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Removal of odorants from animal waste using Fenton's reaction

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Abstract. The purpose of this study was to evaluate Fenton's reaction as a means of mitigating the problem of offensive odors emitted from livestock manures. The hypothesis to be tested was that hydroxyl radicals generated during this reaction would oxidize odorant compounds, breaking them down to nonodorous products. The deodorization effect was assessed using various chromatographic techniques to determine the concentration of selected odor indicators present in swine slurry and reactor headspaces before and after treatment. The indicators included seven volatile fatty acids, three phenols, and two indoles that were positively correlated with malodors from animal manure. The extent of their removal strongly depended on the concentration of Fenton's reagents (0 to 40 mM FeCl3, and 0 to 800 mM H2O2), the initial pH of swine slurry (2.0 to 6.5), and the total solids content (0.6 to 2.9% TSC). Control samples treated with no FeCl3 or H2O2 did not show significant reduction of odorant concentration at all pH and TSC levels tested. Acceptable removals of total odorants (65 to 90%) were observed between pH 3.5 and 5.5. When swine slurry (0.7% TSC, pH 5.0) was treated for 2 h with 40 mM FeCl3 at 400 mM H2O2, all odorants were removed completely (100%), except for small amounts of propionic acid. Odorant removal from swine slurry was in good agreement with that from the headspace air (90-100% removal for most measured odorants). Pilot-scale treatment produced encouraging results, surpassing the expectations based on the outcome of laboratory experiments.

Keywords. deodorization, Fenton's reaction, animal waste, swine slurry, odorants.

Introduction

Presently, animal malodors are not a trivial problem. Pork production, for instance, is a $50 billion industry that provides jobs for 800,000 workers according to the National Pork Producers Council (2005). Confined animal feeding operations (CAFOs) involve collection, storage, transport and disposal of animal manures, which are sources of offensive odors and pose quality of life issues for surrounding communities. According to a *Newsweek* report of July 12, 2004, a Nebraska appeals court ruled that a hog producer (Progressive Swine Technologies) must compensate its neighbors for forcing them to live with lower air quality. In a similar case, the Iowa Supreme Court recently decided that neighbors of large livestock operations could sue livestock producers, striking down the state's Right-to-Farm law. Livestock industries in other parts of the country also risk facing similar legal issues.

The federal government is recognizing the problem. Recent evaluation of air emissions from animal feeding operations (AFOs) by the U.S. Department of Agriculture (USDA) and the U.S. Environmental Protection Agency (EPA) indicated that odor is primarily of concern in terms of human life quality, and is of

major importance at local scales (National Research Council, 2003). Societal clashes over malodor may therefore create a threat to the viability of livestock industries. Work on technologies to control odors is underway in industry and academia. A variety of techniques have been proposed for manure deodorization, ranging from aeration, to diet modifications, to the application of manure additives (American Society of Agricultural Engineers, 2001), but none of these techniques has proven to be entirely satisfactory.

The purpose of this project was to evaluate Fenton's reagent treatment as a novel approach to the problem of air quality degradation by offensive odors emitted from livestock manures. Fenton's process involves mixing ferrous or ferric iron (e.g., $FeCl_2$, $FeCl_3$) with hydrogen peroxide (H_2O_2). As shown below in Equation 1, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}) with the release of a hydroxyl radical ($^{\cdot}OH$) (Walling, 1975; Wardman and Candeias, 1996; U.S. Peroxide Reference Library, 2004). The ferric iron then reacts with another molecule of H_2O_2 (Equation 2), generating a different form of hydroxyl radical ($^{\cdot}OOH$) with the recovery of ferrous iron that can again react with H_2O_2, generating more hydroxyl radicals.

$$\mathbf{Fe^{2+} + H_2O_2 \text{ ----> } Fe^{3+} + {}^{\cdot}OH + OH^-} \quad (1)$$

$$\mathbf{Fe^{3+} + H_2O_2 \text{ ----> } Fe^{2+} + {}^{\cdot}OOH + H^+} \quad (2)$$

