

**ELIMINATION OF H_2S FROM CHICKEN MANURE BY REACTION
WITH H_2O_2 & TITRATING WITH KMnO_4**

MUHAMAD AZHAR BIN AZMAN

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS♦

JUDUL : **ELIMINATION OF H₂S FROM CHICKEN MANURE BY
REACTION WITH H₂O₂ & TITRATING WITH KMnO₄**

SESI PENGAJIAN : 2010/2011

Saya

MUHAMAD AZHAR BIN AZMAN

mengaku membenarkan tesis Projek Sarjana Muda (PSM) ini disimpan di Perpustakaan Universiti Malaysia Pahang dengan syarat-syarat kegunaan seperti berikut:

1. Hakmilik kertas projek adalah di bawah nama penulis melainkan penulisan sebagai projek bersama dan dibiayai oleh UMP, hakmiliknya adalah kepunyaan UMP.
2. Naskah salinan di dalam bentuk kertas atau mikro hanya boleh dibuat dengan kebenaran bertulis daripada penulis.
3. Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian mereka.
4. Kertas projek hanya boleh diterbitkan dengan kebenaran penulis. Bayaran royalti adalah mengikut kadar yang dipersetujui kelak.
5. *Saya membenarkan/tidak membenarkan Perpustakaan membuat salinan kertas projek ini sebagai bahan pertukaran di antara institusi pengajian tinggi.
6. **Sila tandakan (✓)

☐

SULIT

(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)

☐

TERHAD

(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan).

☒

TIDAK
TERHAD

Disahkan oleh:

(TANDATANGAN PENULIS)

(TANDATANGAN PENYELIA)

Alamat
Tetap

54-A Jln Dato Musa

Kg. Pasir 81200 Tampoi

Johor bahru

Nama Penyelia:

Prof Ir Dr. Jailani Salihon

Tarikh

13.DISEMBER.2010

Tarikh

22.DISEMBER.2010

CATATAN : * Potong yang tidak berkenaan.

** Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT atau TERHAD.

♦ Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertai bagi pengajian secara kerja kursus dan penyelidikan atau Laporan Projek Sarjana Muda (PSM).

“I hereby declare that I have read this thesis and in my opinion this thesis has fulfilled the requirement for the award of the Degree of Bachelor of Engineering (Chemical)”

Signature : _____

Name of Supervisor : PROFESOR IR. DR. JAILANI
SALIHON

Date : 22.DECEMBER.2010

**ELIMINATION OF H_2S FROM CHICKEN MANURE BY REACTION
WITH H_2O_2 & TITRATING WITH KMnO_4**

MUHAMAD AZHAR BIN AZMAN

**A thesis submitted in fulfillment for the award of the degree of Bachelor of
Chemical Engineering (Biotechnology)**

**Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang**

DECEMBER 2010

I declare that this thesis entitled '*Elimination of H_2S from Chicken Manure by Reaction with H_2O_2 & Titrating with $KMnO_4$* ' is the result of my own research except as cited in references. The thesis has not been accepted for any degree and it is not concurrently submitted in candidature of any degree.

Signature :

Name : MUHAMAD AZHAR BIN AZMAN

Date : 12.DECEMBER.2010

*Specially dedicated to my beloved family, lecturers and to all my friends who are
always in my prayers.....*

ACKNOWLEDGEMENT

First of all, praise to The Almighty for its guidance, I can complete my undergraduate research project even through there are some problems that have occurred

I also like to express special thanks to my beloved family for their strong support and infinite blessing for me to finish my Bachelor Degree

Not forget my supervisor Prof Ir Dr Jailani Salihon for his support and sincere guidance. Also to my academic advisor Dr. Norazwina Zainol who always was taking care of my education. Once again thank you so much to both of you.

Lastly thank you so much to all my lecturers and my fellow friends for their support and knowledge given to me.

THANK YOU SO MUCH...

ABSTRACT

The process of odor removal from the chicken manure (H_2S) can be done in several ways. One of them is the chemical reaction of chicken manure with H_2O_2 and titration with KMnO_4 . This research was done according to an improvised method with cautious handling of H_2O_2 and chicken manure. The research by using human smell detection used a scale of between 0 until 10 based on the odor strength; the value 0 for no odor and 10 for strangest chicken manure odor. For a volume of 1000mL chicken manure sample comprising 1 kg of improved sample with the addition of 500mL of 11ppm H_2O_2 , it was found that there was no more odor of chicken manure and takes 3 hours for reaction between chicken manure and H_2O_2 to get 0 odor of chicken manure. Stiochiometric calculation showed that when zero odors were reached in the first experiment 0.0001618 mol H_2O_2 would have reacted with 0.0001618 mol H_2S . Actually by using the human smell detection the results at zero odors may not unrespond with complete removal with H_2S because of the limits of sensitivity of the human nose. That means there may still exists some balance of H_2S in chicken manure after reaction with H_2O_2 by using human detection to zero odors. So, the solution for this problem was using titration with KMnO_4 for the balance of H_2S in chicken manure to get to true zero odors or complete removal of H_2S . The detector of H_2S for this titration was the changing color of KMnO_4 from dark purple to light pink. That means not changing color of KMnO_4 indicates that the odor (H_2S) was fully removed. The result obtained from the second experiment is 0.000451 mol KMnO_4 react with 0.0003383 mol H_2S . In calculations one tone of chicken manure contains 17.05g of H_2S . In this research the pH value of the sample was maintained at near neutral condition of pH 7.28.

ABSTRAK

Proses penghilangan bau tahi ayam (H_2S) dapat dilakukan dengan pelbagai cara. Salah satunya ialah dengan tindak balas tahi ayam dengan H_2O_2 . Kajian ini dikendalikan mengikut prosedur yang diperbaharui serta berwaspada dengan penggunaan H_2O_2 dan tahi ayam. Keputusan untuk kajian ini dikesan dengan menggunakan deria bau manusia yang berdasarkan kadar bau iaitu diantara 0 sehingga 10.0 tiada bau dan 10 paling tinggi bau tahi ayam. Dan keputusan untuk mendapat 0 bau tahi ayam ialah pada kadar kandungan 500mL (100ppm H_2O_2) dan proses ini memerlukan 3 jam untuk bertindak balas tahi ayam dengan H_2O_2 bagi mendapatkan keputusan 0 bau tahi ayam. Kajian ini dijalankan dengan mengekalkan nilai pH pada keadaan neutral iaitu pada pH 6 sehingga pH 7. Proses penghilangan bau tahi ayam dapat dipercepatkan dalam lingkungan 1 jam dengan menggunakan H_3PO_4 sebagai mangkin dan ini juga dapat mengurangkan penggunaan H_2O_2 dalam kajian tersebut. Tetapi apabila menggunakan H_3PO_4 sebagai mangkin, ia akan menyebabkan proses pencernaan anaerobic tidak akan berlaku kerana pH sampel akan berada di bawah pH 6 iaitu asid dan ini juga akan menyebabkan bekteria di dalam tahi ayam akan mati. Kajian kedua ialah untuk mengetahui berapa banyak kandungan gas CH_4 yang terdapat didalam sampel yang telah ditindak balaskan bersama 500mL (100ppm H_2O_2) dan dikesan dengan menggunakan Micro GC. Tetapi kajian ini dijalankan pada kadar 100g tahi ayam 100mL (100ppm H_2O_2). Dan keputusan yang dikeluarkan oleh Micro GC telah didapati dengan hanya 0.05% gas CH_4 . Ini menunjukkan hanya sedikit kandungan gas CH_4 di dalam sampel kerana sampel yang digunakan hanyalah sedikit, ini bermakna, sampel tahi ayam diperlukan dengan banyak untuk menghasilkan kandungan gas CH_4 yang banyak. Proses ini dapat dikomersialkan dan dijual kepada penternak ayam serta menyahut cabaran kerajaan Malaysia iaitu 'Zero waste'. Dan proses dapat diperbaiki dengan menggunakan alat pengesan bau berbanding deria bau manusia kerana batasan terhadap deria bau manusia.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	ACKNOWLEDGEMENT	i
	ABSTRACT	ii
	ABSTRAK	iii
	TABLE OF CONTENTS	iv
	LIST OF FIGURES	vi
	LIST OF TABLES	vii
	LIST OF ABBREVIATIONS	viii
	LIST OF APPENDIX	ix
1	INTRODUCTION	1
	1.1 Introduction	1
	1.2 Research Background	3
	1.2 Problem Statements	5
	1.3 Research Objectives	7
	1.4 Research Scopes of Study	7
2	LITERATURE REVIEW	8
	2.1 Introduction of Chicken Manure	8
	2.2 How Can H ₂ O ₂ Can Remove H ₂ S & SO ₂ from Waste	10
	2.3 Hydrogen Peroxide	11
	2.3.1 Physical Properties of H ₂ O ₂ Aqueous Solution	11
	2.3.2 Industrial Application Uses	12
	2.3.3 H ₂ O ₂ Safety	13
	2.4 Potassium Permanganate	14
	2.4.1 Disadvantages of KMnO ₄	14
	2.5 Gas Methane	15
	2.6 Additional Information	18
	2.6.1 Alkaline Mineralization of Organic Waste	18
	2.6.2 Alkaline Materials	19
	2.6.3 Solubility of Phosphorus	19
	2.7 Basic Anaerobic Digestion	21
	2.7.1 Process Description of Waste to Energy (WTE) Facility Based on Livestock Manure	22
	2.7.2 Fermentation	24
	2.7.3 Acidity	24

	2.7.4	Carbon Nitrogen Ratio	25
	2.7.5	Temperature	25
	2.7.6	Percentage of Solids	25
	2.7.7	The Advantages of This Process	26
	2.7.8	The Disadvantages of This Process	26
3		METHODOLOGY	27
	3.1	Material Selection	27
	3.1.1	H ₂ O ₂ is Very Economical to Use	27
	3.1.2	Usage of KMnO ₄	28
	3.2	Research Apparatus	28
	3.2.1	Remove Odor from Chicken Manure	28
	3.3	Research Conditions	30
	3.4	Research Parameters	30
	3.5	Research Stages	31
	3.6	Research Summary Stages	32
4		RESULT AND DISCUSSION	33
	4.1	Results & Discussions for H ₂ O ₂ to Eliminate H ₂ S from the Chicken Manure	33
	4.1.1	Calculation for H ₂ O ₂ to Eliminate H ₂ S (odorless) from the Chicken Manure	
	4.2	Results & Discussions for Titration of KMnO ₄ to remove The Balance of H ₂ S (Odorless) From the First Experiment Sample.	36
	4.2.1	Calculation for the Titration of KMnO ₄ to remove The Balance of H ₂ S (Odorless) From the First Experiment Sample	
5		CONCLUSION AND RECOMMENDATION	40
	5.1	Conclusion	40
	5.2	Recommendation	41
6		REFERENCES	42
7		APPENDIX	44

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Anaerobic decomposition of animal waste	3
2.6.1	pH Versus Percentage of Total Solid in Indicated Form	18
2.6 3:	Solubility of phosphorus from mineralized chicken manure	20
2.7.1	Process of waste to energy based on the livestock manure	23
4.2.1(A)	Graph for the first reading	37
4.2.1 (B)	Graph for the second reading	37
4.2.1 (C)	Graph for the third reading	38

LIST OF TABLES

TABLE NO.	TITLE	PAGE
1.1	Compounds found in animal manure	2
2.4.1	pH and composition of a phosphoric acid aqueous solution	14
4.1(A)	Result for experiment based data on the journal	33
4.1(B)	Result for the constant value of H_3PO_4	34
4.1(C)	Result for the constant value of H_2O_2	35
4.2.1	Standard for the Micro GC	36
4.2.1(A)	Result for the figure 4.2.1 (A)	37
4.2.1(B)	Result for the figure 4.2.1(B)	38
4.2.1(C)	Result for the figure 4.2.1(C)	38

LIST OF ABBREVIATIONS

CH ₄	-	Gas Methane
CO ₂	-	Gas Carbon Dioxide
H ₂ S	-	Hydrogen Sulphide
NH ₃	-	Ammonia
H ₂ O ₂	-	Hydrogen Peroxide
H ₃ PO ₄	-	Phosphoric acid
CH ₃ NH ₂	-	Methylamine
CH ₃ OH	-	Methanol
Micro GC	-	Micro gas chromatography
V/w	-	Volume over weight
T	-	Temperature
W	-	Weight
%	-	Percent

LIST OF APPENDIX

TITLE	PAGE
Standard of Micro GC	45
Result Micro GC (1)	48
Result Micro GC (2)	50
Result Micro GC (3)	52
Hydrogen Peroxide dilution Chart	54
Hydrogen Peroxide Safety & Handling	56
Determination Hydrogen Peroxide Concentration	61

CHAPTER 1

INTRODUCTION

1.1 Introduction

Many years, livestock operations such as animal feedlots and poultry have operated with little concern from the public. These operations were very small in nature and rural populations were quite accustomed to the low levels of the odor emitted from these operations. Currently, these operations are getting larger in size and hence producing large amounts of wastes which are causing air, water and soil pollution.

In addition, non agricultural populations have their first or second residence in farming areas and are largely responsible for the air pollution complains. Animal manure contains various complex organic and inorganic compounds as shown in Table 1.1. When handling animal manure, extremely noxious odors arise. The odorous compounds originate during the anaerobic decomposition of animal waste. Anaerobic decomposition of animal waste is a complex biochemical process (Fig. 1.1) that involves a consortium of microorganisms including several groups of acid producing and methane forming bacteria. The acid formers are the primary producer of organic acid, while the methane formers use the acids to produce methane and carbon dioxide.

