by inserting into the column a probe with a digital pH/Temp/mV/ORP meter equipped with automatic temperature compensation (Cat: 5938-10, Cole Parmer Instrument Company). Three probes were running simultaneously to get triplicate data. The pH of each sample was measured by a pH meter (Model 720A, Fisher Company) immediately after sampling. Total phosphorus was measured after digestion with H$_2$SO$_4$–H$_2$O$_2$ (acid extraction) and dilution to 100 mL. Soluble orthophosphate and NH$_4^+$ were extracted by filtering ten-fold diluted manure using a Whatman filter paper. Orthophosphate was determined colorimetrically as the phosphomolybdate complex after reduction with ascorbic acid (APHA, 1998) and NH$_4^+$ was measured by Nesler’s method (Adams, 1990). Total Kjeldahl nitrogen was measured using the Kjeldahl method (APHA, 1998). Organic nitrogen was calculated as the difference between total Kjeldahl nitrogen and NH$_4^+$. Organic carbon was measured by the tube digestion method, which is recommended in determination of soil organic carbon (SSSA & ASA, 1996). Total solids and total volatile solids were determined using standard laboratory methods (APHA, 1998).

3. Results and discussion

3.1. Redox potential and pH variation

The variations of redox potential with aeration time are presented in Fig. 2. On the first day, for both aeration treatments, the redox potential increased dramatically up to about $-170$ mV for the first 4–5h, and then decreased rapidly to around $-300$ mV on the second day and fluctuated slightly in the rest of the aeration period. The initial increase in redox potential could be due to the build-up of oxygen in the liquid prior to the activation of aerobic growth, while the subsequent decrease in redox potential might indicate the acceleration of aerobic growth that consumed oxygen at a faster rate. At the end of test, both dropped to the same level as that in the non-aerated manure, which remained almost constant at around $-333 \pm 9$ mV throughout the test. Although the intermittent aeration delivered half the amount of air as compared to the continuous aeration, the redox potential in the manure was slightly higher than that of the latter during the test. The results also show that both aeration schemes only increased the redox potential significantly on the first day and did not establish the oxidizing condition during the test.

The pH of manure (Fig. 3) was significantly increased by aeration within the first 2 days from 6.5 to 7.5. This phenomenon was also observed by past researchers (Stevens & Cornforth, 1974). In the rest of the aeration period, the pH continued to increase but at a much lower rate. The continuous aeration resulted in a little higher pH increase than the intermittent aeration but followed a similar pattern. This pH change, caused by aeration, may be associated with the conversion of NH$_4^+$-N into ammonia. Stevens and Cornforth (1974) reported that pH would increase to between 8 and 9 by purging the dissolved CO$_2$ out of a solution, which forms NH$_4^+$ bicarbonate that keeps the pH neutral.

3.2. Removal of organic carbon

The changes in organic carbon during aeration treatment of manure are presented in Fig. 4. The non-aerated treatment shows a slight decrease in the content of organic carbon. Significant reduction of organic
3.3. Removal of total Kjeldahl nitrogen

The changes in total Kjeldahl nitrogen (TKN) during the aeration processes are presented in Fig. 5. The reductions of TKN in the non-aerated, the intermittently aerated and the continuously aerated manure are approximately 4-6, 16-5 and 26-5%, respectively. The total Kjeldahl nitrogen removal occurs soon after the aeration starts and the continuous aeration is more efficient than the intermittent aeration. The reduction of TKN observed in the present study is lower than that reported by Osada et al. (1991) who observed that aeration removes 72-2% of total nitrogen from pig wastewater. The main reason for the low removal efficiency of TKN may be due to the relatively low redox potential under which no nitrification would occur.