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The free hydroxyl radical is one of the most reactive chemical species (Walling, 1975). Its relative oxidation power is 2.06, second only to that of elemental fluorine (2.23), equal to that of ozone (2.1), and greater than those of atomic oxygen (1.78), hydrogen peroxide (1.31), permanganate (1.24), and chlorine (1.0) (Walling, 1975; U.S. Peroxide Reference Library, 2004). Because of this high oxidative potential of hydroxyl radicals, Fenton's reaction has been proposed for treatment of a variety of industrial wastes containing a range of toxic organic compounds, such as phenols, formaldehyde, BTEX, and complex wastes derived from dyes, pesticides, wood preservatives, plastics additives, and rubber chemicals (Leung et al., 1992; Schrader and Hess, 2004). The process is being applied to industrial wastewaters, sludges, and contaminated soils (U.S. Peroxide Reference Library, 2004).

As demonstrated in this study, hydroxyl radicals generated during Fenton's reaction can break down odorant compounds present in animal manures, probably to CO_2 and other non-odorous products:

$$\mathbf{OH + {}^{\cdot}OOH + odorants \text{ ----> } CO_2 + odorless\ breakdown\ products} \quad (3)$$

The long-term goal of this study is to develop an effective deodorization method based on Fenton's reagent treatment. In this part of the project, experiments were carried out to: (1) optimize Fenton's process for the treatment of swine slurry by monitoring the extent of odorant degradation as a function of Fenton's reagents concentration, initial pH of swine slurry, and total solids content, and (2) to carry out a pilot-scale experiment, in which 20-L increments of swine slurry were added daily up to a total of 180 L on Day 9, when the last treatment took place. In so doing, it was possible to assess the potential of Fenton's reaction for a full-scale treatment of animal wastes.

1. Materials and Methods

1.1. Reagents

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), which was used for the laboratory experiments, was bought from Fisher Scientific (Pittsburgh, PA). Anhydrous ferric chloride ($FeCl_3$), used in the pilot-scale experiment, and hydrogen peroxide (H_2O_2, 35% w/v and 50% w/v) were purchased from Sigma-Aldrich (St. Louis, MO). Standards of the chemicals that served as malodor indicators (propionic acid, isobutyric acid, *n*-butyric acid, isovaleric acid, *n*-valeric acid, isocaproic acid, *n*-caproic acid phenol, *p*-cresol, *p*-ethylphenol, indole, skatole) were purchased from Sigma-Aldrich (St. Louis, MO).

1.2. Swine slurry samples: collection and physiochemical analyses

Swine manure slurry samples for both laboratory and pilot-scale testing were collected in large volumes (20 L) from a concrete swine slurry storage pit (capacity: 6,000 gallons, or 23,000 L) at the Swine Center operated by the Department of Dairy and Animal Science at Penn State. The pH, before and after adjusting to desired levels with concentrated HCl, was measured after the sample had equilibrated to room temperature using a ThermoOrion model 525A Plus pH meter with a pH electrode (ThermoOrion Model No. 9165). The total solids content (TSC) of the original, centrifuged, and sedimented swine slurry samples was determined based on dry weight after 24-h heating at 103°C.

1.3. The effect of Fenton's reagent concentrations on the extent of odorants removal

The concentration of $FeCl_3 \cdot 6H_2O$ in this series of experiments ranged from 0 to 10, 20, and 40 mM, and that of H_2O_2 ranged from 0 to 200, 400, and 600 mM. The pH of the swine slurry was adjusted (with concentrated, 11.6 M, HCl) so that the initial pH prior to Fenton treatment was 3.5, 5.0, or 6.5 (unadjusted). Two types of swine slurry samples were tested: (1) centrifuged samples with a total solids content (TSC) of 0.7%, and (2) centrifuged samples mixed with the original slurry to result in a TSC of 1.5%. The experimental setup was as follows: triplicate 10-mL samples of swine slurry with 0.7% or 1.5% TSC were placed in 30-mL test tubes. The slurry was thoroughly mixed with $FeCl_3 \cdot 6H_2O$, then H_2O_2 was added (with continued mixing). The samples were left for 2 h without further mixing, and analyzed for odorant concentrations by gas chromatography (GC).