The decomposition process of organic matter involves the breakdown of protein, carbohydrates and fats into a number of end products. In general, the decomposition process results in the formation of several compounds including alcohols, esters, carbonyls, sulfides, mercaptans, amines, amino acids, organic acids and different gases. The organic acids may include formic, acetic, propionic and bacteria. Amino acids may also change to amines by decarboxylation. The breakdown of protein may result in sulfur related amino acids which may produce various sulfides and mercaptans.

The breakdown of fats is an energy releasing process that results in the formation of alcohols and fatty acids which may be broken down to acetic acid. The breakdown of carbohydrates leads to the production of alcohols, Aldehydes, ketons and organic acids. Among the compounds of anaerobic decomposition, hydrogen sulfide (H_2S), ammonia (NH_3) and methylamine (CH_3NH_2) are largely responsible for the animal manure odors.

Amines, alcohols, carbohydrates, sulfides, disulfide and mercaptans as volatiles from animal waste and found amine and sulfides to be the most important in terms of the amount of malodorous materials. The formation of organic acids (including butyric, valeric, isobutyric and isovaleric) in liquid chicken manure when the pH was below 8.

Table 1.1: Compounds found in animal manure

Protein	B-lactoglobuline, σ -lactoalbumin, Immunoglobuline, Protosses, Peptones, Poly peptides, Peptides, Enzymes, Amino acids, Arginine, Cysteine, Histidine, Isoleucine, Leucine, Lysine, Methionine, Phenylalanine, Threonine, Tryptophan, Tyrosine & Valine
Non-Protein-N	Ammonia, Urea, Creatinine, Creatine, Uric Acid & Amine Phosphoethanolamine, β - Phosphoglyceroethanolamine, Phynyleacetylglutamine, Hippuric acid, Ortic acid & Indican
Fats	Triglycerides, Diglycerides, Monoglycerides, Ketoacid glycerides,

	Ketonogenic glycerides, Lactonogenic glycerides, Nevtrm plasmatorens, Phospholipids, Sphinolipids, Sterols, Squalene, Caretonides, Vitemins (A, D, E, K), Fatty acids, Butric, Caproic, Coprylic, Capric, Lauric, Myristic, Myristoleic, Pentadelanol, Pelmitic, Palmitoleic, Marganl, Stearic, Oleic, Linoteic & Linoleni
Carbohydrates	Cellulose, Hemicellulose, Lignin & Sugars
Minerals	Ca, P, S, Zn, Fe, Cu, K, Na, Cl, Mg, F, I, Mo, Mn & Co
Others	Waxes, Hydrocarbons, Oils & Plastics

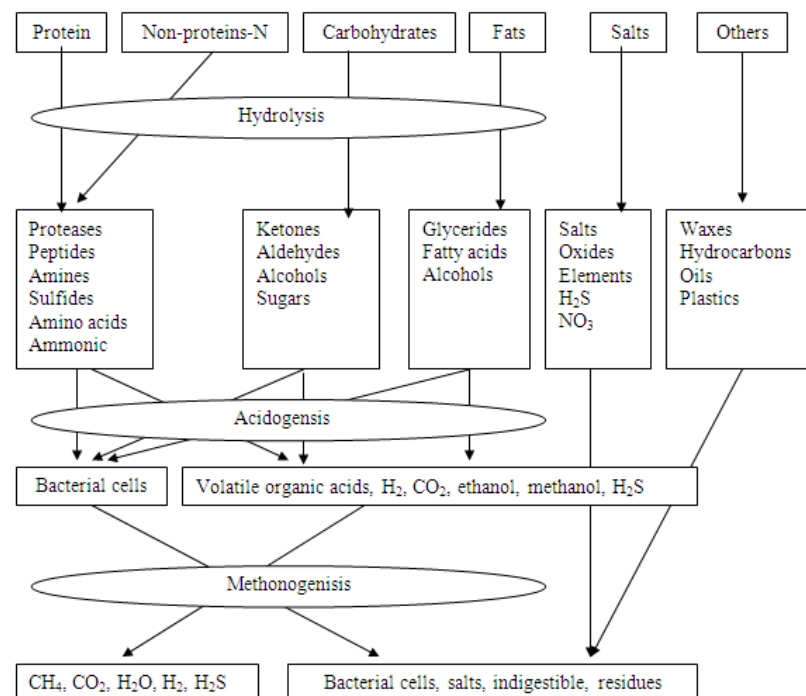


Figure 1.1: Anaerobic decomposition of animal waste

1.2 Background of Study

In this era of globalization in our country. There are some poultry farmers, that story of manure outside for long periods of time is a problem. Every second of the day and night, animals are producing waste products inside their bodies. If those waste products are not removed from the body, the animal may become ill or die. One of the most dangerous of all such waste products is the chemical resulting from the normal breakdown of amino acids (which make up protein) and nucleic acids (of which our genetic material is composed). The main waste product formed during this decomposition is ammonia, NH_3 , which is toxic (poisonous)

In mammals such as us humans, our waste ammonia is combined with carbon dioxide, CO_2 , and converted into urea, $\text{CO}(\text{NH}_3)_2$, which is less toxic than ammonia and which dissolves very easily in water. Our bodies dissolve their urea in water, making urine. In other words, when we go pee, basically what we're doing is getting rid of our urea. If we didn't, that urea would build up in our systems and poison us.

Unfortunately, urinating is fairly wasteful of water. Reptiles and birds have developed a different, less water wasting process for dealing with their bodies' ammonia. Instead of converting their ammonia to urea, they mostly convert it to uric acid, $\text{C}_5\text{H}_4\text{N}_3\text{O}_3$, which is excreted as a white paste or even a dry, white powder.

It seems that birds and reptiles have developed an ammonia-disposal system that in many ways is better than our mammalian system. If our bodies could convert our ammonia to pasty uric acid instead of urea, we wouldn't have to drink nearly as much water, nor would we have to go pee nearly as often.

But chicken manure is the best as far as sheer nutrients go. It's rich in nitrogen; an application of chicken manure will grow some of the best corn you can imagine. However, chicken manure is what's known as 'hot' manure; it will burn plants, and cannot be applied directly to the soil. In order to use it, let it compost for at least three months (six months to a year is better) in an out-of-the-way corner of the garden, then apply it sparingly to your unplanted beds and wait at least two

weeks and one good rain before planting in it. Or, mix it with dry matter, such as leaf mold or sawdust, to cut down on the heat. (Unfortunately, this also dilutes the nutrients. But chicken manure diluted this way makes an excellent organic fertilizer because it can be applied directly to the beds, left two weeks and one good rain, and then planted.

Nowadays in Malaysia wastes generated from the chicken farm are keeping increasing as a result of rapid growth of chicken farm industry. Thus, the application of chicken farm wastes as sources of nutrients for the agricultural production has become an important area of research. Usually, chicken farm wastes such as chicken manures were used directly as an organic fertilizer for crops farming. Direct application of chicken manure into agricultural soil may cause environmental problems such as the foul odor generated, and it may become the breeding ground of pests such as flies. The biological transformation of chicken manure via composting technique has its disadvantage because the process may take several weeks to complete. Chicken manure contains rich plant nutrients that are vital for their growth including nitrogen, phosphorus, and potassium.

In addition to supply of nutrients, the application of chicken farm waste also improves the chemical, physical and biological properties of soil. Therefore, transformation of chicken manure into environmental friendly and easy to handle organic fertilizer is necessary. In this work, chicken manure is transformed into organic fertilizer via chemical mineralization. The mineralization technique was chosen due to its ability to produce mineralized product at very short period.

1.3 Problem Statement

Over 19.5 million tons of chicken and turkey manure produced each year by the industry is no simple task, but a government poultry nutritionist is looking at ways to more carefully balance chicken diets and reduce waste.

The options for manure use are many, but the more practical ones are fuel, feed and fertilizer. Chicken manure can be burned, producing one third the fuel value of coal, or converted to methane in biomass converts. Chicken manure can also be used to feed ruminant animals, such as cattle, that can extract unused nutrients. However, the most common use for chicken manure today is as a fertilizer for agricultural fields.

Excess nutrients in fertilizer are a source of non point source pollution targeted by environmental initiatives like the Chesapeake Bay Pollution Program. The two components of chicken manure that cause the most concern for runoff are nitrogen and phosphorous, but both elements are necessary for good bird health, egg laying and weight gain.

Farmers can control the nitrogen content of manure by using better feed formulation, lower protein diets, and feed additives. In many cases, these approaches save money as well as control the nitrogen output of the birds. Modern breeds of laying and meat birds are more efficient than older varieties. By looking at available rather than total protein, farmers can lower the protein content of feeds and reduce the amounts of nitrogen in manure. Synthetic amino acids are also cost effective and reduce nitrogen waste.

Controlling excess phosphorus centers around supplying phosphorus in a form the birds can use. Feeds such as corn and sorghum contain only 19 to 22 percent bio-available phosphorus with the rest in a chemical form difficult for the birds to digest. The phosphorus in meat or fish meal is 81 to 100 percent bio-available so birds require less phosphorus in their feed thereby reducing the amount of phosphorus in the manure.

Reducing the nitrogen and phosphorus in feeds, in many cases, decreases the cost of the feed. Lowering the nitrogen and phosphorus levels in the manure can also reduce disposal costs for the enormous amounts of chicken manure produced by the poultry industry each year.

1.4. **Research Objectives**

The objectives of this research are to determine how much of the parameters H_2O_2 and KMnO_4 quantity to remove the H_2S (odorless) of the chicken manure and how much H_2S was fully removed from the one tone of the chicken manure when process will be done.

1.5 **Research Scope of Study**

Regarding this particular research, there are several scopes that need to be fulfilling to ensure that research will achieve the objective that had been set.

First scope of this research is to study about how the hydrogen sulfide can remove from the chicken manure when react with hydrogen peroxide and potassium permanganate. Secondly is to analyze how much the hydrogen peroxide and potassium permanganate react with the hydrogen sulfide when hydrogen sulfide is fully removed from the chicken manure. And the last one is to study how the safety precautions are required when doing that research by using hydrogen peroxide and potassium permanganate react with hydrogen sulfide.

This research will focus at the second scope of that experiment. The second scope has the parameters to define. These parameters is more important thing when want to do the experiment of the research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Chicken Manure

The chicken manure contained aerobic heterotrophs, total fungi and crude oil degrading bacteria. The crude oil degraders were identified as species of *Micrococcus*, *Bacillus*, *Pseudomonas*, *Enterobacter*, *Proteus*, *Klebsiella*, *Aspergillus*, *Rhizopus*, and *Penicillium*. *Pseudomonas aeruginosa* CDB-06 and species of *Bacillus* CDB-08 and *Penicillium* CDF-10 degraded the crude oil at exceedingly high rates. *Pseudomonas aeruginosa* CDB-06 degraded 65.5 percent of the crude oil after 16 days, while *Bacillus* sp. CDB-08 and *Penicillium* sp. CDF-10 degraded 65.3 percent, and 53.3 percent, respectively of the crude oil over the same period.

The chicken manure also had a pH 7.3, 18.5 percent moisture content, 2.3 percent total nitrogen, and 0.5 percent available phosphorus. Addition of oil polluted soil 10 percent (v/w) pollution level with chicken manure enhanced degradation of the crude oil in the soil. 68.2 percent of the crude oil was degraded in the soil amended with chicken manure, whereas only 50.7 percent of the crude oil was degraded in the un-amended soil after 16 days. The amendment raised the acidic reaction (pH 5.7) of the oil-polluted soil to alkaline (pH 7.2) within 16 days. Chicken manure could, therefore be used in an integrated oil pollution abatement program.

For other way chicken manure is cyclic use of chicken manure incinerated ash as a phosphorus source for feed to chicken? The possibility of utilizing the phosphorus contained in chicken manure incinerated ash as a phosphorus source for

feed to chicken and pig by circulation. It was proven that even if chicken manure incinerated ash was mixed with the feed for broilers and laying hens, the growth performance of broilers and the layer performance of laying hens were not lowered, which showed the possibility of recycling use as a phosphorus source in the feed for chickens.

The effective utilization of chicken manure, although incineration processing using combustion heat has advanced, combustion ash has not been effectively utilized. The fertilizer effects using spinach and tomato as subjects. Chicken manure combustion ash has strong alkalinity such as pH between 11.5 and 13.5 also contains high content of potassium, phosphate and calcium as well as trace elements of iron, manganese, boron and silicate. It is necessary to use the ash by combining with nitrogen fertilizer. Since it does not contain nitrogen component. In a cultivation test, good results were obtained by jointly using CDU, ammonium sulfate, or LP30 as a nitrogen source. The effectiveness of chicken manure combustion ash especially as a PK fertilizer has been done.

Fresh chicken manure may contain disease organisms that could contaminate root crops (carrots, radishes, beets) and leaves (lettuce, spinach), so DO NOT spread un-composted manure on the soil in your vegetable garden. The following “Safety Tips” are summarized.

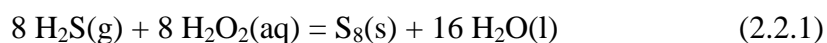
- Apply only aged or composted manure to your soil.
- Always wear gloves when handling livestock manure.
- Thoroughly wash raw vegetables before eating.
- Do not use cat or dog manure in compost piles.
- People who are susceptible to food borne illnesses should avoid eating uncooked vegetables from manure gardens. Those who face risks from food borne illness include pregnant women, very young children, and persons with cancer, kidney failure, liver disease, diabetes or AIDS.

2.2 How Can Hydrogen Peroxide Remove Hydrogen Sulfide & Sulfur Dioxide From Wastes?

Would hydrogen sulfide and sulfur dioxide both be oxidized by hydrogen peroxide? (If the gases were bubbled through a solution of hydrogen peroxide). Would the result be an acidic solution because of sulfuric acid formation?

