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Deodorization of swine manure slurry using horseradish peroxidase and peroxides

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ABSTRACT

Considering the development of highly confined piggery and increasing complaints about livestock manure odors, it is pressing to develop a practical way to reduce the odors. Peroxidase, which has been proved to be capable of removing toxic phenolic compounds from wastewater, may also be effective in deodorizing the swine manures. Horseradish peroxidase (HRP) (0.1–3.0 U/mL) with hydrogen peroxide (H_2O_2, 0.5–6%) or calcium peroxide (CaO_2, 0.1–3.0 g) was examined for the efficiency of controlling the release of seven malodor compounds, including three volatile fatty acids (isobutyric acid, isocaproic acid and isovaleric acid), two phenolic compounds (phenol and *p*-cresol) and two indolic compounds (indole and skatole) from swine manure slurry. Odor intensity and total nitrogen content in swine manure were also measured. The results showed almost 100% reduction in *p*-cresol, 54–84% reduction in odor intensity, 32–54% reduction in indolic compounds and 28–41% reduction of VFAs. The effect of deodorization can last for at least 48 h.

1. Introduction

In China, livestock production is in a time of significant transition. The traditional small farm practice of having a few pigs is declining. The trend toward high-density, confined feeding of swine has increased tremendously in recent years. The storage and processing of large amounts of swine manure becomes a serious management and environmental issue. Swine manures consist of concentrated organic materials, decomposition of which can result in the production of malodorous, volatile low molecular weight compounds such as volatile fatty acids (VFAs), and aromatic compounds such as phenol, indoles and cresols as well as ammonia and hydrogen sulfide. More than 160 odorous compounds have been identified in livestock wastes [1]. Among these compounds, the volatile phenolic and indolic metabolites are among the most malodorous of the compounds found in swine manure slurry. During storage of manure the odor offensiveness increased, as did the concentration of malodorous compounds, which include phenol, *p*-cresol, skatole and VFAs [2]. In addition to causing nuisance and unpleasure, elevated odor in confinement building may decrease growth rate of livestock, increase the incidence of infection, and adversely affect the health of farm workers. Odor management is currently a great challenge of farm operators, environmental regulators, agricultural and environmental engineers because it creates a major threat to the sustainability, profitability and growth of animal industry. As a consequence, there exists an impetus to develop technologies for reducing the impact of odor on the surrounding community.

Solutions to manure odor control were proposed to control livestock manure odor. Manure additives [3,4], diet modifications [5] and aeration [6–9] or ozonation [10] have been applied to reduce odor, but the costs were high. None of these techniques were proved to be entirely satisfactory. There is thus a need to develop cheap and effective methods to control odor from intensive livestock production.

Conventional technologies, based on chemical treatment and/or use of microorganisms, pose serious limitations. Then the proposed enzymatic methods have generated great interest. Oxidoreductive enzymes, such as peroxidase and tyrosinase, are capable of oxidizing phenols and aromatic amines to free radicals or quinones. It has been demonstrated that horseradish peroxidase (HRP) could be exploited for the removal of aromatic compounds, particularly phenols and anilines from industrial wastewater [11–14]. Subsequently, several other oxidoreductive enzymes, such as tyrosinase and laccase have been successfully tested [12,15]. Considerable progress has been made in elucidating the mechanism of the oxidative coupling reactions [12].

Presently, HRP is the most widely studied enzyme used in the decontamination processes. Since phenols, the target pollutants in the above-discussed decontamination investigations, were known as major odorants in livestock manure slurry [1,16]. Govere et al. [17,18] employed minced horseradish roots, which contains large

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amount of this enzyme, to deodorize swine manure successfully. This study was aimed at evaluating the effectiveness of HRP with peroxides (H_2O_2 and CaO_2) in reducing odor intensity and the concentrations of the odorants from livestock, which include two phenolic compounds (phenol and *p*-cresol), three VFAs (isobutyric acid, isocaproic acid, isovaleric acid), and two indolic compounds (indole and skatole). These target chemicals were chosen because they were found to be positively correlated with malodors from animal manure [19,20].