1.4. The effect of pH on odorant removal

The experiments described in section 1.2. indicated that Fenton treatment might strongly depend on pH, so, in the follow up experiments, carried out in order to further evaluate this dependence, pH was adjusted to range from 2 to 6.5 in half-unit increments. Two separate sub-experiments were carried out, in which 10-mL samples (with 0.7% TSC) were treated at different pH with 20 or 40 mM $FeCl_3$, using 400 mM H_2O_2 in either case. Non-treated samples (0 mM $FeCl_3$ and 0 mM H_2O_2) served as controls). As in section 1.2., the treatment time was 2 h, involving an initial mixing without further agitation, and the samples were analyzed for odorant concentration by GC.

1.5. The effect of total solids content (TSC) on odor removal

This experiment was designed to further evaluate the dependence of Fenton treatment on total solids present in the swine slurry, after the initial experiment indicated the significant effect of TSC. TSC was adjusted by mixing the centrifuged swine slurry (0.7% TSC) with the original slurry (2.9% TSC), so that TSC ranged from 0.7 to 2.9% at 0.2% increments. The experiment was run (for 2 h with an initial mixing) at pH 4.0 with 20 or 40 mM $FeCl_3$, and 400 mM H_2O_2, and monitored by GC for odorant concentrations. Non-treated samples (0 mM $FeCl_3$ and H_2O_2) served as controls.

1.6. Pilot-scale experiment

The pilot-scale experiment was conducted using a 200-L plastic, cylindrical reactor (h = 71 cm, dial. = 60 cm) equipped with a ball valve at the bottom, and covered with a plastic lid with a central 1.1-inch opening for inserting a stirrer, which was used for mixing the contents when necessary. The stirrer consisted of a 60-cm long rod (one inch in diameter), with a hand crank device outside the reactor, and a set of welded 25-cm baffles. The lid was equipped with two capped ports, through which Fenton reagents were added (anhydrous $FeCl_3$, and 50% H_2O_2).

The reactor was installed outdoors, at the underground manure storage unit located in the Penn State's Swine Center (air temperature and swine slurry temperature were monitored shortly before each treatment, ranging from 7 to 19°C and from 11 to 17°C, respectively, and averaging each at 14°C). The experiment was run for 9 days, with daily additions of 20-L increments of settled swine slurry until the reactor was filled to a volume of 180 L on Day 9. Sedimentation was a way to adjust the total solids content of the slurry to treatable levels (0.6-1.5% TSC). For that purpose, after 1 h of mechanical mixing of the slurry in the concrete swine slurry storage pit, the slurry was left undisturbed for 1 h to sediment, and the 20-L volumes were taken for pilot-scale testing from the top layer of the storage pit content. Immediately after each addition of fresh slurry to the previously treated one(s), the content of the plastic reactor was mixed first with 217 g of $FeCl_3$ (on Days 1, 2, 3, 4 and 5), then with 545 mL of 50% H_2O_2 (on Days 1 through 9). Each day, before treatment and 2 h after treatment, the slurry was briefly mixed and triplicate 10-mL samples were withdrawn from the reactor for GC, pH, and TSC measurements. Additionally, on Days 1, 5, and 9, triplicate 10-mL samples were taken for gas chronmatography/mass spectrometric (GC/MS) analysis, and quadruplicate 30-mL samples were taken to determine odorants concentration in the headspaces by multidimensional gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O). Before the first treatment, pH of the slurry was reduced from the original pH 7.4 to pH 4.6 by mixing the slurry with 150 mL of concentrated (11.6 M) HCl; all the remaining eight treatments were carried out without prior pH adjustment.