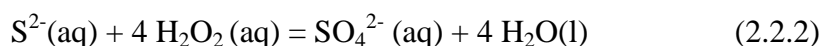
Hydrogen sulfide and sulfur dioxide are waste products of several manufacturing processes, and reaction with peroxide is one fairly cost-effective method of removing them from industrial wastes.

The sulfur in hydrogen sulfide (H_2S) is in the -2 state. In a neutral solution, hydrogen peroxide will oxidize hydrogen sulfide to elemental sulfur via the following reaction:



No acid is produced. The reaction takes a while, so if you're bubbling the hydrogen sulfide through the peroxide solution, you need to recycle the gas stream through the peroxide solution. Metal ions catalyze the reaction.

In alkaline solution, you get a completely different reaction. The hydrogen sulfide is present as sulfide ion, and you'll get sulfate after oxidation:

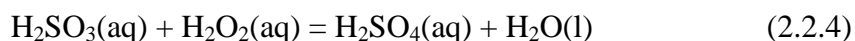


The reaction is exothermic and much more rapid than the neutral pH reaction above, but again, no acid is produced.

Acid is produced when SO₂ is bubbled through a hydrogen peroxide solution, though. First the SO₂ dissolves and reacts with water to form sulfurous acid:



The sulfurous acid is then oxidized to sulfuric acid by the peroxide:



2.3 Hydrogen Peroxide (H₂O₂)

Hydrogen peroxide (H₂O₂) is a very pale blue liquid, slightly more viscous than water that appears colorless in dilute solution. It has strong oxidizing properties, and is a powerful bleaching agent. It is used as a disinfectant, antiseptic, oxidizer, and in rocketry as a propellant. The oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species.

Hydrogen peroxide is naturally produced in organisms as a by-product of oxidative metabolism. Nearly all living things (specifically, all obligate and facultative aerobes) possess enzymes known as peroxidases, which harmlessly and catalytically decompose low concentrations of hydrogen peroxide to water and oxygen.

2.3.1 Physical Properties of Hydrogen Peroxide Solutions

Aqueous hydrogen peroxide solutions have specific properties that are different from those of the pure chemical due to hydrogen bonding between water and hydrogen peroxide molecules. Specifically, hydrogen peroxide and water form a eutectic mixture, exhibiting freezing-point depression. While pure water melts and freezes at approximately 273K, and pure hydrogen peroxide just 0.4K below that, a 50% (by volume) solution melts and freezes at 221 K.

2.3.2 Industrial Applications Uses

About 50% of the world's production of hydrogen peroxide in 1994 was used for pulp- and paper-bleaching. Other bleaching applications are becoming more important as hydrogen peroxide is seen as an environmentally benign alternative to chlorine-based bleaches.

Other major industrial applications for hydrogen peroxide include the manufacture of sodium per carbonate and sodium per borate, used as mild bleaches in laundry detergents. It is used in the production of certain organic peroxides such as dibenzoyl peroxide, used in polymerizations and other chemical processes. Hydrogen peroxide is also used in the production of epoxides such as propylene oxide. Reaction with carboxylic acids produces a corresponding peroxy acid. Per acetic acid and meta-chloroperoxybenzoic acid (commonly abbreviated mCPBA) are prepared from acetic acid and *meta*-chlorobenzoic acid, respectively. The latter is commonly reacted with alkenes to give the corresponding epoxide.

In the PCB manufacturing process, hydrogen peroxide mixed with sulfuric acid was used as the micro etch chemical for copper surface roughening preparation. A combination of a powdered precious metal-based catalyst, hydrogen peroxide, methanol and water can produce superheated steam in one to two seconds, releasing only CO₂ and high-temperature steam for a variety of purposes.

Recently, there has been increased use of vaporized hydrogen peroxide in the validation and bio-decontamination of half-suit and glove-port isolators in pharmaceutical production.

Nuclear pressurized water reactors (PWRs) use hydrogen peroxide during the plant shutdown to force the oxidation and dissolution of activated corrosion products deposited on the fuel. The corrosion products are then removed with the cleanup systems before the reactor is disassembled.

Hydrogen peroxide is also used in the oil and gas exploration industry to oxidize rock matrix in preparation for micro-fossil analysis.

2.3.3 Hydrogen Peroxide Safety

Regulations vary, but low concentrations, such as 3%, are widely available and legal to buy for medical use. Higher concentrations may be considered hazardous and are typically accompanied by a Material Safety Data Sheet (MSDS). In high concentrations, hydrogen peroxide is an aggressive oxidizer and will corrode many materials, including human skin. In the presence of a reducing agent, high concentrations of H_2O_2 will react violently.

High-concentration hydrogen peroxide streams, typically above 40%, should be considered a D001 hazardous waste, due to concentrated hydrogen peroxide's meeting the definition of a DOT oxidizer, if released into the environment. The EPA Reportable Quantity (RQ) for D001 hazardous wastes is 100 pounds, or approximately ten gallons, of concentrated hydrogen peroxide.

Hydrogen peroxide should be stored in a cool, dry, well-ventilated area and away from any flammable or combustible substances. It should be stored in a container composed of non-reactive materials such as stainless steel or glass (other materials including some plastics and aluminium alloys may also be suitable). Because it breaks down quickly when exposed to light, it should be stored in an opaque container, and pharmaceutical formulations typically come in brown bottles that filter out light.

2.4 Potassium Permanganate (KMnO₄)

Potassium permanganate is a strong oxidizing agent that can react with hydrogen sulfide in a variety of ways, depending on whether the stream is acidic or alkaline. In acidic conditions, the following reaction takes place:



Under alkaline conditions the following takes place:



Under conditions that are in between acidic and alkaline pHs a variety of reactions occur yielding elemental sulfur, sulfate, thionates, dithionates and manganese sulfide end of the products. Potassium permanganate has been fairly effective when added to the waste production operation.

2.4.1 Disadvantages of Potassium Permanganate (KMnO₄)

Dosages are difficult to predict and control in most liquid applications. The high cost and high dose, 6 or 7 parts of potassium permanganate are needed to each part of hydrogen sulfide are discouraging. Safety precautions are required for handling and storage.

2.5 Methane (CH₄)

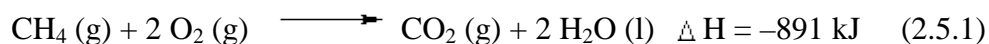
Methane is a colorless, odorless gas with a wide distribution in nature. It is the principal component of natural gas, a mixture containing about 75% CH₄, 15% ethane (C₂H₆), and 5% other hydrocarbons, such as propane (C₃H₈) and butane (C₄H₁₀). Anaerobic bacterial decomposition of plant and animal matter, such as occurs under water, produces marsh gas, which is also methane.

At room temperature, methane is a gas less dense than air. It melts at -183°C and boils at -164°C . It is not very soluble in water. Methane is combustible, and mixtures of about 5 to 15 percent in air are explosive. Methane is not toxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen inhaled. A trace amount of smelly organic sulfur compounds (*tertiary*-butyl mercaptan, (CH₃)₃CSH and dimethyl sulfide, CH₃-S-CH₃) is added to give commercial natural gas a detectable odor. This is done to make gas leaks readily detectible.

Methane is synthesized commercially by the distillation of bituminous coal and by heating a mixture of carbon and hydrogen. It can be produced in the laboratory by heating sodium acetate with sodium hydroxide and by the reaction of aluminum carbide (Al₄C₃) with water.

In the chemical industry, methane is a raw material for the manufacture of methanol (CH₃OH), formaldehyde (CH₂O), nitro methane (CH₃NO₂), chloroform (CH₃Cl), carbon tetrachloride (CCl₄), and some Freon's (compounds containing carbon and fluorine, and perhaps chlorine and hydrogen). The reactions of methane with chlorine and fluorine are triggered by light. When exposed to bright visible light, mixtures of methane with chlorine or fluorine react explosively.

The principal use of methane is as a fuel. The combustion of methane is highly exothermic.



The energy released by the combustion of methane, in the form of natural gas, is used directly to heat homes and commercial buildings. It is also used in the generation of electric power. During the past decade natural gas accounted for about 1/5 of the total energy consumption worldwide, and about 1/3 in the United States.

Natural gas occurs in reservoirs beneath the surface of the earth. It is often found in conjunction with petroleum deposits. Before it is distributed, natural gas usually undergoes some sort of processing. Usually, the heavier hydrocarbons (propane and butane) are removed and marketed separately. Non-hydrocarbon gases, such as hydrogen sulfide, must also be removed. The cleaned gas is then distributed throughout the country through thousands of miles of pipeline. Local utility companies add an odorant before delivering the gas to their customers.

Some methane is manufactured by the distillation of coal. Coal is a combustible rock formed from the remains of decayed vegetation. It is the only rock containing significant amounts of elemental carbon. The composition of coal varies between 60% and 95% carbon. Coal also contains hydrogen and oxygen, with small concentrations of nitrogen, chlorine, sulfur, and several metals. Coals are classified by the amount of volatile material they contain, that is, by how much of the mass is vaporized when the coal is heated to about 900°C in the absence of air. Coal that contains more than 15% volatile material is called bituminous coal. Substances released from bituminous coal when it is distilled, in addition to methane, include water, carbon dioxide, ammonia, benzene, toluene, naphthalene, and anthracene. In addition, the distillation also yields oils, tars, and sulfur-containing products. The non-volatile component of coal, which remains after distillation, is coke. Coke is almost pure carbon and is an excellent fuel. However, it may contain metals, such as arsenic and lead that can be serious pollutants if the combustion products are released into the atmosphere.

2.6 Additional Information

2.6.1 Alkaline Mineralization of Organic Waste

The nitrogen compounds contained in most of bio-solids such as chicken manure include soluble ammonium ion, organic nitrogen, nitrates and nitrites. Ammonium ions in alkaline conditions are converted into ammonia gas.



The higher the pH, the more gaseous ammonia (NH_3) is released from the alkaline stabilized bio-solids. Equation above shows the effect of pH on ammonia release at various pH levels. At the pH of 11, all ammonium ions are converted to ammonia gas, which if not controlled, can cause considerable odors

On the other hand, high pH levels essentially eliminate odors due to hydrogen sulphide and possibly other sulphur-containing odor pollutants such as mercaptans and organic sulphides.

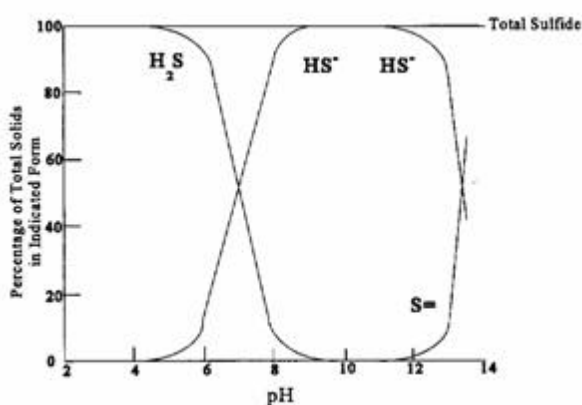
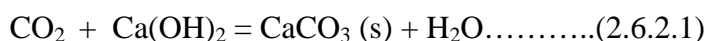


Figure 2.6.1: pH Versus Percentage of Total Solid in Indicated Form

Figure 2.6.1 illustrates that as pH increases, the gaseous hydrogen sulphide (H_2S) decreases while water soluble HS^- and S^{2-} increase. At pH of 9, H_2S gaseous release is essentially at 0%.

2.6.2 Alkaline Materials

Lime in its various forms, as quicklime and hydrated lime, is the principal and also the lowest cost alkali. Lime is a general term, but by strict definition it only embraces burned forms of lime; quicklime, hydrated lime, and hydraulic lime. Both quicklime (CaO) and hydrated lime [Ca(OH)₂] are used in this study. Ca(OH)₂ is added to neutralize any free acids that may be presented in the water. CO₂ is the principal acid present in unpolluted, naturally occurring water.



Calcium present in the waste makes them alkaline and thus promotes ammonia loss. The loss and odor dissipation may be even greater when heated, which promotes volatilization. Sodium hydroxide, commonly known as caustic soda, can be added to control sulphides. The addition of NaOH to waste elevates pH, reduces the concentration of protons (H⁺) that form the aqueous hydrogen sulphide, and thus prevents aqueous hydrogen sulphide formation. Caustic is not flammable or combustible. The 50% caustic solution has a very low corrosion rate, and iron and steel equipment is usually adequate if operated at moderate temperatures.

2.6.3 Solubility of Phosphorus

Effect of the applied mineralized samples on the availability, and the concentration of phosphorus in water were investigated. Results show (see figure 7a and 7b) that the concentration of phosphorus in water increased more readily within one month. The mineralized sample with 90 % chicken farm waste has the highest concentration of orthophosphate. Meanwhile, the 50 % chicken farm waste in the mineralized sample has the lowest soluble phosphorus in water.