2. Materials and methods

2.1. Swine manure treatment with HRP and peroxides

HRP was purchased from Sigma Co., while CaO_2 (power, 60%, w/v) and H_2O_2 (30%, w/w) were purchased from Sinopharm Group Chemical Reagent Co. Ltd., Shanghai, China. The HRP was prepared in solution and stored at 4 °C until used. H_2O_2 was diluted when used.

Swine manure slurry samples were collected from a concrete swine manure storage pit at a piggery in Ningbo, China. Before the samples were collected, the swine manure was mixed for half an hour. 2 kg of the wet swine manure samples were distributed in 21 L plastic pails (inner diameter 25 cm, height 22 cm) with cover and sprayed with 15 mL HRP solution. The reaction was initiated with the addition of a specified amount of either H_2O_2 or CaO_2. In the first experiment, HRP solution with different concentrations (0.1–3.0 U/mL) were sprayed on the surface of swine manure, then sprayed with 15 mL H_2O_2 solution (6%) to asses the optimal dosage of HRP. In the second experiment, 15 mL 2.0 U/mL HRP solution were sprayed on the surface of swine manure, then sprayed with 15 mL H_2O_2 solution of different concentrations (0.5–6%) to asses the optimal dosage of H_2O_2. In the third experiment, 15 mL 2.0 U/mL HRP solution were sprayed on the surface of swine manure, then sprayed with CaO_2 power (0.5–3.0 g) to investigate the optimal dosage of CaO_2. In the fourth experiment, in six plastic pails with swine manure, 15 mL 2.0 U/mL HRP solution were sprayed on the surface of swine manure, then sprayed with 15 mL H_2O_2 solution (3%) in three plastic pails, and sprayed with 1.68 g CaO_2 power (60%) in other three plastic pails to compare the effect of different electron acceptor. In the fifth experiment, in three plastic pails with swine manure, 15 mL 2.0 U/mL HRP solution were sprayed on the surface of swine manure, and then sprayed with 15 mL H_2O_2 solution (3%). The swine slurry was incubated for 2, 24, 48, and 72 h after treatment to evaluate duration of deodorization. In the first four experiments, three plastic pails were used as control, only 30 mL distilled water was sprayed on the surface of the swine manure without HRP and H_2O_2 solution or CaO_2 power.

All tests were conducted in a 22 °C temperature-controlled room. If not specified, the treatment time was 2 h.

2.2. Odor intensity measured using olfactometry

Odor intensity was estimated according to the procedure developed by Green et al. [21]. A panel consisted of six trained evaluators who independently recorded their estimates of odor intensity using qualitative scales on a set of computer displays. The scale for odor intensity ranged from strongest odor imaginable to very strong, strong, moderate, weak, and no odor. When recorded, the estimates were electronically assigned with numerical values, ranging from 100 (strong odor imaginable) to 0 (no odor). The samples were presented to panelists in a random order (sniffing order) after 2 h treatment. All panelists evaluated each sample three times (sniffing replication by panelist) during individual sessions.

2.3. Odorant extraction and quantification

Using the modified procedure developed by Ohta and Ikeda [22], and utilized by Govere et al. [17], 10 mL aliquots of the manure sample were withdrawn from the pail and acidified with 2.0 mL of 1 M HCl. The odorants were extracted for 4 h at 4 °C into a 2.5 mL layer of diethyl ether placed on the top of the acidified manure and then quantified by gas chromatography using a chromatograph with a flame ionization detector (FID). The injection and detection temperatures were 220 °C. The column temperature was gradually increased: initial temperature of 35 °C for 1 min; firstly 15 °C per min for 7.73 min and held at 150 °C for 2 min; secondly 25 °C per min for 2.5 min to 210 °C; final temperature of 210 °C for 5 min. The injection volume was 1 μL.