1.7. Determination of odorant concentrations in swine manure samples

GC analysis of odorants present in swine slurry involved five volatile fatty acids (VFAs), three phenols, and two indoles. GC/MS was used to verify the identity of odorant compounds in swine slurry samples from the pilot-scale reactor. The odorants were extracted by ethyl ether and quantified using a Hewlett-Packard5890 chromatograph with a HP G1030A ChemStation Controller according to our previous study (Govere et al., 2005). MDGC-MS-O analysis of odorants present in headspaces of swine slurry samples was preceded by solid phase microextraction (SPME) according to Koziel et al. (2006). The quadruplicate swine slurry samples (30 mL) were shipped overnight to the Atmospheric Air Quality Laboratory (AAQL) in Iowa State University and refrigerated for no more than 4 days. Twenty four h before analysis they were equilibrated at room temperature in the fume hood, and adjusted to pH 1. Ten-mL aliquots were transferred to 22 mL glass vial with PTFE stir bar, and headspace gases emitted from swine manure were collected (for 40 min at constant stirring) using 85 µm Carboxen/PDMS SPME fiber (Supelco, Bellefonte, PA), and the fiber was then analyzed on a MDGC-MS-O system (Microanalytics, Round Rock, TX). The system integrated GC-O with conventional GC-MS (Agilent 6890N GC / 5973 MS, Agilent Inc., Wilmington, DE) as the base platform with the addition of an olfactory port. The system was equipped with a non-polar precolumn and polar analytical column in series as well as system automation and data acquisition software (MultiTrax™ V. 6.00 and AromaTrax™ V. 6.61, Microanalytics and ChemStation™, Agilent). The identity of compounds was verified by combination of (a) high purity reference standards (Sigma-Aldrich, Fisher, and Fluka) and matching their retention time on the MDGC capillary column and mass spectra; (b) matching mass spectra of unknown compounds with BenchTop/PBM (Palisade Mass Spectrometry, Ithaca, NY) MS library search system and spectra of pure compounds, and (c) matching the description of odor characteristics. The relative % reduction was used to evaluate the effectiveness of Fenton treatments: %Reduction = [(Ci – Ti)/Ci] x 100%, where: Ci is peak area count of compound or odor "i" for the control, and Ti is peak area count of compound or odor "i" for the treatment.

2. Results and Discussion

2.1. Laboratory experiments

Laboratory experiments demonstrated that the removal of odorants increased at increased concentrations of Fenton's reagents, reduced pH, and reduced TSC (Figures 1-3). Control samples treated with no $FeCl_3$ and H_2O_2, or with only one of the Fenton reagents, did not show significant reduction of odorant concentration at all pH and TSC levels tested.

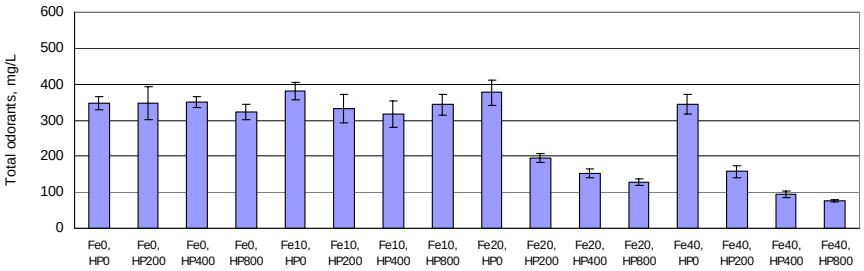

Figure 1. Odorant concentrations (total VFAs, phenols and indoles) in swine slurry (0.7% TSC) incubated for 2 h with 0, 10, 20 and 40 mM $FeCl_3 \cdot 6H_2O$ (Fe0, Fe10, Fe20, Fe40), and 0, 200, 400 and 800 mM hydrogen peroxide (HP0, HP200, HP400, HP800), at pH 3.5.

As shown in Figure 1, presenting the outcome of Fenton treatment carried out at pH 3.5, for swine slurry with 0.7% TSC, odorant removal required a sufficient increase in $FeCl_3 \cdot 6H_2O$ concentration. At 10 mM $FeCl_3 \cdot 6H_2O$ no significant removal of total odorants occurred despite increasing the concentration of H_2O_2, but when $FeCl_3 \cdot 6H_2O$ was used at 20 mM, the concentration of total odorants dropped by about 40% for 200 mM H_2O_2, and by about 60% for 800 mM H_2O_2. At 40 mM $FeCl_3 \cdot 6H_2O$, a further decrease of total odorants was observed – down to about 20% for 400 and 800 mM H_2O_2. The odorant remaining in these latter samples was propionic acid; as all other VFAs were completely removed (so were all phenols and indoles).