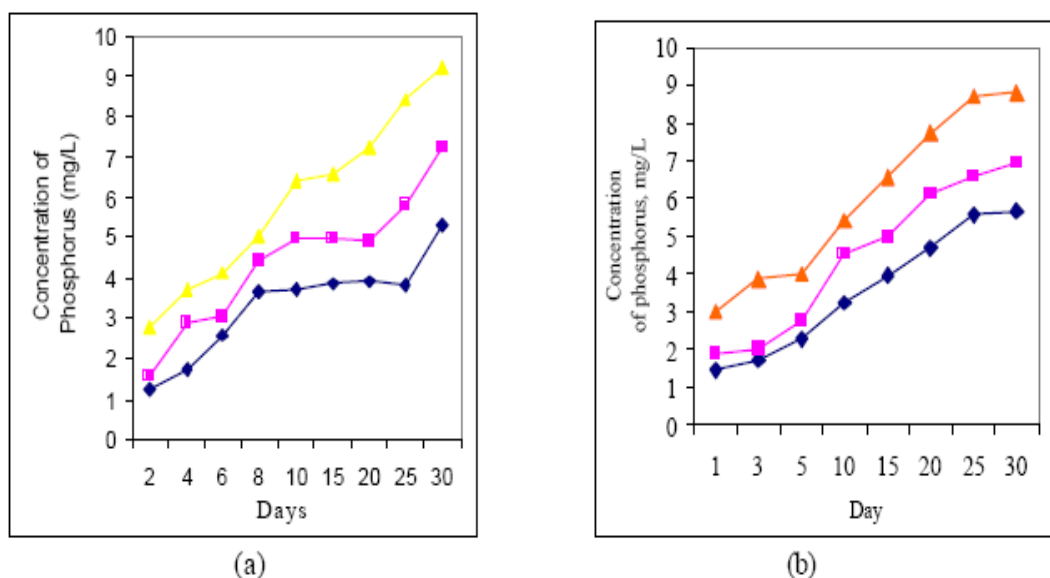


Figure 2.6 3: Solubility of phosphorus from mineralized chicken manure

(a) With Ca(OH)_2 and

(b) With CaO (Chicken manure content in mineralized sample:-50%;
70%;- 90%)

Tremendous increases in agriculture products indirectly contribute to the great demand on effective organic fertilizer. Direct application of chicken farm waste as an organic fertilizer causes environmental problem. Therefore, fast chemical mineralization process was introduced to overcome the shortcomings of direct application and composting. The application of Ca(OH)_2 and CaO on chicken manure and its subsequent heat treatment produces valuable organic fertilizers. The nitrogen and phosphorus present could be easily dissolved in water. The percentage of available nitrogen in the solid mineralized sample increased with the increasing of chicken manure composition in the mineralized sample. Meanwhile, concentration of soluble nitrogen and phosphorus in water increased with time also indicating a slow release capability of the mineralized organic fertilizer.

2.7 Basic Anaerobic Digestion

By definition, anaerobic means lacking air or lacking oxygen. Anaerobic digestion is the process in which volatile organic materials are broken down in the absence of oxygen. This biological process produces a gas, sometimes called biogas, principally composed of methane and carbon dioxide.

Anaerobic digestion and aerobic treatment have been used, or are being adopted, on livestock farms to provide treatment for animal manure prior to storage. These methodologies have the potential to significantly reduce gaseous emissions from manure management systems. The air quality impact of anaerobic digestion and aerobic treatment technologies on animal manure focused mainly on odor control. The effectiveness of aeration on odor control for various types of animal manure that aerobically treated manure had lower odor intensity than untreated manure. The odor characteristics of untreated and an aerobically dairy manure over a three-month anaerobic storage period and found that untreated manure had strong odors with high concentrations of volatile fatty acids (VFAs), hydrogen sulfide (H_2S) and methyl mercaptan (CH_3SH) in the emitted gases, while an aerobically digested manure had lower odors, VFAs and low or no detectable sulfur gases. Most of the research regarding volatile organic compound (VOCs) emissions from confined animal feeding operations has been focused on compounds associated with odors. However besides causing odors, VOCs also contribute to the formation of ozone by reacting with nitrogen oxides in the air in the presence of sunlight. Reducing the emissions of VOC from livestock operations is an important task with respect to the reduction in ozone formation, as well as odor control.

In light of the increased need for greenhouse gas emission reduction, it is important to quantify the effects of various treatment technologies for the reduction of methane and nitrous oxide. Gaseous emissions from animal manure occur in two major steps: the production of gas in the manure and the release of the gas from the manure. The production of methane and VOCs from treated and untreated manure during storage, as the production of the gasses was directly correlated to the emission of the gases. Reductions in the mass production of gasses in manure storage translate

directly into the reductions in their emission. The gases produced from the anaerobic treatment processes were collected and combusted for energy production. The gases produced from the aerobic treatment process were released into the atmosphere. The impact of the gases released during the anaerobic or aerobic treatment processes was happen in this process.

Anaerobic digestion of high solids chicken manure was conducted in a batch screening assay. Different mixtures of the fresh manure and an aerobically digested sludge or pit manure, resulting in different total solids levels, were incubated at 35°C. The efficiency of organic matter conversion to methane was found to decrease with increasing organic loads to the digesters. The highest solid at which the digestion was still feasible was around 10% total solids. The methanogenesis took place at free ammonia (NH_3) concentrations of up to maximum. The efficiency of organic nitrogen conversion to ammonia ($\text{NH}_3 + \text{NH}_4^+$) ranging from 62.6% to as high as 80.3% was achieved in most digestions.

2.7.1 Process Description of Waste to Energy (WTE) Facility Based on Livestock Manure

The layout below of a typical biogas facility using livestock manure as raw material is shown in Fig 2.7.1. The fresh animal manure is stored in a collection tank before its processing to the homogenization tank which is equipped with a mixer to facilitate homogenization of the waste stream. The uniformly mixed waste with H_2O_2 to remove the odor of the manure through a macerator to obtain uniform particle size of 5-10 mm and pumped into suitable-capacity anaerobic digesters where stabilization of organic waste takes place.

In anaerobic digestion, organic material is converted to biogas by a series of bacteria groups into methane and carbon dioxide. The majority of commercially operating digesters are plugging flow and complete-mix reactors operating at mesophilic temperatures. The type of digester used varies with the consistency and

solids content of the feedstock, with capital investment factors and with the primary purpose of digestion.

Biogas contains a significant amount of hydrogen sulfide (H_2S) gas which needs to be stripped off due to its highly corrosive nature. The removal of H_2S takes place in a biological desulphurization unit in which a limited quantity of air is added to biogas in the presence of specialized aerobic bacteria which oxidizes H_2S into elemental sulfur.

Gas is dried and vented into a CHP unit to a generator to produce electricity and heat. The size of the CHP system depends on the amount of biogas produced daily. The digested substrate is passed through screw presses for dewatering and then subjected to solar drying and conditioning to give high-quality organic fertilizer. The press water is treated in an effluent treatment plant based on activated sludge process which consists of an aeration tank and a secondary clarifier. The treated wastewater is recycled to meet in-house plant requirements. A chemical laboratory is necessary to continuously monitor important environmental parameters such as BOD, COD, VFA, pH, ammonia, C:N ratio at different locations for efficient and proper functioning of the process.

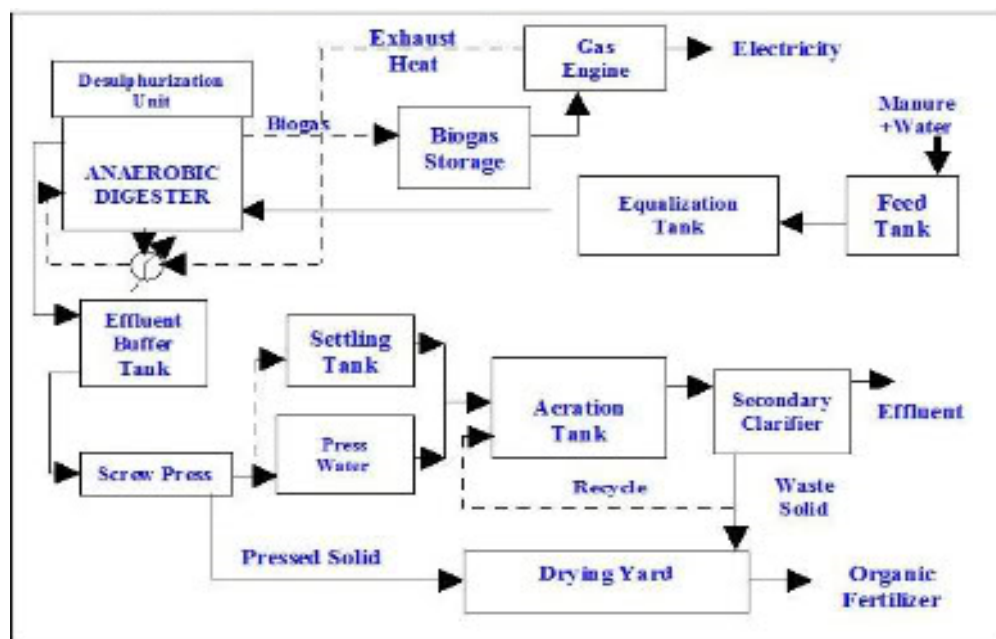


Figure 2.7.1: Process of waste to energy based on the livestock manure

2.7.2 Fermentation

There are two basic types of organic decomposition that can occur. Aerobic (in the presence of oxygen) and anaerobic (in the absence of oxygen) decomposition. All organic material, both animal and vegetable can be broken down by these two processes, but the products of decomposition will be quite different in the two cases. Aerobic decomposition (fermentation) will produce carbon dioxide, ammonia and some other gases in small quantities, heat in large quantities and a final product that can be used as a fertilizer. Anaerobic decomposition will produce methane, carbon dioxide, some hydrogen and other gases in traces, very little heat and a final product with a higher nitrogen content than is produced by aerobic fermentation.

Anaerobic decomposition is a two-stage process as specific bacteria feed on certain organic materials. In the first stage, acidic bacteria dismantle the complex organic molecules into peptides, glycerol, alcohol and the simpler sugars. When these compounds have been produced in sufficient quantities, a second type of bacteria starts to convert these simpler compounds into methane. These methane producing bacteria are particularly influenced by the ambient conditions, which can slow or halt the process completely if they do not lie within a fairly narrow band.

2.7.3 Acidity

Anaerobic digestion will occur best within a pH range of 6.8 to 8.0. More acidic or basic mixtures will ferment at a lower speed. The introduction of raw material will often lower the pH (make the mixture more acidic). Digestion will stop or slow dramatically until the bacteria have absorbed the acids. A high pH will encourage the production of acidic carbon dioxide to neutralize the mixture again.

2.7.4 Carbon-Nitrogen Ratio

The bacteria responsible for the anaerobic process require both elements, as do all living organisms, but they consume carbon roughly 30 times faster than nitrogen. Assuming all other conditions are favorable for biogas production, a carbon - nitrogen ratio of about 30 - 1 is ideal for the raw material fed into a biogas plant. A higher ratio will leave carbon still available after the nitrogen has been consumed, starving some of the bacteria of this element. These will in turn die, returning nitrogen to the mixture, but slowing the process. Too much nitrogen will cause this to be left over at the end of digestion (which stops when the carbon has been consumed) and reduce the quality of the fertilizer produced by the biogas plant. The correct ratio of carbon to nitrogen will prevent loss of either fertilizer quality or methane content.

2.7.5 Temperature

Anaerobic breakdown of waste occurs at temperatures lying between 0°C and 69°C, but the action of the digesting bacteria will decrease sharply below 16°C. Production of gas is most rapid between 29°C and 41°C or between 49°C and 60°C. This is due to the fact that two different types of bacteria multiply best in these two different ranges, but the high temperature bacteria are much more sensitive to ambient influences. A temperature between 32°C and 35°C has proven most efficient for stable and continuous production of methane. Biogas produced outside this range will have a higher percentage of carbon dioxide and other gases than within this range.

2.7.6 Percentage of Solids

Anaerobic digestion of organics will proceed best if the input material consists of roughly 8 % solids. In the case of fresh cow manure, this is the equivalent of dilution with roughly an equal quantity of water.

2.7.7 The Advantages of This Process:

The organic content of the chicken manure is significantly reduced by conversion into gaseous end-products. The obnoxious odor of the sludge is removed and the final digested sludge has a characteristic 'tarry' odor, fats and greases are broken down by the process. There is a significant reduction in the quality of pathogenic bacteria. There is a marked chemical change after digestion. The liquid fraction of chicken manure (supernatant) contains increased levels of ammonia as a result of the breakdown of organic nitrogen (proteins). This makes the digested chicken manure liquor potentially suitable for agricultural use the biogas that is formed is a mixture of carbon dioxide (CO₂) and methane (CH₄) that can be used for digester heating or to generate power.

2.7.8 The Disadvantages of This Process:

The slow rate of bacterial growth requires long periods of time for start-up and limits the flexibility of the process to adjust to changing feed loads, temperatures and other environmental conditions. The process is prone to upsets if not regularly monitored and if corrective action is not taken in time.

Anaerobic digestion is a multi-stage biological chicken manure treatment process whereby bacteria, in the absence of oxygen, decompose organic matter to carbon dioxide, methane and water. In this way, the chicken manure sludge is stabilized and the obnoxious odor is removed. The process can, however be described adequately and simply as occurring in two stages, involving two different types of bacteria. The first stage, the organic material present in the feed sludge is converted into organic acids (also called volatile fatty acids) by acid forming bacteria. In the second stage, these organic acids serve as the substrate (food) for the strictly anaerobic methane-producing bacteria, which converts the acids into methane and carbon dioxide. The end result of the process is a well-established sludge in which 40 to 60% of the volatile solids are destroyed. Finally, a combustible gas consisting of 60 to 75% methane and the remainder largely being carbon dioxide.

CHAPTER 3

RESEARCH AND METHODOLOGY

3.1 Materials Selection

In order to remove the odor of chicken manure toward the capacity of Hydrogen Peroxide (H_2O_2) and titration of potassium permanganate ($KMnO_4$) that chemicals is an important material used in my research. In this research, the odors removed and produced some gases like methane (CH_4) gas and Hydrogen Sulfide gas (H_2S).

3.1.1 Hydrogen Peroxide (H_2O_2) is Very Economical to Use:

In this experiment H_2O_2 was used for process to remove odor from chicken manure. Peroxide application into the well waste water, also remove odor from the animal can best be accomplished by a metering device, which keeps the application more constant and thorough (although manual application can be a second best). Automatic injection pumps can administer 10 ppm to over 1000 ppm with a digital control box that allows better accuracy and water metering capabilities. The rule of thumb is 8 to 10 oz. of 35% hydrogen peroxide to 1000 gallons water striving to attain a reading 30 ppm after application. This same ratio is used for all waste animals: likes a cows, pigs, poultry, sheep, goats, rabbits, and birds.