The extracted odorants were identified based on the identity of their retention times with the retention times of seven chemicals that served as malodor indicators. The standards of these seven chemicals (phenol, *p*-cresol, isobutyric acid, isocaproic acid, isovaleric acid, indole and skatole) were purchased from Sigma Co. External standard calibration procedure was employed. First, primary stock standard solution of each odorant was prepared in methanol using pure reagents. Then a composite stock standard solution was prepared by mixing individual primary stock standard solutions and diluting them with diethyl ether. Triplicate calibration standards were prepared at five different concentrations by using the composite stock standard solution.

Calibration curve of each malodor indicator was gained by a linear regression of the detector response (i.e., peak area versus the concentration of the calibration standard). Where no signal was detectable in the ether which was extracted from swine manure samples, then it was assumed the absence of the compound. The retention times (min), R^2 values of calibration curves, percent odorant recoveries, and precision of odorant measurements are shown in Table 1.

3. Results and discussion

3.1. Different concentration of HRP treatment with 6% H_2O_2 solution

The mean concentrations of three replicates for each compound in treated and control swine slurry samples (i.e. 0 U/mL HRP concentration) are presented in Fig. 1. The results showed the concentrations of seven chemicals, and the odor intensity reduced with the increase of concentrations of HRP. But when the concentration of HRP was over 1.5 U/mL, the removal effect was not significant. The HRP and H_2O_2 treatment had no significant effect on the concentration of skatole. When the swine manure treated with 1.0 U/mL HRP and 6% H_2O_2, the removal efficiencies of HRP and H_2O_2 on phenolic compounds, indolic compounds and VFAs were 80, 32, and 28%, respectively, and odor intensity of swine slurry was reduced by 54%. The HRP and H_2O_2 treatment resulted in a complete, 100%, removal of *p*-cresol. The results showed that the HRP with addition of peroxides can significantly reduce the odor from swine manure, and the optimum concentration of HRP is 1.0–2.0 U/mL, namely, the dosage of HRP is about 7.5–15 U/kg of swine slurry. Total nitrogen (TN) content of swine slurry after treatment was comparable with the control, which indicated that the HRP treatment do not decrease the function of manure as fertilizer due to the loss of nitrogen (data was not shown). The results also implied that the offensive odor potential was not only correlated with single kind of chemicals. A large quantity of chemicals was attributed to the malodors of swine manure. Therefore, it is not reasonable to choose one, or two kinds of chemicals as indicators for malodors of swine manure.

Manure odors are a complex mixture of VFA, aromatic compounds, amides and sulfides produced during digestion and

Table 1
Quality assessment parameters for the GC method.

Odorants	Mean retention times (min) ($n = 4$)	Mean R^2 values for calibration curves ($n = 4$)	Mean recovery of odorants (%) from swine slurry extracts ($n = 3$)	Mean precision (%) for odorant measurements in swine slurry extracts ($n = 3$)
Phenol	10.542	0.9966	98.4	101.4
p-Cresol	12.103	0.9959	97.1	99.5
Isobutyric acid	6.287	0.9981	99.6	99.2
Isovaleric acid	7.865	0.9967	101.1	98.7
Isocaproic acid	9.926	0.9991	102.4	97.9
Indole	14.896	0.9980	102.2	102.3
Skatole	17.336	0.9968	98.2	103.8

subsequent manure storage. Research on the major indicators for malodors of swine manure has been carried out for many years. Air and manure concentrations of VFAs, phenolics, indoles, and cresols have been shown to be good indicators of odor emission potential and offensiveness [19,23]. However, in recent years, it has been shown by a few investigations that different VFAs will have different contribution to the odor generation. Although the short chain acids are present in much higher concentration and have higher volatility, the VFAs with higher carbon number have lower odor detection threshold thus are more offensive in nature. The offensive odor potential was not directly associated with the total concentration of VFAs in the manure. It was depending on the types and characteristics of certain acids, which not necessarily existing in high concentrations in the manure. The proportion of individual VFA to total VFA concentration has been deemed extremely significant in relation to odor offensiveness [1]. Thus, of the VFA, acetic and propionic acid concentrations have considered unimportant when investigating odor quality. The VFAs responsible for odor were those with long carbon chains or branchings [24]. Therefore, the three branching VFAs were chosen for odor indicator in this study.