It thus appears that VFAs with larger molecules were gradually degraded (via smaller molecules) to propionic acid, which is the reason propionic acid was not completely removed from the reaction mixture.

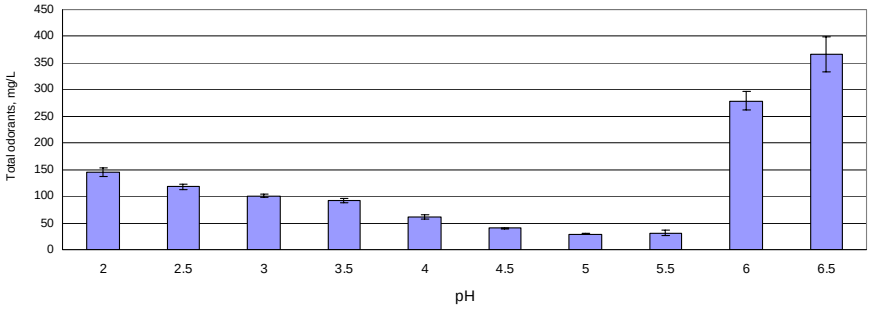

Figure 2. Odorant concentrations (total VFAs, phenols and indoles) in swine slurry (0.7% total solids content) incubated for 2 h with 40 mM $FeCl_3 \cdot 6H_2O$ and 400 mM H_2O_2 at different pH.

The effect of Fenton's reagents was tested also at pH 5.0 and 6.5, and for increased TSC (1.5%). At higher pH levels and TSC, odorant removal significantly decreased (at pH 5), or did not occur at all (at pH 6.5) (data not shown). Figure 2 presents the results of follow up experiments aimed at assessing the changes in odorant concentration as pH changed in (half-unit increments) from 2.0 to 6.5. The experiment was carried out with 0.7% TSC samples. The concentration of total odorants in the control samples (no $FeCl_3 \cdot 6H_2O$, and no H_2O_2) did not change significantly with pH, averaging at 340 mg/L (data not shown). With 40 mM $FeCl_3$ (and 400 mM H_2O_2), an efficient odorant removal occurred at a broad range of pH (from pH 2.0 to 5.5). The maximal odorant removal (91%) was observed at pH 5.0 and 5.5, with no removal at pH 6.0 and 6.5. In swine slurry samples treated with 20 mM $FeCl_3 \cdot 6H_2O$ (and 400 mM H_2O_2), the maximal removal total odorants was somewhat lower (72% at pH 4.0) than that observed for 40 mM $FeCl_3 \cdot 6H_2O$, and it occurred at a narrower pH range (pH 2.0 to 4.5) (data not shown).

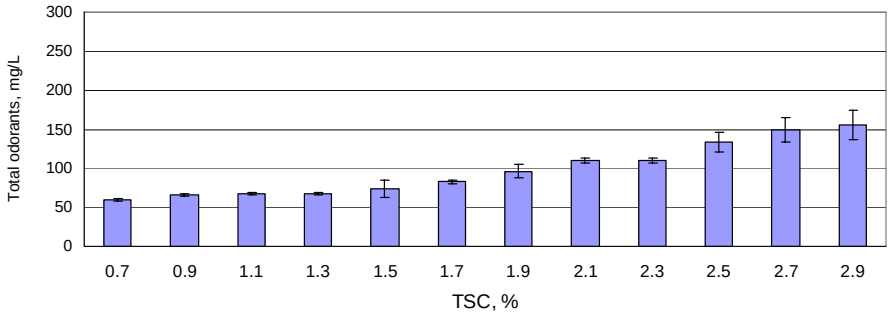

Figure 3. Odorant concentrations (total VFAs, phenols and indoles) in swine slurry with different TSC incubated for 2 h (at pH 4.0) with 40 mM $FeCl_3 \cdot 6H_2O$, and 400 mM H_2O_2.