In order to get a true reading of the amount of oxygen remaining in the waste after the application, use peroxide test strips, designed especially for this very purpose. When peroxide is being applied throughout the entire watering system, with a reading of 30 ppm at the end of the line, all the waste water should stay clean of rust, bacteria, and algae, plus some other foreign materials found in waste water.

Thus the waste waters stay clean and help to stop the spread of diseases. Through this method of waste water purification, there have been many reports of cows passing worms, hogs without even parasite eggs in the fecal matter (with no previous worming medication for over an extended period of time). Some animals cut back on feed (depending on the nutrient level in their feed program). This process of water purification is especially helpful in a confinement barn of any animal and to remove odor from the animal.

3.1.2 Usage of Potassium Permanganate (KMnO_4)

The effectiveness of oxidizing agents when he found a 1% solution of KMnO_4 to be highly effective in controlling odor from a cattle feedlot and was used to control the odor from stockyard manure. KMnO_4 was effective in controlling odors for 72 h in dairy slurry at concentrations of 480 and 240 mg L chicken slurry during short-term tests.

3.2 Research Apparatus

3.2.1 Remove Odor From chicken Manure

In my experiment to remove odor I used one set of apparatus.

- One 1L beaker
- Two 500mL beaker
- Glass Rod
- Stopwatch
- Weighing Scale
- To detect odor using human smell detection

3.3 Research Conditions

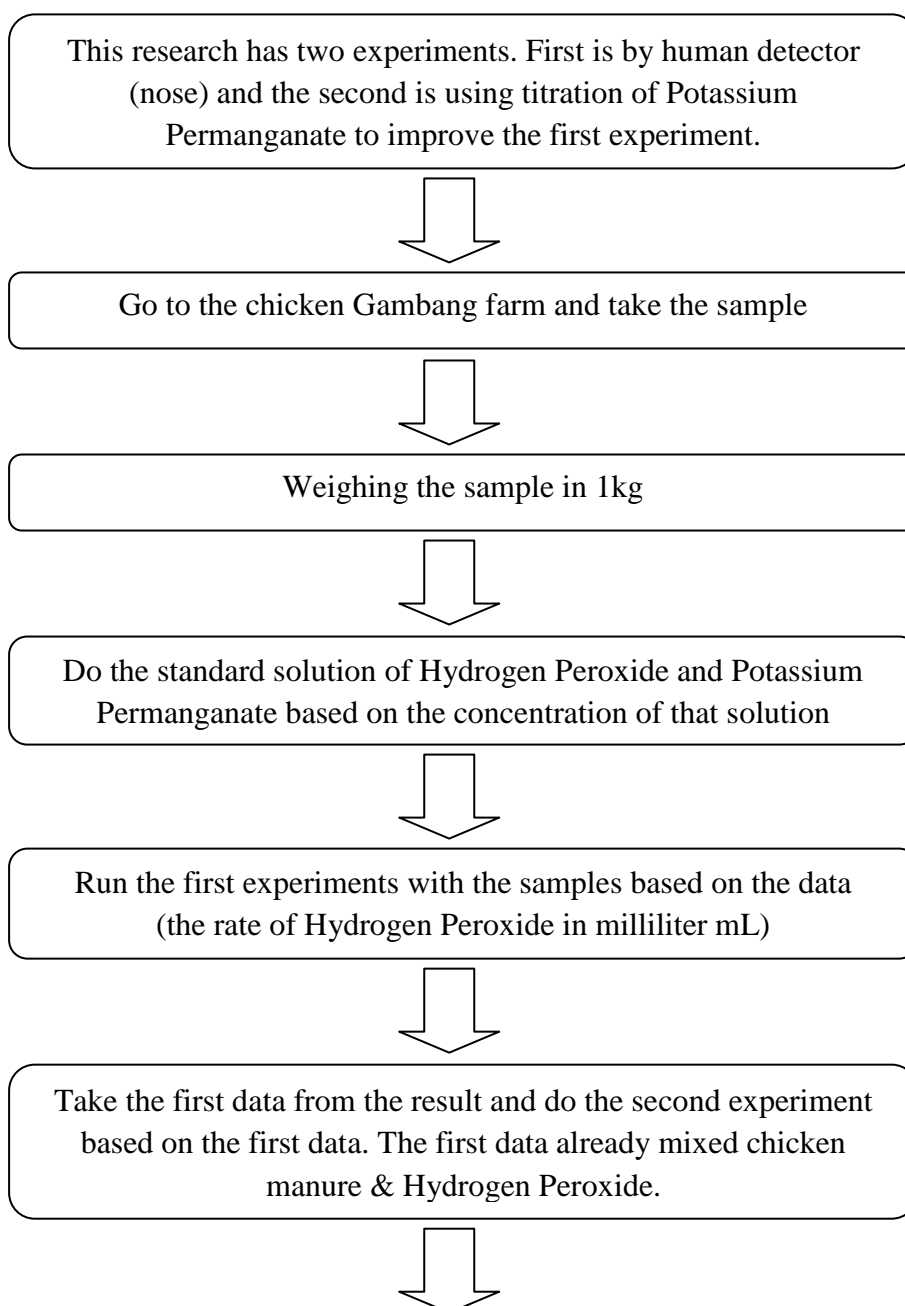
The sample was subjected to treatment with a various amounts of hydrogen peroxide (H_2O_2). After the sample was contacted with the chemical treating agent, the sample was mixed mechanically by hand in about 15 minutes in room

temperature 27°C. After mixing, then titration with KMnO_4 until no color changing from dark purple to light pink in room temperature 28°C.

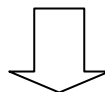
3.4 Research Parameters

In this research, will consider two parameters. Firstly are how much of the hydrogen peroxide and potassium permanganate of materials in order to remove hydrogen sulfide (odorless) from the chicken manure when doing the experiment.

3.5 Research Stages



Then filter the sample above to remove the waste (sand or small rock) and titrate the Potassium Permanganate into the beaker of the sample above after filtration until no changing color of Potassium Permanganate (dark purple to light pink)



Collect the data from the first experiment and second experiment

3.6 Research Summary Stages

Go to the chicken Gambang farm and take the sample of chicken manure. The chicken manure it's not too dry or wet. Before take the sample, must wearing the PPE (Proper Protection Equipment) like a glove, glasses to avoid the hazard form the chicken manure. Bring sample to the lab to do the next step.

Before run the 1 kg sample, the equipment and apparatus should be ready first. After that, run the experiment with the sample by using hydrogen peroxide (H_2O_2) to get the data in 15 minutes. The data are all about the rate amount of hydrogen peroxide in millimeter (mL). The data must be recorded based on the human smell detection. And repeated the experiment more times until get the data closely. After that, settling rate the experiment. Clean and wash the apparatus and equipments.

Then run the second experiment to convinced the first experiment data by using titration of potassium permanganate (KMnO_4) Then collect the data after titration until no color changing but when the color is changing form dark purple to light pink that's mean the sample still has the hydrogen sulfide (H_2S). So hydrogen sulfide still not fully removed from the sample.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Results & Discussions for H₂O₂ to Eliminate H₂S from the chicken manure.

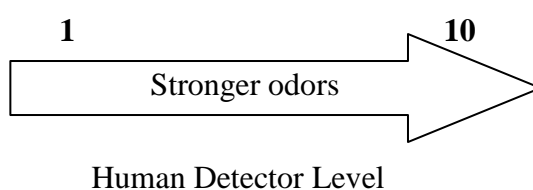


Table 4.1(A)

Stirrer rotation = 100 rpm , Time = 15 minutes		
11 PPM H ₂ O ₂ (mL)	Sample (kg)	Result / Odor
0	1	10
100	1	8
100	1	6
100	1	5
100	1	2
200	1	1
500	1	0

This is a result that data based on the journal for them. This result got after do the stirrer at 15 minutes on speed 100 rpm. The experiment that was similar with the journal. So the best amount of 500mL for 11 ppm H₂O₂ can remove the entire hydrogen sulfide (odorless) of the chicken by using human smell detection.

Table 4.1(B)

11 PPM H ₂ O ₂ (mL)	Sample (kg)	Result / Odor
50	1	8
100	1	8
150	1	7
200	1	6
250	1	5
300	1	4
350	1	3
400	1	2
450	1	1
500	1	0

This above experiment was repeated from the first experiment to ensure that data same with the first experiment by the way the data is not exactly with the first experiment. But in this experiment the data of the H₂O₂ was increasing 50mL to 500mL until same with the data of the journal but more accurate. This experiment in the neutral condition. The result was showed decreased smoothly very fast with strong skatole until no skatole smell by using human smell detection. So the last results still show the 500mL of 11ppm H₂O₂ was fully remove the hydrogen sulfide in the chicken manure by using human detector. But this experiment takes a long time about three hours to fully remove the hydrogen sulfide (odorless) of the chicken manure.

4.1.1 Calculation for H₂O₂ to Eliminate H₂S (odorless) from the chicken manure.

The equation for this experiment:



➔ The result above show when increase the H₂O₂ the odor of chicken manure was decreased by using human detector. The result shows 500 mL of H₂O₂ get 0 odor of chicken manure.

➔ In this experiment the concentration of H₂O₂ is 11 ppm or 11 mg/Kg. So:

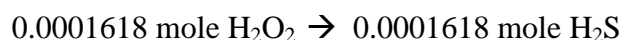
$$\frac{11}{1000000} \times 500 = 0.0055g \text{ of } \text{H}_2\text{O}_2$$

➔ The value of H₂O₂ in mole after divide with molecular weight of H₂O₂:

$$\frac{0.0055}{34} = 0.0001618 \text{ mole } \text{H}_2\text{O}_2$$

➔ So based on the stiochiometry of this equation:

1 mole H₂O₂ react with 1 mole H₂S



In conclusion for this experiment was 0.0001618 moles H₂O₂ react with 0.0001618 moles H₂S in 1 kg chicken manure.

4.2 Results & Discussions for Titration of KMnO_4 to remove The Balance of H_2S (Odorless) From the First Experiment Sample.

Table 4.2(A)

Sample (mL)	KMnO_4 (mL)	Duration (min)
100	10	15
100	20	35
100	30	45
100	40	60
100	50	No color changing

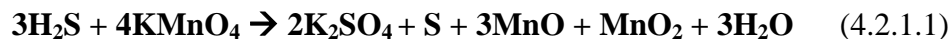
The table above shows the results for the titration 99.2ppm of KMnO_4 to remove all the H_2S from the balance of the first experiment. That's mean in the first experiment still have balance of H_2S so to proof or convinced the first data will do the second experiment. The final result show that between 40-50mL 99.2ppm of KMnO_4 was no color changing from dark purple to light pink that's mean dark purple color only to removed fully H_2S from that sample.

Table 4.2(B)

Sample (mL)	KMnO_4 (mL)	Duration (min)
10	41	70
10	42	75
10	43	83
10	44	92
10	45	106
10	46	No color changing

The 4.2(B) table shows the final result was taken from the 4.2(A) table. The final result from that table was 40-50mL 99.2ppm of KMnO_4 . So the result shows at 46mL was no color changing from dark purple to light pink that's mean dark purple color only to removed fully H_2S from that sample. That's mean that the amount of KMnO_4 was using to remove the balance of H_2S from the first experiment by using H_2O_2 .

4.2.1 Calculation for the Titration of KMnO_4 to remove The Balance of H_2S (Odorless) From the First Experiment Sample



➔ The result show 46 mL of 99.2 ppm KMnO_4 react with 560 mL sample

$$\frac{99.2}{1000000} \times 46 = 0.004563 \text{ g of } \text{KMnO}_4$$

➔ The value of KMnO_4 in mole after divide with molecular weight of KMnO_4 :

$$\frac{0.004563}{158.04} = 0.00002891 \text{ mole } \text{KMnO}_4$$

➔ 100 mL using in 1260 mL of samples

$$\frac{100}{1560} = 0.0641$$

➔ So;

$$\frac{0.00002891}{0.0641} = 0.000451 \text{ mole } \text{KMnO}_4$$

➔ Based on the stiochiometry of this equation:

3 mole H_2S react with 4 mole KMnO_4

$$\frac{0.000451}{4} \times 3 = 0.0003383 \text{ mole } \text{H}_2\text{S}$$

➔ Total of the H_2S for two experiment above:

$$\begin{aligned} \text{Total mole } \text{H}_2\text{S} &= 0.0001618 + 0.0003383 \\ &= 0.0005 \text{ mole } \text{H}_2\text{S} \end{aligned}$$

➔ Multiply total of H₂S with molecular weight H₂S:

$$0.0005 \times 34.1 = 0.01705\text{g H}_2\text{S}$$

In conclusion 0.01705g H₂S in 1Kg chicken manure. So that's mean 17.05g H₂S in 1 tone chicken manure. For the reaction in this experiment was 0.0003383 moles H₂S react with 0.000451 moles KMnO₄. So the total amount H₂S in the first and second experiment was 0.0005 moles H₂S.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, a process to remove odor from the chicken manure can be done by using H_2O_2 but the process takes a long time on about 3 hours. This process can either case on a farmer or a user who wants to deal with chicken manure and they can easily remove the odor of chicken manure first. This research has two experiments. First experiment is reaction of H_2O_2 with H_2S . That experiment got 0.0001618 moles H_2O_2 react with 0.0001618 moles H_2S in 1 kg chicken manure based on their stiochometric equation and for the volume of H_2O_2 was 500mL. And for the second experiment is titration of KMnO_4 .to react with H_2S based on changing color of KMnO_4 from dark purple to light pink. That experiment got 0.0003383 moles H_2S react with 0.000451 moles KMnO_4 without no color changing that's mean no H_2S in that sample and the volume of KMnO_4 was 46mL. So the best data from the result are the 500mL of 11 ppm H_2O_2 plus 46mL of 99.2 ppm KMnO_4 can remove 0.01705g of H_2S in 1 kg chicken manure. The main advantages for small scale farmer when follow that procedure was the quantity of the parameters also can minimize the budget of plant odor treatment.