The underlying phenomenon of HRP treatment involved enzymatic oxidation of phenolic compounds, leading to the formation of reactive phenoxyl radicals; the subsequent coupling of the oxidation products was completed without further involvement of peroxidase. Through this so-called oxidative coupling, the contaminants were transformed to less toxic polymers or underwent binding to organic matter in manure, both of which were expected to reduce the toxicity and mobility of the parent compounds.

3.2. Different concentration of H_2O_2 treatment with 2.0 U/mL HRP

Fig. 2 shows the results of the experiment to achieve the optimum dosage of H_2O_2, in which the H_2O_2 concentration ranged from 0.5 to 6%, with the same HRP concentration (2.0 U/mL). The concentrations of isovaleric acid, indole, and *p*-cresol were essentially the

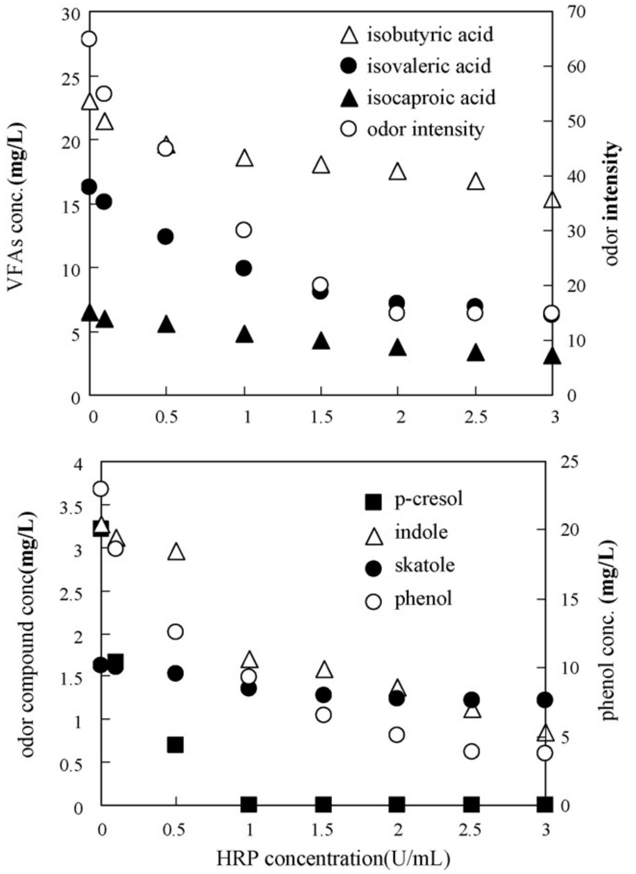

Fig. 1. Concentration (mg/L) of seven chemicals and odor intensity in swine slurry treated with different concentrations of HRP and with same 6% H_2O_2 solution.