The effect of TSC is presented in Figure 3. The experiment was carried out at pH 4.0. The concentration of odorants in the control swine slurry samples (no $FeCl_3 \cdot 6H_2O$, and no H_2O_2) did not change significantly with the increasing TSC (from 0.7 to 2.9%), averaging at 300 mg/L (data not shown). In treated samples, odorant removal decreased with increasing TSC. When swine slurry was treated with 40 mM $FeCl_3 \cdot 6H_2O$ (and 400 mM H_2O_2), significant removal (by 60 to 81%) was observed at the entire range of TSC. Decreasing $FeCl_3 \cdot 6H_2O$ concentration to 20 mM resulted in a decreased odorant removal, which ranged from 17 to 71% for TSC ranging from 0.7 to 2.1% (beginning from 2.3%TSC no removal was observed) (data not shown).

2.2. Pilot-scale experiment

The pilot-scale experiment essentially confirmed the outcome of laboratory studies (Figure 4), and, simultaneously, it provided evidence for self-regulating mechanisms that were activated once the first treatment has been done.

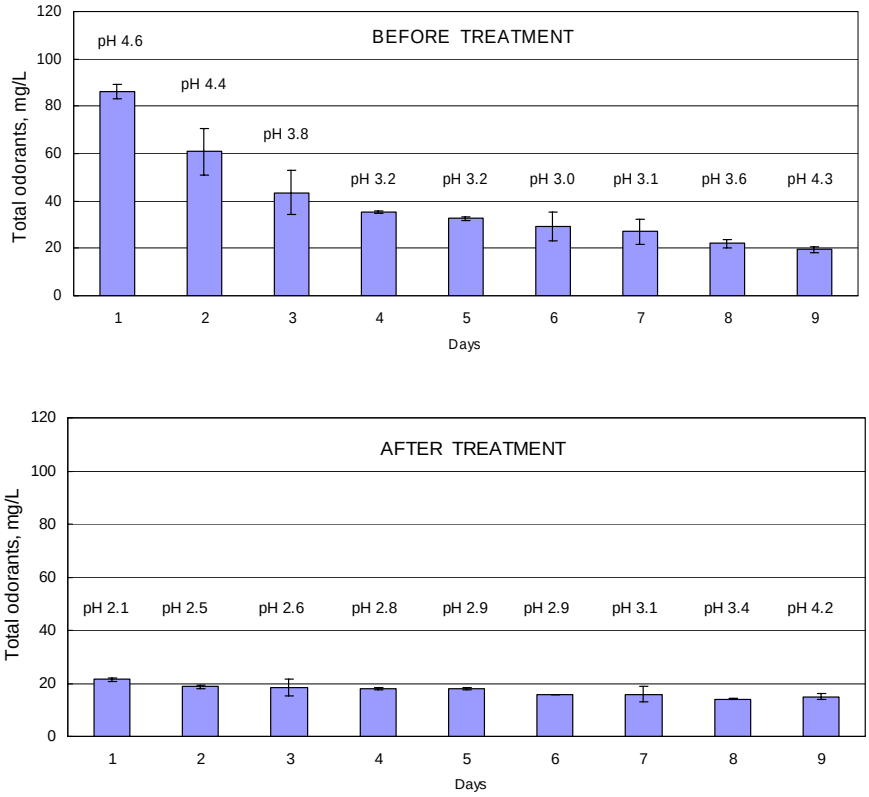

Figure 4. Changes in odorant concentrations (total VFAs, phenols and indoles) in swine slurry during the 9-day pilot-scale experiment, in which the increasing volume of the slurry (from 20 to 180 L) was treated for 2 h with 217 g of $FeCl_3$ (on Days 1, 2, 3, 4 and 5), and 545 mL of 50% H_2O_2 (on Days 1 through 9).