5.2 Recommendation

The process of chicken manure odor removal can be upgraded by using odor detector kit or gas analyzer instead of using human smell detection because:

- More effective and accurate to detect the odor from the chicken manure
- More sensitive and easy to detect the odor from the chicken manure
- Unlimited usage instead of human smell detection
- Fast and more systematic while running the detection of odor from the chicken manure process

Through this research, the H_2O_2 can be commercialize and sold in niche market in the world as well as support the zero waste policy.

REFERENCES

1. Anonymous (2004) UPM – Faculty of Environmental Studies, list of chicken farms, being produced for the CHIMATRA project, unpublished
2. Burton, C.H.; Turner C. (2003): Manure Management – Treatment Strategies for Sustainable Agriculture, 2nd Edition, ISBN: 0 9531282 6 1
3. Glenn J. (1998) 300,000,000 Tons of Manure, BioCycle, January, Vol.39, Iss.1, pp.47-50 Haga, K. (2001): Managing Manure on Japanese Livestock and Poultry Farms, BioCycle, June, Vol.42, Iss.4, pp.66
4. Khan, S. (2005) Pelletizing of chicken manure, project work at the Department of Waste Management, Hamburg University of Technology TUHH, unpublished
5. Koerner, I.; Trevino-Garza, E.; Stegmann R. (2003) Concepts for the treatment of chicken manure: Investigations regarding the production of agglomerats, Proceedings of ORBIT 2003, pp. 805-817
6. Ruihong Zhang, Jeffery A. McGarvey, Yanguo Ma, Frank M. Mitloehner. Effects of anaerobic digestion and aerobic treatment on the reduction of gaseous emissions from dairy manure storages. Int J Agric & Biol Eng. 2008; 1(2):15 - 20.
7. Proceedings Sardinia 2005, Tenth International Waste Management and Landfill Symposium S. Margherita di Pula, Cagliari, Italy; 3 - 7 October 2005 2005 by CISA, Environmental Sanitary Engineering Centre, Italy
8. J. agric. Engng Res. (2000) 76, 51d60 High Solid Anaerobic Digestion of Chicken Manure G. Bujoczek¹; J. Oleszkiewicz¹; R. Sparling²; S. Cenkowski³ doi.10.1006/jaer.2000.0529

9. Feedstocks for Anaerobic Digestion Steffen, R.; Szolar, O. and Braun, R. Institute for Agrobiotechnology Tulln University of Agricultural Sciences Vienna 1998-09-30
10. Fahad Nasser Alkoai, Ozone Treatment of Animal Manure for Odor Control, American Journal of Environmental Sciences 5 (6): 765-771, 2009
11. Heinz Baumann, Method of Making Fertilizer from Chicken Manure, Feb 27, 1973
12. Helmet Junkermann, Process for Deodorizing Liquid Manure & Removing Harmful Gases, July 10, 1979
13. Eugene T O'Neill, William H. Kibble, Jr, Animal Waste Ofor Treatment, June 29, 1976

APPENDIX

Safety Data Sheet

According to EC Directive 91/155/EEC

Date of issue: 10.03.2004
Supersedes edition of 26.02.2004

1. Identification of the substance/preparation and of the company/undertaking

Identification of the product

Catalogue No.: 106097
Product name: Hydrogen peroxide solution 31% Ultrapur®

Use of the substance/preparation

Auxiliary material for semiconductor industry

Company/undertaking identification

Company: Merck KGaA * 64271 Darmstadt * Germany * Phone: +49 6151 72-0
Emergency telephone No.: Please contact the regional Merck representation in your country.

2. Composition/information on ingredients

Aqueous solution.

Hazardous ingredients:

Name according to EC Directives:

CAS-No.	EC No.	EC-Index-No.	Classification	Content:
Hydrogen peroxide 7722-84-1	231-765-0	008-003-00-9	O; R8 C; R34	31 %

(Full text of R-Phrases in heading 16)

3. Hazards identification

Causes burns.

4. First aid measures

After inhalation: fresh air. Call in physician.
After skin contact: wash off with plenty of water. Dab with polyethylene glycol 400. Immediately remove contaminated clothing.
After eye contact: rinse out with plenty of water for at least 10 minutes with the eyelid held wide open. Immediately call in ophthalmologist.
After swallowing: make victim drink plenty of water (if necessary several litres), avoid vomiting (risk of perforation!). Immediately call in physician. Do not attempt to neutralize.

Merck Safety Data Sheet

According to EC Directive 91/155/EEC

Catalogue No.: 106097
Product name: Hydrogen peroxide solution 31% Ultrapur®

5. Fire-fighting measures

Suitable extinguishing media:
In adaption to materials stored in the immediate neighbourhood.

Special risks:
Non-combustible. Ambient fire may liberate hazardous vapours.

Special protective equipment for fire fighting:
Do not stay in dangerous zone without self-contained breathing apparatus. In order to avoid contact with skin, keep a safety distance and wear suitable protective clothing.

Other information:
Prevent fire-fighting water from entering surface water or groundwater. Contain escaping vapours with water.

6. Accidental release measures

Person-related precautionary measures:
Do not inhale vapours/aerosols. Avoid substance contact. Ensure supply of fresh air in enclosed rooms.

Environmental-protection measures:
Do not allow to enter sewerage system.

Procedures for cleaning / absorption:
Take up with liquid-absorbent and neutralizing material (e.g. Chemizorb® H⁺, Art. No. 101595). Forward for disposal. Clean up affected area.

7. Handling and storage

Handling:

Small containers must be emptied within 2 years.
No further requirements.

Storage:

Tightly closed. Away from combustible materials and sources of ignition and heat. Below +30°C.
Requirements for storage rooms and containers:
Close containers in such a way to enable internal pressure to escape (e.g. excess pressure valve).

8. Exposure controls/personal protection

Personal protective equipment:

Protective clothing should be selected specifically for the working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.

Respiratory protection: required when vapours/aerosols are generated.

Eye protection: required.

Merck Safety Data Sheet

According to EC Directive 91/155/EEC

Catalogue No.: 106097
Product name: Hydrogen peroxide solution 31% Ultrapur®

Hand protection:

In full contact:

Glove material: natural latex
Layer thickness: 0.6 mm
Breakthrough time: > 480 Min.

In splash contact:

Glove material: nitrile rubber
Layer thickness: 0.11 mm
Breakthrough time: > 30 Min.

The protective gloves to be used must comply with the specifications of EC directive 89/686/EEC and the resultant standard EN374, for example KCL 706 Lapren® (full contact), 740 Dermatrill® (splash contact). The breakthrough times stated above were determined by KCL in laboratory tests acc. to EN374 with samples of the recommended glove types.

This recommendation applies only to the product stated in the safety data sheet and supplied by us as well as to the purpose specified by us. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN374 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).

Other protective equipment:

Suitable protective clothing.

Industrial hygiene:

Immediately change contaminated clothing. Apply skin-protective barrier cream. Wash hands and face after working with substance.

9. Physical and chemical properties

Form:	<u>liquid</u>	
Colour:	colourless	
Odour:	slightly pungent	
pH value	(20 °C)	2-4
Melting point		~ -25.5 °C
Boiling point		~ 108 °C
Ignition temperature		not applicable
Flash point		not applicable
Explosion limits	lower	not applicable
	upper	not applicable
Vapour pressure	(20 °C)	~ 18 hPa
Relative vapour density		1.2
Density	(20 °C)	1.11 g/cm ³
Solubility in water	(20 °C)	soluble
Thermal decomposition		> 100 °C

Merck Safety Data Sheet

According to EC Directive 91/155/EEC

Catalogue No.: 106097
Product name: Hydrogen peroxide solution 31% Ultrapur®

10. Stability and reactivity

Conditions to be avoided

Heating.

Substances to be avoided

alkali metals, alkali salts, alkali hydroxides, alkaline earth metals, metals, metals in powder form, metallic oxides, metallic salts, nonmetals, nonmetallic oxides, aldehydes, alcohols, amines, ammonia, hydrazine and derivatives, hydrides, combustible substances, ethers, acids, anhydrides, oxidizing agent, organic substances, peroxi compounds, impurities/dust, permanganates, organic solvents, organic nitro compounds, brass.

Hazardous decomposition products

no information available

Further information

light-sensitive; heat-sensitive.

11. Toxicological information

Acute toxicity

LD₅₀ (dermal, rabbit): >2000 mg/kg (35% solution).

LD₅₀ (oral, rat): 1232 mg/kg (35% solution).

Specific symptoms in animal studies:

Eye irritation test (rabbit): burns (35% solution).

Skin irritation test (rabbit): Irritations (35% solution).

Subacute to chronic toxicity

Sensitization:

Sensitization test (guinea pig): No sensitizing effect.

Mutagenicity (mammal cell test): micronucleus negative.

Further toxicological information

Property that must be anticipated on the basis from the components of the preparation:

After inhalation of vapours: mucosal irritations.

Possible effects: damage of respiratory tract.

After skin contact: After long-term exposure to the chemical: burns.

After eye contact: Burns. Risk of blindness!

After swallowing: burns in mouth, throat, oesophagus and gastrointestinal tract.

Further data

The product should be handled with the care usual when dealing with chemicals.

Merck Safety Data Sheet

According to EC Directive 91/155/EEC

Catalogue No.: 106097
Product name: Hydrogen peroxide solution 31% Ultrapur®

12. Ecological information

Biologic degradation:
Readily biodegradable.

Decomposition products: water and oxygen.

Ecotoxic effects:

Biological effects:

In high concentrations: Toxic effect on fish and plankton.

When used properly, no impairments in the function of waste- water-treatment plants are to be expected.

Fish toxicity: *P. promelas* LC₅₀: 16.4 mg/l /96 h.

Algal toxicity: *Chlorella vulgaris* IC₅₀: 2.5 mg/l /72 h.

Daphnia toxicity: *Daphnia magna* EC₅₀: 7.7 mg/l /24 h.

Further ecologic data:

No ecological problems are to be expected when the product is handled and used with due care and attention.

13. Disposal considerations

Product:

Chemicals must be disposed of in compliance with the respective national regulations. Under www.retrologistik.de you will find country- and substance-specific information as well as contact partners.

Packaging:

Merck product packaging must be disposed of in compliance with the country-specific regulations or must be passed to a packaging return system. Under www.retrologistik.de you will find special information on the respective national conditions as well as contact partners.

14. Transport information

Road & Rail ADR, RID

UN 2014 WASSERSTOFFPEROXID, WAESSRIGE LOESUNG, 5.1, (8), II

Inland waterway ADN, ADNR not tested

Sea IMDG-Code

UN 2014 HYDROGEN PEROXIDE, AQUEOUS SOLUTION, 5.1, II

Ems F-H S-Q

Air CAO, PAX

HYDROGEN PEROXIDE, AQUEOUS SOLUTION, 5.1, UN 2014, II, 8

The transport regulations are cited according to international regulations and in the form applicable in Germany. Possible national deviations in other countries are not considered.

Merck Safety Data Sheet

According to EC Directive 91/155/EEC

Catalogue No.: 106097
Product name: Hydrogen peroxide solution 31% Ultrapur®

15. Regulatory information

Labelling according to EC Directives

Symbol:	C	Corrosive
R-phrases:	34	Causes burns.
S-phrases:	3-26-36/37/39-45	Keep in a cool place. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

16. Other information

Text of any R phrases referred to under heading 2:

8 Contact with combustible material may cause fire.
34 Causes burns.

Reason for alteration

Chapter 8: personal protective equipment.

General update.

Regional representation:

This information is given on the authorised Safety Data Sheet for your country.

The information contained herein is based on the present state of our knowledge. It characterizes the product with regard to the appropriate safety precautions. It does not represent a guarantee of the properties of the product.

Redox reactions



This section **does not cite any references or sources**.

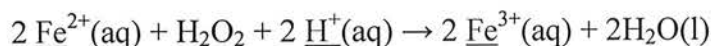
Please help [improve this article](#) by adding citations to [reliable sources](#). Unsourced material may be [challenged](#) and [removed](#). (July 2010) Find sources: "[Hydrogen peroxide](#)" – [news](#) · [books](#) · [scholar](#) · [images](#)

In acidic solution, H_2O_2 is one of the most powerful oxidizers known—stronger than [chlorine](#), [chlorine dioxide](#), and [potassium permanganate](#). Also, through catalysis, H_2O_2 can be converted into hydroxyl radicals ($\cdot\text{OH}$), which are highly reactive.

<u>Oxidant/Reduced product</u>	<u>Oxidation potential, V</u>
Fluorine / Hydrogen fluoride	3.0
Ozone / Oxygen	2.1
Hydrogen peroxide / Water	1.8
Potassium permanganate / Manganese dioxide	1.7
Chlorine dioxide / HClO	1.5
Chlorine / Chloride	1.4

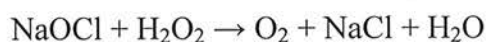
In aqueous solution, hydrogen peroxide can [oxidize](#) or [reduce](#) a variety of inorganic ions. When it acts as a reducing agent, [oxygen](#) gas is also produced.

In [acidic](#) solutions Fe^{2+} is oxidized to Fe^{3+} (hydrogen peroxide acting as an oxidizing agent),

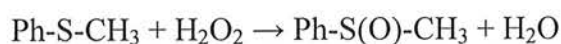


and [sulfite](#) (SO_3^{2-}) is oxidized to [sulfate](#) (SO_4^{2-}). However, [potassium permanganate](#) is reduced to Mn^{2+} by acidic H_2O_2 . Under [alkaline](#) conditions, however, some of these reactions reverse; for example, Mn^{2+} is oxidized to Mn^{4+} (as [MnO₂](#)).