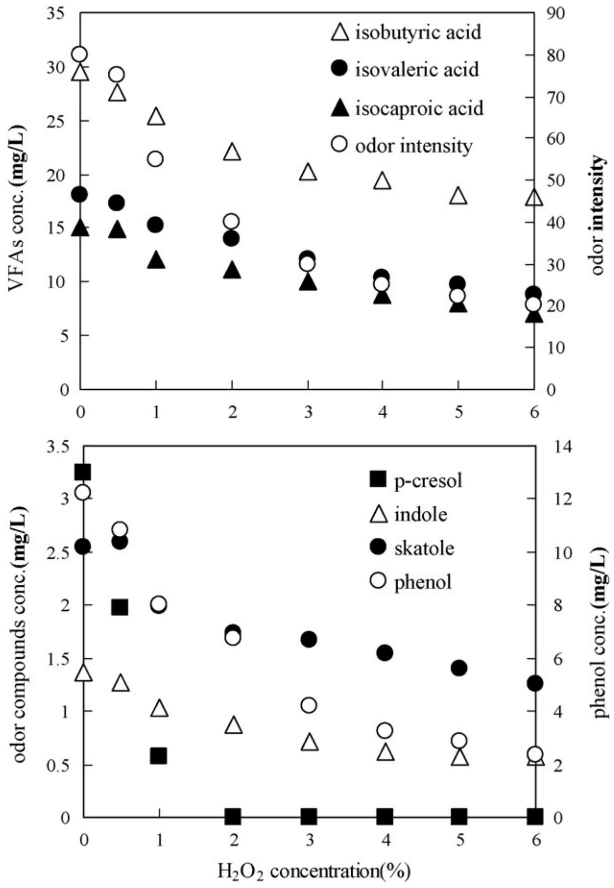

Fig. 2. Concentration (mg/L) of seven chemicals and odor intensity in swine slurry treated with different concentrations of H_2O_2 (0.5–6%) and same dosage of HRP (15 U/kg manure).

same in both experiments, but the concentrations of isobutyric acid, isocaproic acid and skatole were a little higher than that of previous experiment, while the concentration of phenol was a little lower than that of the first experiment. Increasing H_2O_2 concentration from 0.5 to 3% seemed to have a significant effect on the concentration of VFAs, indolic and phenolic compounds, because they were all reduced by 33, 41, and 83%, respectively. The 2% H_2O_2 treatment with HRP together achieved 100% removal of *p*-cresol. But the removal effect of VFAs, indolic and phenolic compounds were not distinct when treated with more than 4% H_2O_2. Odor intensity of swine slurry after treated by 15 mL 2.0 U/mL HRP and 15 mL 3% H_2O_2 was reduced by 63%. Thus, the optimum concentration of H_2O_2 should be 1–3%, namely, the dosage of H_2O_2 was about 75–225 mg/kg of swine slurry. This amount is higher compared to others reports in which K-2BP dye was decolorized by using ligninolytic enzymes promoted by 0.1 mM of H_2O_2 [25]. It maybe attributed to three factors: (1) the catalytic mechanisms of lignin peroxidase and HRP, and catalytic target pollutants were different in spite of H_2O_2 used in two studies; (2) decolorization of K-2BP dye, not degradation was investigated in their study. It is reasonable that much more enzyme and H_2O_2 were needed to degrade dye completely into CO_2, other than decolorization; (3) a lot of components, including organic matter, in the swine manure, instead of K-2BP dye could react with HRP and H_2O_2. In addition, hydrogen peroxide is so easy to decompose, it is impossible to measure the residual H_2O_2 concentration. However, a finer H_2O_2 feeding strategy to reduce cost, thus making HRP treatment more economically attractive to livestock producers should be developed in future investigation.