As shown in the top graph of Figure 4, with each 20-L addition of fresh swine slurry, there was a steady decrease in the initial concentration of total odorants, apparently due to two factors: (1) the considerable reduction in odorant concentration in the preceding 20-L swine slurry volume (Figure 4, bottom), and (2) the dilution of freshly added swine slurry by the previously treated 20-L volume. As a result, a 75% removal of total odorants observed during Day 1 treatment dropped to 20% removal in Day 9, but the initial total odorant concentration on that day was already reduced by 80% as compared to that on Day 1. As in laboratory experiments, the 20% remainder was represented exclusively by residues of propionic acid; all other odorants were completely removed.

Laboratory experiments seemed to indicate that Fenton treatment might require adjusting pH with HCl after each cycle, a discouraging prospect. The pilot-scale study, however, demonstrated that pH adjustment was only necessary in the first cycle (from the original pH 7.4 to the initial pH 4.6). After the first cycle, the system took care of itself, automatically maintaining pH at acceptable levels for an efficient odorant removal, simply as a result of adding $FeCl_3 \cdot 6H_2O$, which on its own led to pH adjustment. Specifically, pH that was initially adjusted from 7.4 to 4.6 (Figure 4, top), dropped to 2.10 after the first treatment (Figure 4, bottom), and increased back to 4.4 when the second 20-L volume of swine slurry was added the next day, dropping again to 2.5 after the second treatment, and increasing again to 3.80, and so on. In fact, there was a steady decrease in the initial pH, down to pH 3.0 on Day 6, but it never reached an unacceptable level that would drastically affect odorant removal. Beginning from Day 7, initial pH started to increase again, first imperceptibly (from 3.0 to 3.1 on Day 7), and then up to 4.3 on Day 9, which was the result of ceasing the

application of $FeCl_3 \cdot 6H_2O$ after Day 5, as a way of maintaining pH on an acceptable level, on the one hand, and of reducing the input of one of the Fenton reagents, on the other. As shown in the bottom graph of Figure 4, stopping the application of $FeCl_3 \cdot 6H_2O$ did not lead to a reduction of odorant removal. On the contrary, it was maintained on an established level, apparently because the amount of $FeCl_3 \cdot 6H_2O$ introduced into the system in the previous five cycles was sufficient to sustain the efficient odorant degradation.

Allowing swine slurry to settle in the storage pit before subjecting it to Fenton treatment, so that the initial TSC remained between 0.6 and 1.5% (data not shown) provided for considerable odorant removals. It remains to be determined, however, if the self-regulating mechanisms that revealed themselves in the course of the pilot-scale experiment would also allow for treating swine slurries with higher TSC levels than those tested.

The results of MDGC-MS-O analysis of headspace gases were consistent with those of the GC analysis of swine slurry. Both total ion chromatograms and aromagrams of swine manure headspaces (data not shown) had a very complex pattern, especially for the control samples, with several major compounds responsible for the offensive odor designed as "foul, fecal" (methyl mercaptan), "onion, garlic" (dimethyl sulfide), "skunky" (3-methyl thiophene), "body odor" (isovaleric acid), "barnyard" (4-methyl phenol), "barnyard, piggy" (indole) and "naphthalenic" (skatole). Most of the offensive odors were removed or dramatically decreased after the Fenton treatment, especially sulfides, VFAs, phenolic and indolic compounds. Effects of the Fenton treatment on 18 target headspace gases on day 1, 5 and 9 are shown in Table 1. Average reduction of target compounds on day 1, 5 and 9 were 96.9%, 81.6% and 71.0%, respectively.

Table 1 Effectiveness of Fenton treatment on target odorants in swine manure headspace.