Another example of hydrogen peroxide's acting as a reducing agent is the reaction with [sodium hypochlorite](#), which is a convenient method for preparing [oxygen](#) in the laboratory.



Hydrogen peroxide is frequently used as an [oxidizing agent](#) in organic chemistry. One application is for the oxidation of [thioethers](#) to [sulfoxides](#).^{[\[citation needed\]](#)} For example, [methyl phenyl sulfide](#) was oxidized to [methyl phenyl sulfoxide](#) in 99% yield in methanol in 18 hours (or 20 minutes using a [TiCl₃](#) catalyst).^{[\[citation needed\]](#)}



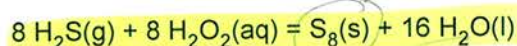
Alkaline hydrogen peroxide is used for [epoxidation](#) of electron-deficient alkenes such as [acrylic acids](#), and also for oxidation of [alkylboranes](#) to [alcohols](#), the second step of [hydroboration-oxidation](#).

How can peroxide remove hydrogen sulfide and sulfur dioxide from wastes?

Would hydrogen sulfide and sulfur dioxide both be oxidized by hydrogen peroxide? (if the gases were bubbled through a solution of hydrogen peroxide). Would the result result be an acidic solution because of sulfuric acid formation.

Hydrogen sulfide and sulfur dioxide are waste products of several manufacturing processes, and reaction with peroxide is one fairly cost-effective method of removing them from industrial wastes.

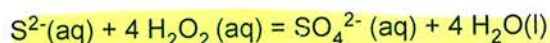
The sulfur in hydrogen sulfide (H_2S) is in the -2 state. In a neutral solution, hydrogen peroxide will oxidize hydrogen sulfide to elemental sulfur via the following reaction:



cyclooctasulfur

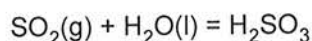
No acid is produced. The reaction takes a while, so if you're bubbling the hydrogen sulfide through the peroxide solution, you need to recycle the gas stream through the peroxide solution. Metal ions catalyze the reaction.

In alkaline solution, you get a completely different reaction. The hydrogen sulfide is present as sulfide ion, and you'll get sulfate after oxidation:

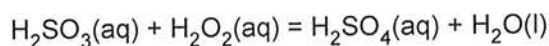


The reaction is exothermic and much more rapid than the neutral pH reaction above, but again, no acid is produced.

Acid is produced when SO_2 is bubbled through a hydrogen peroxide solution, though. First the SO_2 dissolves and reacts with water to form sulfurous acid:



The sulfurous acid is then oxidized to sulfuric acid by the peroxide:



Author: Fred Senese senese@antoine.frostburg.edu

General Chemistry Online! How can peroxide remove hydrogen sulfide and sulfur dioxide from wastes?

Copyright © 1997-2010 by Fred Senese

Comments & questions to fsenese@frostburg.edu

Last Revised 02/15/10. URL: <http://antoine.frostburg.edu/chem/senese/101/redox/faq/print-h2o2-h2s-so2.shtml>

- Manholes
- Lift Stations
- Toxicity Reduction
- Thickeners
- Clarifiers
- Acid Mine Drainage

Technical Brief

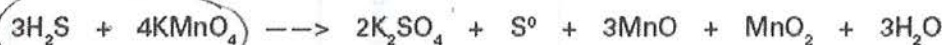
Sulfides and other organic and inorganic compounds can form in the biosolids handling operation of a wastewater system due to anaerobic conditions. These gases can be released during the dewatering step causing the rotten egg odor of toxic hydrogen sulfide and other sewage related compounds. Sulfides can react with moisture in the atmosphere to form acids, that will corrode equipment. Aqueous solutions of permanganate will destroy the odors caused by hydrogen sulfide, mercaptans, amines, and other organic nitrogen and sulfur based compounds and prevent the formation of corrosive acids. The result is a safe, odor-free environment that minimizes corrosion due to sulfides. Permanganate will not oxidize ammonia. In the treatment of sanitary sewage, biosolids are separated from the liquid. These biosolids are concentrated and dewatered using filter presses, centrifuges, or other devices. Hydrogen sulfide is released during the dewatering operation.

Application of Permanganate

Hydrogen sulfide measurements are made around the dewatering equipment. Permanganate (1% to 20% solution) is then applied at a convenient point either into the biosolids holding tank or directly ahead of the solids transfer pumps. The reaction with sulfides is immediate. Feed rates are adjusted to adapt to changing conditions such as flow and temperature. The direct injection of aqueous potassium permanganate solutions into the wastewater biosolids eliminates odors except ammonia.

Hydrogen Sulfide Chemistry

For hydrogen sulfide:



Dosage

For each part of hydrogen sulfide, 4-6 parts of permanganate are required. For biosolids odor control, testing usually starts at 100 ppm KMnO₄ (10 lbs. per dry ton). The dosage is normally reduced to 5 to 8 lbs. KMnO₄ per dry ton after the system is stabilized.

Facility Requirements

To effectively introduce permanganate into the system, proper feed equipment is necessary and available from Carus. No other changes are needed. Operators should be properly trained to handle permanganate and be aware of safety and emergency procedure.

Benefits to Permanganate Treatment

Permanganate reacts rapidly with the functional groups of the odorous compounds, destroying the odor without having to fully mineralize (degrade) the compound. Dewatering improvements have been shown when permanganate is added to septic biosolids to eliminate hydrogen sulfide. In some cases the reduction in polymer is dramatic and offsets the cost of permanganate addition.

Employees are no longer subjected to toxic hydrogen sulfide and neighbor complaints about odors are reduced or completely eliminated.

References

Pisarczyk, K. S., Rossi, L. A., Sludge Odor Control and Improved Dewatering with Potassium Permanganate, 55th Annual Conference of the Water Pollution Control Federation, St. Louis, Mo. (Oct 1982). Carus Form CX #4005

alkaline

H = 6
S = 3
O = 16
K = 4
Mn = 4

H = 6
S = 3
O = 16
K = 4
Mn = 4

KMnO₄ = 158.04 g/mol

impurities in order to improve the color, taste or properties of the fluid. R.O. uses a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting other ions and contaminants from passing. This technology uses a process known as crossflow to allow the r.o. membrane to continually clean itself. This is the reason of why an r.o. element can last many years before clogging or need replacement. This water purification process requires a driving force to push the fluid through the membrane, and the most common force is household water pressure or pressure from a booster pump. The higher the pressure, the larger the driving force and efficiency.

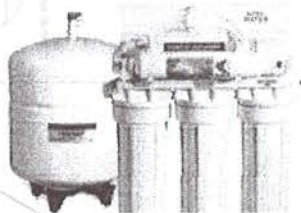
be removed by filtration. Low to moderate concentrations of hydrogen sulfide can be eliminated through use of an oxidizing filter of the same type satisfactory for iron removal. Because the elemental sulfur precipitate tends to clog the filter material, it is usually necessary to replace this material from time to time.

Chemical treatment is recommended for medium to high concentrations of hydrogen sulfide. In such cases, solutions of household bleach or potassium permanganate serve as satisfactory oxidizing agents. When these oxidizing agents-such as household bleach and permanganate solution are used, a small chemical feed pump will serve to feed the agent into the water. A ratio of 2 mg/l chlorine per 1 mg/l H_2S is suggested as a starting dosage. This level will normally provide a high enough chlorine residue to insure complete oxidation of the sulfide to sulfur. The feeding rate of the chlorine solution may be adjusted from the original settings to provide the most efficient operation. As in the case of iron, the chlorine solution should enter the water upstream from the mixing or storage tank to provide sufficient contact time. A contact time of at least 20 minutes should be allowed for complete reaction. After this contact time, the water should pass through an activated carbon filter to remove the now insoluble sulfur and excess chlorine

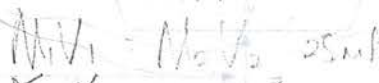
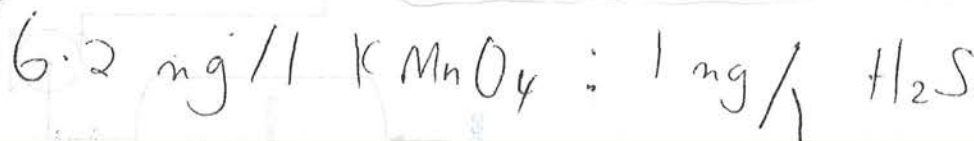
If potassium permanganate can be used as the oxidizing agent, an iron filter is recommended to remove the insoluble products from the water. (Theoretically, 6.2 mg/l of pure $KMnO_4$ are necessary to oxidize 1 mg/l H_2S) However, a slight excess of permanganate, as shown by a light pink color, should be fed to keep the filter in a "regenerated" state. In this way it acts as a reserve to protect against any unexpected increase in the hydrogen sulfide content of the water.

An activated carbon filter alone will remove, trace amounts of hydrogen sulfide. In this process the carbon simply adsorbs the gas on its surface areas. The use of an activated carbon filter can be economical when extremely small amounts of the gas are present. Regeneration of the activated carbon is not usually practical. Periodic replacement is necessary. With moderate to high concentrations of hydrogen sulfide this becomes impractical from an economic standpoint.

Some large users of water depend on aeration to remove hydrogen sulfide from water. Although this is the simplest basic method, it's not normally used for household applications. It has the disadvantage of high initial cost and incomplete removal of the gas. There has been some use of the ion exchange process for removal of hydrogen sulfide. The ion exchange material for this purpose is a strong base anion substance which can be regenerated with salt or a mixture of salt and sodium bicarbonate. This technique has the advantage of simplicity in operation. On the other hand, it offers relatively low flow rate and an effluent water that has all chloride anions.



$M = 0.01 M$
 $V = 15 - 22 ml$



$$\frac{M_1 V_1}{M_2 V_2} = \frac{4}{3}$$

0.1 M

UMP

FAKULTI KEJURUTERAAN KIMIA & SUMBER ASLI

UNIVERSITI MALAYSIA PAHANG

KARUNG BERKUNCI 12, 25000 KUANTAN
PAHANG DARUL MAKMUR

TESTING RECORD

PERSONNEL

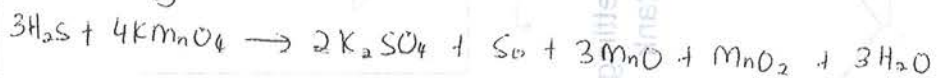
Operator Name / ID No : NORA - 0667
Date & Time : 10/04/07
Telephone : 019-9860193
Purpose : ~~BIODIESEL PROJECT~~ IDENTIFICATION OF H_2S .

MATERIAL & METHOD

Material/Sample/Product : Water from scrubber (500 mL) - 2 bottles.
Agent/Solvent :
Equipment : No
Equipment parameter : Titration
- oxidation agent ($KMnO_4$).
Work description : to identify the presence of H_2S in water sample via ^{redox} titration
($KMnO_4$ titration).

REPORT

Theoretically:




Complete rxn between H_2S and $KMnO_4$ occur at ratio $3H_2S : 4KMnO_4$.

The ^{purple} solution is converted to pink colour as endpoint.

RECORD VERIFICATION

Reported by : NOR HAFIZAH
Designation : SCIENCE OFFICER.

Date : 16/04/07.
Signature : 

Determination of H_2S by Titration:

10/04/04

① $KMnO_4$ (oxidizing agent)

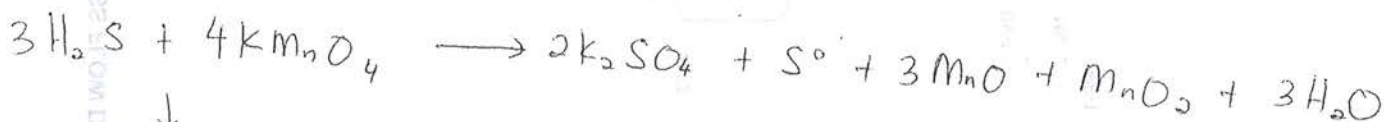
$$\begin{array}{r} 2 : 3 \\ - : 1 \end{array}$$

$$\frac{2}{3} = 1$$

Theory:

$$6.2 \text{ mg/L } KMnO_4 : 1 \text{ mg/L } H_2S$$

Chemical Rxn:



↓

$$3 : 4$$

Use $M_1V_1 = M_2V_2$ by titration method.

① Prepare $KMnO_4$ at 0.01 M
Use 10 ml ($H_2S + Di$) solution.

② Indicator : \rightarrow pink (light)

Do Replicate !!

③ 0.01 M $KMnO_4$ (158 g)

$\Rightarrow M_1$

$$0.01 \frac{M}{L} = 0.01 \frac{\text{mol}}{L}$$

$$\text{mass} = 0.01 \frac{\text{mol}}{L} \times 158 \frac{g}{\text{mol}}$$

$$= 1.58 \frac{g}{L}$$

\therefore dilute 1.58 g in 1 L of H_2O

1000 g = 1 g

V_1 = the volume of KMnO_4 after titration

M_2 = Concentration of H_2S that we want to find out.

V_2 = Volume of sample (water) used in the titration.