3.3. Different dosage of CaO_2 treatment with 2.0 U/mL HRP

Fig. 3 shows the results of an experiment to achieve the optimum dosage of CaO_2, in which the CaO_2 dosage ranging from 0.1 to 3 g, with the same HRP concentration (2.0 U/mL). The initial concentrations of the odorants in untreated samples were comparative to the previous two experiments, except for the concentration of isocaproic acid. It seemed that increase of CaO_2 dosage from 1.0 to 2.0 g does have a significant effect on the concentration of VFAs, indolic and phenolic compounds and odor intensity, resulting in reduction of 41, 54, 91 and 71%, respectively. Compared with the results from treatment with H_2O_2, the removal efficiencies of VFAs, indolic and phenolic compounds and odor intensity by CaO_2 were obviously higher. But the removal effect of VFAs, indolic and phenolic compounds were not notable when treated with more than 2.5 g CaO_2. Odor intensity of swine slurry after treated by 15 mL 2.0 U/mL HRP and 1.0 g CaO_2 was reduced by 84%. Consequently, the suggested concentration of CaO_2 should be 1.0–2.0 g, namely, the dosage of CaO_2 was about 0.375–0.75 g/kg of swine slurry. Better performance of CaO_2 than H_2O_2 maybe due to the slow release of H_2O_2 from CaO_2 powder to the aqueous phase of the swine manure. Flanders et al. [26] who investigated horseradish-mediated binding of ^{14}C-labeled 2,4-dichlorophenol to soil found that horseradish-mediated binding/immobilization was enhanced by a factor of two when CaO_2 was used instead of H_2O_2. H_2O_2 is known to decompose quickly once in contact with dissolved or particulate organic matter.

3.4. Different electron acceptor treatment (CaO_2 and H_2O_2) with 2.0 U/mL HRP

Fig. 4 shows the results of the experiment in which the CaO_2 and H_2O_2 dosage were 2.0 g and 15 mL (3%) respectively, with the same HRP concentration (2.0 U/mL) to compare the effect of CaO_2 and H_2O_2, the two different electron acceptor on the removal of odorants. The concentrations of VFAs, indolic and phenolic com-

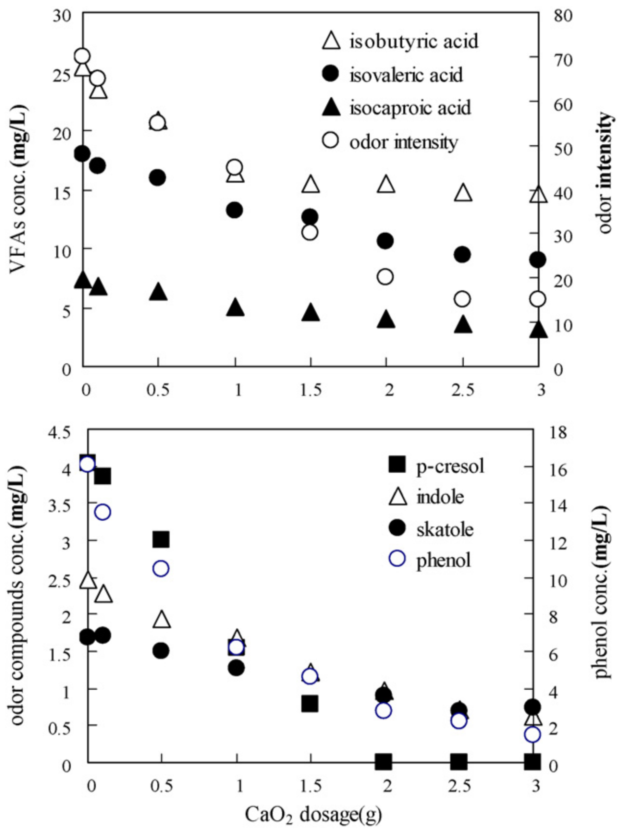

Fig. 3. Concentration (mg/L) of seven chemicals and odor intensity in swine slurry treated with different concentrations of CaO_2 (0.1–3 g) and same dosage of HRP (15 U/kg manure).