Aeration may cause nitrogen loss by: (1) volatilization of ammonia (Webb & Archer, 1994); and (2) nitrification/denitrification process if the oxygen concentration is appropriately adjusted (Fallowfield et al., 1994). However, no nitrification can possibly occur when redox potential is lower than +100 mV (Charpentier et al., 1987). While Fallowfield et al. (1994) and Webb and Archer (1994) state that increasing volatilization of ammonia by aeration could cause a loss of 30-40% of total nitrogen in manure. Therefore, under low redox potential conditions, all nitrogen loss is attributed to volatilization of ammonia. This might be the reason why high nitrogen removal efficiency is not achieved in this study.

3.4. Variation of ammonium nitrogen

Figure 6 presents the concentration of \( \text{NH}_4^+ \)-N in manure during the aeration processes. It is clear that carbon is observed after the first week for the continuous aeration, but not for the intermittent aeration. The overall removal efficiencies of organic carbon were 13/9, 24/0 and 7/3% for the intermittent aeration, the continuous aeration and the control, respectively.

Many researchers reported much higher efficiencies of organic carbon removal by aeration than those presented above. For example, Bicudo (1996) noted that the efficiency of carbon removal by aeration was about 90% as indicated by total COD at a DO level of 2.5 mg l\(^{-1}\). Obviously, in this case, the redox potential must have been +100 mV or higher since DO could be detected. Osada et al. (1991) reported that more than 90% of the total organic carbon was removed by aeration at an airflow rate of 0.325 l min\(^{-1}\)l\(^{-1}\) of manure which was substantially higher than the airflow rate used in the present study. Therefore, the low efficiency of carbon removal here may be related to the low redox potential.

Charpentier et al. (1987) stated that organic matter could go only through a fermentative pathway to be decomposed into volatile acids when redox potential was around –300 mV. The results by Hashimoto (1974) well documented the importance of redox potential in organic carbon removal. He found that aeration at a rate of 0.125 l min\(^{-1}\) per litre of manure could bring the redox potential to not more than –300 mV and the corresponding removal of carbon was 17-7%. When the redox potential increased to +10 mV by a higher flow rate of 3.74 l min\(^{-1}\)l\(^{-1}\), the carbon removal increased to 29.5%. The results in our experiment suggest that low aeration rates may not result in efficient organic carbon removal because of the low redox potential. Similar findings were also reported by Evans et al. (1986a, 1986b).
NH$_4^+$-N does not vary much during the first week of aeration. The treatment without aeration shows the highest NH$_4^+$-N concentration followed by the intermittent aeration and the continuous aeration. During the second week, sharp decreases in NH$_4^+$-N were observed in both the continuous and the intermittent aeration processes, with a reduction of 32.3 and 14.5% in NH$_4^+$, respectively.

Although NH$_4^+$-N is supposed to be converted into NH$_3$ due to aeration, thus leaving the manure under high pH, the NH$_4^+$-N concentration was not significantly reduced in the first week of treatment. This might be explained by the dynamic equilibrium between different nitrogen forms in the manure. In our experiment, the transformation of nitrogen can be expressed as

$$\text{Organic Nitrogen (N}_o\text{) } \leftrightarrow \text{NH}_4^+\text{-N } \leftrightarrow \text{NH}_3\uparrow$$  \hspace{1cm} (1)

Aeration can cause the decrease of NH$_4^+$-N level through both volatilization that results in the loss of total nitrogen and microbial assimilation that retains nitrogen in suspended solids. At the same time, aeration can also result in the increase of NH$_4^+$-N in liquid fraction derived from the mineralization of a labile organic nitrogen fraction since manure contains two similar-sized fraction, i.e. convertible nitrogen and non-convertible nitrogen (Fallowfield et al., 1994). Evans et al. (1986a, 1986b) showed that the readily mineralized convertible nitrogen could be conserved as ammonia/ammonium nitrogen. This process may offset the reduction of NH$_4^+$-N to some extent, thus keeping NH$_4^+$-N at a relatively stable level as observed in the first week of test (Fig. 6). In the second week, NH$_4^+$-N decreased sharply because the depletion of degradable organic nitrogen reduced the release of NH$_4^+$-N. Also, there could be an increase in organic nitrogen in microbial assimilation. This argument is evidenced by the change of organic nitrogen in the manure (Fig. 7). It can be seen that the organic nitrogen in the treatment without aeration decreased almost at a constant rate, while organic nitrogen in both aeration treatments sharply decreased between day 2 and day 3, indicating the significant transformation of organic nitrogen into inorganic forms. In the last 4 days, the concentration of organic nitrogen in the aeration processes was higher than that in the control. This is obviously attributed to the microbial assimilation. Therefore, after 1 week of aeration, NH$_4^+$-N was sharply decreased when the NH$_4^+$-N released from the organic matter was not enough to compensate for the loss of nitrogen by volatilization of ammonia and the assimilation by microbes (Fig. 6).