		Day 1		**Day 5**		**Day 9**	
No	**Compound**	**% Reduction**	**p-value**	**% Reduction**	**p-value**	**% Reduction**	**p-value**
1	Methyl mercaptan	100.0	0.0323	n/a	n/a	n/a	n/a
2	Dimethyl sulfide	100.0	0.0100	n/a	n/a	n/a	n/a
3	Dimethyl disulfide	100.0	0.0014	100.0	0.0000	100.0	0.0003
4	2-Methyl thiophene	100.0	0.0067	100.0	0.0046	100.0	0.0005
5	3-Methyl thiophene	100.0	0.0031	100.0	0.0012	100.0	0.0017
6	Dimethyl trisulfide	100.0	0.0002	100.0	0.0002	100.0	0.0317
7	Propionic acid	59.3	0.0008	49.2	0.0011	34.8	0.0010
8	n-Butyric acid	97.6	0.0001	87.9	0.0000	81.8	0.00004
9	Isovaleric acid	99.2	0.0001	92.8	0.0000	88.1	0.00002
10	n-Valeric acid	99.5	0.0002	97.0	0.0000	94.0	0.0002
11	Isocaproic acid	100.0	0.0022	100.0	0.0306	100.0	0.0183
12	n-Caproic acid	98.4	0.0005	91.6	0.0003	69.9	0.0870
13	Heptanoic acid	94.8	0.0007	64.8	0.0103	31.5	0.1780
14	Phenol	99.1	0.0002	93.7	0.0596	88.4	0.0007
15	4-Methyl phenol	99.1	0.0003	96.2	0.0618	97.4	0.0002
16	4-Ethyl phenol	99.0	0.0019	95.2	0.0628	95.9	0.0006
17	Indole	100.0	0.00004	100.0	0.0011	25.2	0.7642
18	Skatole	98.6	0.0009	100.0	0.0517	-153.6	0.5810
Mean % reduction		96.9		81.6		71.0	

Almost all of the target headspace chemicals were removed by Fenton treatment except skatole on day 9. Skatole was detected in only one (out of n =4) replicate treatment samples and was only found on day 9. Noteworthy is the removal of 4-methyl phenol (or *p*-cresol) by 99.1%, 96.2%, 97.4% on day 1, 5 and 9, as this compound was implicated to be the number 1 odorant responsible for the characteristic swine odor near the source and far downwind (Wright, et al., 2005; Bulliner et al., 2006; Koziel et al., 2006).

Conclusion

The outcome of this study supported the hypothesis that the application of Fenton's reagents to swine slurry would lead to a breakdown of odorous compounds to non-odorous products. The extent of odorant removal strongly depended on the concentration of Fenton's reagents, the initial pH of swine slurry, and the

total solids content. Control samples treated with no $FeCl_3$ or H_2O_2 did not show significant reduction of odorant concentration. Odorant removal from swine slurry was in good agreement with that from the headspace air. Pilot-scale treatment produced results consistent with the outcome of laboratory experiments, and revealed self-regulating mechanisms that could save materials and labor.

In view of the obtained results, it becomes clear that a Fenton reagent deodorization system may not be properly assessed based just on treating individual samples in laboratory studies, with an anticipation of an additive demand for Fenton reagents in scaled-up systems. The investigation cannot be considered complete, and it requires further refining of the treatment strategies, such as determining: (1) whether adjusting pH before the first cycle is at all necessary, (2) whether reducing the total solids content is a necessary step in this technology, (3) whether the application of $FeCl_3 \cdot 6H_2O$ can be stopped sooner than after the fifth cycle, (4) whether the application of H_2O_2 can also be stopped at a certain point, (5) whether the application of $FeCl_3 \cdot 6H_2O$ and H_2O_2 can be stopped simultaneously, or must be done alternatively, (6) how soon the application of either of the reagents must be restored to sustain an efficient odorant removal throughout treatment periods much longer than 9 days, and (7) what would be the advantages and/or disadvantages of Fenton treatment using alternative chemicals, such as ferrous iron (e.g., $FeSO_4$) and calcium peroxide (CaO_2). It has not escaped our attention that, in addition to odorants, Fenton treatment may degrade an array of other unwanted organic chemicals, such as steroid hormones, veterinary antibiotics, and feed additives that are commonly excreted in the animal manure, thus representing a potential threat to the environment.

The chemical components of Fenton's system are commonly used in water and wastewater treatment as coagulants (ferric and ferrous iron) and oxidative agents (H_2O_2). Thus, proven technologies and products already exist to minimize the potential safety risks related with on-site storage of these chemicals. With their low costs, relatively small amounts needed for an efficient application, especially when with the self-regulating mechanisms revealed in this study, Fenton chemicals have potential to emerge as extremely effective deodorizing agents.

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