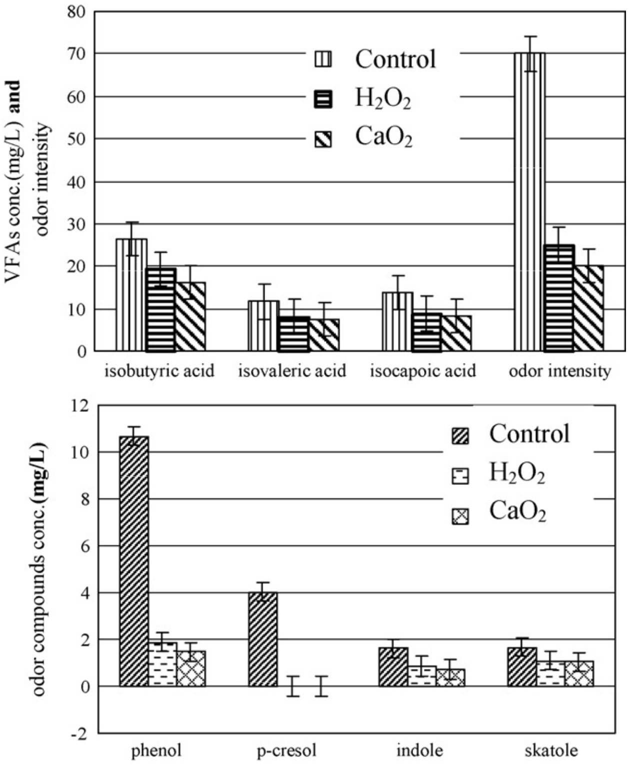

Fig. 4. Concentration (mg/L) of seven chemicals and odor intensity in swine slurry treated with different electron acceptor (0.75 g CaO_2/kg manure; 225 mg H_2O_2/kg manure) and same dosage of HRP (15 U/kg manure).

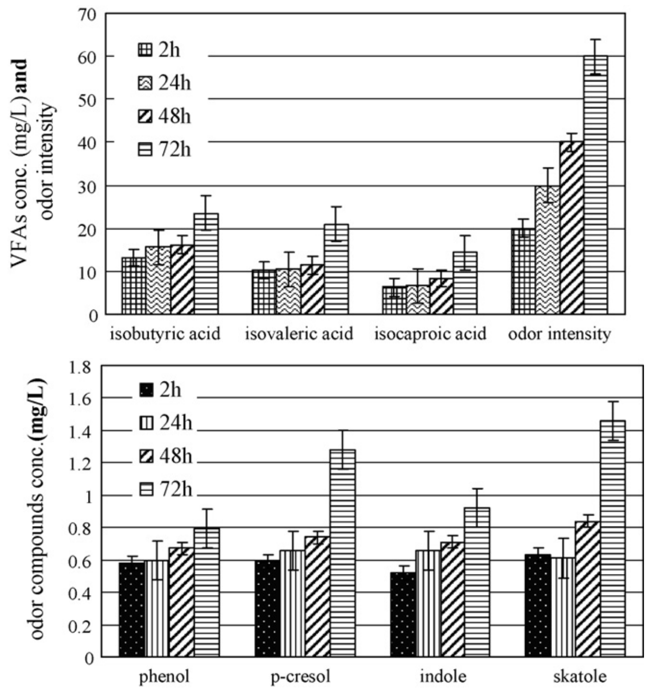

Fig. 5. Concentration (mg/L) of seven chemicals and odor intensity in swine slurry after 2, 24, 48 and 72 h treatment with HRP (15 U/kg manure) and H_2O_2 (225 mg/kg manure).

pounds were reduced by 31, 40, 91%, respectively when sprayed with 15 mL 3% H_2O_2, but the concentrations of VFAs, indolic and phenolic compounds were reduced by 38, 46, 93%, respectively when added with 2.0 g CaO_2. Odor intensities were reduced by 64 and 71% with H_2O_2 and CaO_2 treatment, respectively. It appears that at equal content of O_2^{2-}, CaO_2 is more effective than H_2O_2 in reducing the concentration of malodor indicators in swine slurry.