3.5. **Removal of phosphorus**

After just 1-day aeration, the soluble orthophosphate levels for both aeration treatments dropped dramatically from about 130 to about 30 mg l$^{-1}$ (an approximate reduction of 75%, Fig. 8). There is no statistically significant difference between the two treatments in terms of the soluble orthophosphate removal, indicating a possibility of energy savings. Bicudo and Svoboda (1995) obtained a soluble orthophosphate concentration of 25–60 mg l$^{-1}$ in the effluent of manure treated by aeration with a removal efficiency ranging from 20 to 90%. Bicudo (1996) also reported that soluble orthophosphate concentrations of between 25 and 60 mg l$^{-1}$ in the treated effluent were observed. Osada et al. (1991) reported that the removal efficiencies of orthophosphate by intermittent aeration and continuous aeration were 47.8 and 80.8%, respectively. The results reported here show that aeration can cause a significant decrease in the soluble orthophosphate levels in swine manure.
are strongly in agreement with those reported earlier. Charpentier et al. (1987) stated that the low redox potential resulted in the release of orthophosphate into the solution and that the removal of orthophosphate required the redox potential as high as above 0mV. In this study, redox potential was as low as –300mV that falls into the orthophosphate release range according to Charpentier et al. (1987). However, the soluble orthophosphate removal efficiencies are still quite good as compared to those in early studies. This result suggests that aeration under low redox potential can also remove soluble orthophosphate in pig manure without loss of process efficiency. The reason that low-level aeration could also achieve a similar efficiency in orthophosphate removal may be attributed to the pH rise. Figure 9 shows that there is a good correlation between logarithmic soluble phosphate and pH for intermittent aeration. For continuous aeration, the logarithmic correlation between soluble phosphate and pH appears not as good as in the intermittent aeration, especially when pH goes beyond 7.5. In spite of this, the above results demonstrate that soluble orthophosphate concentration in manure is pH dependent and in situations where nitrogen and carbon are not limiting factors, low-level aeration may be an economical way in removing soluble orthophosphate from pig manure.

4. Conclusion

(1) Aeration at a low rate (0.0667 l/min⁻¹ l⁻¹ of manure) significantly increases the redox potential only in the first day of aeration, but fails to bring redox potential up to oxidative condition.

(2) About 24 and 26% of total nitrogen and organic carbon, respectively, are removed by the continuous aeration process although the efficiency is not as high as under high aeration rates reported by past researchers. Intermittent aeration shows a lower efficiency of carbon and nitrogen removal than continuous aeration.

(3) Under this low airflow rate, NH₄⁺-N in the intermittent and continuous aeration treatments is reduced by 14.5 and 32.3%, respectively. The reduction in NH₄⁺-N is attributed to ammonia volatilization and microbial assimilation, indicated by the gain in organic nitrogen.

(4) Soluble orthophosphate could be successfully decreased approximately by 75% within 24 h aeration under a low aeration rate indicated by low redox potential. Extending aeration time does not increase the removal efficiency. This is similar to the efficiencies reported previously under high aeration rates. The intermittent aeration is not significantly different in removal of soluble orthophosphate from the continuous aeration, suggesting that energy can be saved in the treatment of pig manure for removal of soluble phosphorus.

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