3.5. *Effects of lasting time after HRP treatment on deodorization*

Odors are primarily the products of anaerobic decomposition of manure. One of the more frequent sources of odor complaints is the land application of manure. Another major odor emission source is the manure storage and animal facilities. The regulations recommend that the manure should be treated and disposed as soon as possible, but a post-treatment storage of swine manure maybe a necessity in the highly centralized and congested livestock facilities. Therefore, it was essential to investigate how long time the deodorization effect will last during the storage of manure after treated with HRP and peroxides. This experiment investigated the effect of lasting time on the concentration of odorants and odor intensity after the swine slurry samples were incubated with HRP and H_2O_2 for 2, 24, 48, and 72 h at 22 °C and then analyzed for odorants and odor intensity. Fig. 5 shows that odorants concentration and odor intensity are not significantly different after 2 and 24 h retention periods, increase a little after 48 h, but after 72 h approach these of untreated sample. The results suggested that the deodorization effect by HRP treatment with peroxides could give farm operators 2 days to dispose the treated manure.

The above results showed that HRP treatment is most effective in reducing the concentration of phenolic compounds, especially *p*-cresol with almost 100% removal. It is not surprising that the concentration of VFAs and indolic odorants was not reduced as greatly as that of phenolic odorants. In general, phenolic compounds are preferred substrates over indolic compounds in terms of oxidation rate. It implied that a significant decrease in the concentration of phenolic compounds was directly related to the decrease of odor intensity. Phenolic compounds were found to be correlated with odor intensity in dairy manure [16] or as possible indicators of microbial community changes in swine manure storage systems [27].

In this study, TN did not change markedly in all experiments (data not shown), which implied that the volatile ammonia nitrogen only account for a small percentage and most of the nitrogen may exist in the forms of nitrites, nitrates, or other compounds which are not available for volatilization. On the other hand, it implied that HRP treatment did not effect the ammonia emission of swine manure. However, since the content of ammonia nitrogen did not measured in the test, the potential of control of ammonia emission from swine manure by HRP and peroxides could not be quantitatively determined.

Use of HRP and peroxides to deodorize odor from swine manure may be considered as an environmentally friendly technology because it did not produce any new pollutant. H_2O_2 will provide dissolved oxygen to aerobic bacteria in manure so that these microorganisms can actively decompose the odorous compounds, then resulting in odor reduction. The value of aeration in reducing offensive odors has been demonstrated by a number of reports [6,20]. CaO_2 will provide a nutrient source (Ca^{2+}) for plant production and increase pH of manure. Raising manure pH by CaO_2 addition can attenuate the growth of the odor-causing bacteria, thus reducing odor emission [20]. Moreover, the liming effect of CaO_2 may promote microbial diversity and proliferation in soil, and may also restrict eutrophication of aquatic systems by reducing the concentration of available phosphorus. One study showed that increasing pH of swine slurry from 6.6 to 9.0 resulted in reduction of soluble P concentration up to 91% [28].

4. Conclusions

The results obtained from this study showed that the emission of odor and volatile substances in swine manure slurry can be abated by using small amounts of HRP and peroxides (H_2O_2 or CaO_2). The reduction in odor intensity may not be directly related to the total concentration of VFAs, but may be relevant to the reduction in concentration of phenolic compounds to a certain extent. All treatments reduced odor intensity by 54–84%, and phenolic compounds about 100%. But abatement of indolic and VFAs compounds in swine manure slurry was not significant for any of the treatments in this study. As the electron acceptor of HRP, CaO_2 had a better performance than H_2O_2 in reducing concentration of seven chemicals and odor intensity. The deodorization effect could last for up to 48 h, which may give farmer a more flexible time to dispose treated manure. In addition to deodorization effect, H_2O_2 shows potential to increase concentration of dissolved oxygen, and CaO_2 may supply calcium for soil and exhibit liming effect.

Due to the important role of bacteria in swine manure odor production, studies are underway to investigate the effect of microorganism and other parameters using modern molecular technology. More research is required to find ways to increase the removal of indolic odorants and VFAs from swine slurry.

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