Notes

$$M_1 V_1 = M_2 V_2$$

$$0.01 \text{ M } (V_1) = (M_2) 10 \text{ ml} \rightarrow V_1 = (M_2) \frac{10 \text{ mL}}{0.019} \cdot \frac{\text{L}}{\text{g}}$$

① Find the V_1 first

② Calculate after titration

$$V_1 = M_2 \frac{1000 \text{ mL} \cdot \text{L}}{\text{g}}$$

Table of Experiment

0.01 M (H_2S ①)

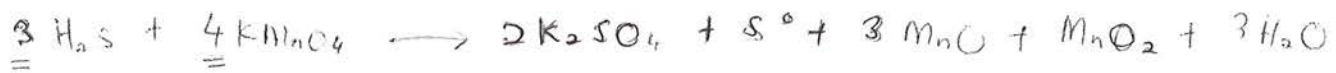
	V_1 (ml)	M_2 (M) g/L
①	2.7	0.0027
②	2.5	0.0025
③	2.7	0.0027
	$\Sigma = 2.63 \text{ ml}$	0.00263

(H_2S ②)
 V_1 (ml)

	M_2 (M)
① 4.1	0.0041
② 4.7	0.0047
③ 3.6	0.0036
Σ 4.13 mL	0.00413

Titration of water sample (containing H_2S) with $KMnO_4$:

Possible chemical rxn:



↓

3 H_2S react with 4 $KMnO_4$ (3:4)

Experimental:

$KMnO_4$ (0.001M after 10X dilution)

Indicator: The purple solution turn to light pink, after titration with $KMnO_4$

Sample 1 (H_2S)

$V_1 = 2.7 \text{ ml}$

2.5 ml

2.7 ml

$\bar{V} = 2.63 \text{ ml of } KMnO_4$

Sample 2 (H_2S)

$V_1 = 4.1 \text{ ml}$

4.7 ml

3.6 ml

$\bar{V} = 4.13 \text{ ml of } KMnO_4$

Sample used for each titration $V_2 = 10 \text{ mL}$

- $m_2 = \text{Molarity of } H_2S \text{ in solution}$

$$M_1 V_1 = M_2 V_2$$

Theoretically:

6.2 mg/L $KMnO_4$ dilute with 1 mg/L H_2S

⑤ Sample 2

KMnO₄ :

$$M_1 = 0.001 \text{ M}$$

$$V_1 = \underline{4.13 \text{ mL}}$$

Sample :

$$M_2 = ?$$

$$V_2 = 10 \text{ mL}$$

$$M_1 V_1 = M_2 V_2$$

From chemical rxn:

$$\frac{M_1 V_1}{M_2 V_2} = \frac{4}{3}$$

$$\rightarrow 3 M_1 V_1 = 4 M_2 V_2$$

$$M_2 = \frac{3 M_1 V_1}{4 V_2}$$

$$\frac{1}{M_2} \left(\frac{M_1 V_1}{V_2} \right) = \frac{4}{3}$$

$$\frac{1}{M_2} = \frac{4}{3} \left(\frac{V_2}{M_1 V_1} \right)$$

$$\frac{1}{M_2} = \frac{4}{3} \left(\frac{10}{0.001 \times 4.13} \right)$$

$$\frac{1}{M_2} = 3228.3$$

$$M_2 = 3.098 \times 10^{-4} \text{ M (x 10 d.f.)}$$

$$= 3.098 \times 10^{-3} \text{ M of H}_2\text{S}$$

$$\frac{3.098 \times 10^{-3} \text{ } \boxed{\text{H}_2\text{S}}}{\text{L}} \quad \left| \quad \frac{34 \text{ g}}{\text{mol}} \quad \right| \quad \frac{1000 \text{ mg}}{1 \text{ g}} = 1053.32 \frac{\text{mg}}{\text{L}}$$

$$= 1053.32 \text{ ppm}$$

Calculations

(i) Sample 1.



KMnO_4 :

$$M_1 = 0.001 \text{ M}$$

$$V_1 = \underline{2.63 \text{ ml}}$$

Sample:

$$M_2 = ?$$

$$V_2 = 10 \text{ ml}$$

$$M_1 V_1 = M_2 V_2$$

from chemical rxn:

$$\frac{M_1 V_1}{M_2 V_2} = \frac{4}{3}$$

$$\frac{1}{M_2} \left(\frac{M_1 V_1}{V_2} \right) = \frac{4}{3}$$

$$\frac{1}{M_2} = \frac{4}{3} \left(\frac{V_2}{M_1 V_1} \right)$$

$$\frac{1}{M_2} = \frac{4}{3} \left(\frac{10}{0.001 \times 2.63} \right)$$

$$\frac{1}{M_2} = 5069.71$$

$$M_2 = 1.972 \times 10^{-4} \text{ M of H}_2\text{S} \quad (\times 10^6 \text{ a.s.})$$
$$= 1.97 \times 10^{-4} \text{ M of H}_2\text{S}$$

$$\frac{1.972 \times 10^{-3} \text{ mol}}{\text{L}} \left| \frac{34 \text{ g}}{\text{mol}} \right| \left| \frac{1000 \text{ mg}}{1 \text{ g}} \right| = 670.48 \frac{\text{mg}}{\text{L}}$$

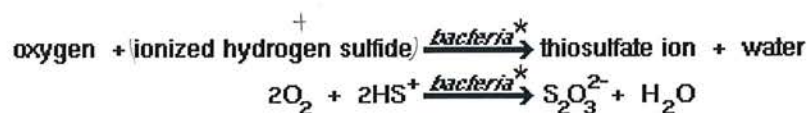
$$= 670.48 \text{ ppm}$$

ALKEN MURRAY CORP.

Solving the Hydrogen Sulfide Odor Problem

Adding Oxygen

Oxygenation assists aerobic and facultative anaerobic bacteria to reproduce faster than anaerobes, thus out-competing them for nutrients.



* anaerobic or facultative anaerobic bacteria

Chemicals Which Have Been Tried to Control Hydrogen Sulfide

Hydrogen Peroxide

Hydrogen peroxide has been injected, upstream of the headworks or primary clarifiers, to react with hydrogen sulfide forming sulfur and water. Excess hydrogen peroxide decomposes to release oxygen and water, thereby increasing the dissolved oxygen in the stream. Generally 90% of the reaction between hydrogen peroxide and hydrogen sulfide takes place within 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes.

Disadvantages: For small installations, 500 lb. drums are purchased. Larger installations buy in tank-trucks or tank-cars. Special safety handling including protective clothing, face shields must be worn during bulk storage loading, and repair and maintenance of the facility. Spontaneous combustion is another possible problem.

hydrogen peroxide + hydrogen sulfide \longrightarrow elemental sulfur + water

pH < 8.5



hydrogen peroxide + sulfide ion \longrightarrow sulfite ion + water

pH > 8.5



Chlorine

Chlorine has been applied to wastewater in a dose that is at least three to nine times the concentration of sulfide to be oxidized. Chlorine combines with water to form hypochlorous and hydrochloric acids.

Disadvantages: Chlorine kills the natural (and Clear-Flo®) waste-degrading bacteria. Chlorine combines with the urine in the waste stream to form chloramines, which are difficult to remove. Toxic or carcinogenic chlorinated hydrocarbons may form during treatment. Chlorine is a hazardous material, requiring special safety precautions.

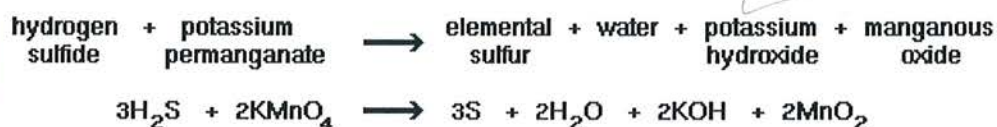
Metal Salts

By reacting certain metal salts, such as ferrous sulfate, with hydrogen sulfide, an insoluble metallic sulfide will be formed. The dose is 4.5 grams of ferrous sulfate for each gram of sulfide to be oxidized. This is less expensive than peroxide or chlorine.

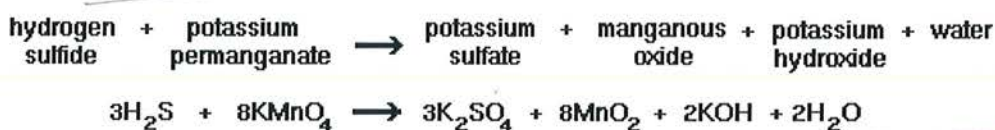
Disadvantages: These products may contain a high free acid content which causes detrimental changes in the pH and alkalinity of the stream, which can interfere with biodegradation of the waste.

Potassium Permanganate

Potassium permanganate is a strong oxidizing agent that can react with hydrogen sulfide in a variety of ways, depending on whether the stream is acidic or alkaline. In **acidic conditions**, the following reaction takes place:



Under alkaline conditions the following takes place:



Under conditions that are in between acidic and alkaline pHs, a variety of reactions occur, yielding elemental sulfur, sulfate, thionates, dithionates and manganese sulfide end products. Potassium permanganate has been fairly effective when added to the sludge dewatering operation, where it is added to the suction side of the sludge pumps feeding the dewatering unit.

Disadvantages: Dosages are difficult to predict and control in most liquid applications. The high cost and high dose, 6 or 7 parts of potassium permanganate are needed for each part of hydrogen sulfide, are discouraging. Safety precautions are required for handling and storage.



Page 1	Page 2	Page 3	Page 4	Page 5	Page 6	Page 7	Page 8	References
--------	--------	--------	--------	--------	--------	--------	--------	------------



United States Patent [19]

O'Neill et al.

[11] 3,966,450

[45] June 29, 1976

[54] ANIMAL WASTE ODOR TREATMENT

[75] Inventors: Eugene T. O'Neill, Hightstown;
William H. Kibbel, Jr., Pennington,
both of N.J.

[73] Assignee: FMC Corporation, Philadelphia, Pa.

[22] Filed: Aug. 12, 1974

[21] Appl. No.: 496,518

[52] U.S. Cl. 71/15; 71/37;
210/63 R

[51] Int. Cl.² C05F 3/00; C02C 1/40

[58] Field of Search 71/11, 15, 20, 21, 37,
71/38, 39, 40, 41; 210/18, 63, 64

[56] References Cited

UNITED STATES PATENTS

3,050,383	9/1962	Wilson	71/21 X
3,705,098	12/1972	Shepherd	210/63

OTHER PUBLICATIONS

The Control of Sulphides in Sewerage Systems, Thistlethwayte, Ed., Ann Arbor Science Pub. Inc., 1972.

Process Design Manual for Sulfide Control in Sanitary Sewage Systems, U.S. EPA, 1974.

Primary Examiner—Charles N. Hart
Assistant Examiner—Ferris H. Lander

[57]

ABSTRACT

Controlling the odor of an animal waste slurry and increasing the plant nutrient values in said animal waste slurry is achieved by contacting an animal waste slurry with about 5 ppm to about 500 ppm hydrogen peroxide, adjusting the pH of the slurry to between about 4.0 and about 8.0 with a mineral acid, mixing the slurry until the odor is no longer objectionable, and recovering the animal waste slurry which contains increased amounts of ammonium salt values.

5 Claims, No Drawings

ANIMAL WASTE ODOR TREATMENT

This invention relates to the treatment of animal waste slurries. In particular, it is concerned with the removal of odorous and noxious gases emanating from animal waste slurries present in storage pits or tanks and with increasing the plant nutrient values in the animal waste.

In recent years the raising of animals in confined areas such as feedlots and similar high animal concentration facilities has become commonplace. This trend is a result of several factors, including increased technology in the livestock industry, and increased population and weight gain of confined animals over pasture and yard animals. A principal drawback of animal confinement raising is the intense odor emanated from the animal wastes which accumulate in the relatively small areas occupied by the animals. Until relatively recently, animal waste odors have not been a problem because the enterprises raising the animals were located at some distance from residential communities, and hence odor dilution by the prevailing winds was adequate. Urban growth, however, has put residential communities much nearer to the animal enterprises and the same odors previously ignored or unnoticed are now offensive and a serious problem.

Numerous procedures have been developed to physically dispose of the animal wastes. Some of these include solid or slurry spreading on fields, oxidation ditches, incineration, and anerobic or aerobic lagoons or digestion systems. Except for field spreading, these treatments involve significant capital expense and/or operating expenditures. Furthermore, these procedures do not eliminate the objectionable odors evolved from the animal wastes except in the aerobic treatment process.

Numerous procedures or systems for dealing with animal waste odors have also been developed. Some involve the use of specifically designed water scrubbers located in the ventilating system of a confinement area. Other procedures involve masking the odors with various

drugs.

An efficient and economic process has been unexpectedly discovered for controlling the odor of an animal waste slurry and increasing the plant nutrient values in the animal waste slurry by contacting the animal waste slurry with about 5 ppm to about 500 ppm hydrogen peroxide as an aqueous hydrogen peroxide solution; adjusting the pH of the slurry to between about 4.0 and about 8.0 with a mineral acid selected from the group consisting of phosphoric acid, sulfuric acid, and nitric acid; mixing the slurry until the animal waste odor is no longer objectionable; and recovering a treated animal waste slurry containing increased amounts of ammonium salts selected from the group consisting of ammonium phosphate salts, ammonium sulfate salts, and ammonium nitrate.

The odors in animal waste slurries are generally noxious gases produced by anaerobic microbial decomposition of organic material present in the waste. The noxious gases include ammonia, hydrogen sulfide, methane, and trace quantities of numerous organic compounds such as mercaptans and skatole. Treatment of an animal waste slurry according to the invention

results in the formation of an odor free animal waste slurry, remaining odor free for several hours, which can be removed and transported from the confinement area or other collection point to a disposal zone such as an open field or a compost station. The treated animal waste slurry is preferably spread as a fertilizer in view of the increased plant nutrient values present in the slurry.

In the process of this invention an animal waste slurry is contacted with an aqueous hydrogen peroxide solution and a mineral acid. The slurry preferably contains about 5% to 25% solids although other pumpable consistencies may be employed.

The aqueous hydrogen peroxide solution is preferably a dilute solution of hydrogen peroxide, containing from 5% to 50% hydrogen peroxide. The amount of hydrogen peroxide necessary to control the unpleasant odors depends upon such factors as the kind of animal waste; feed, age, temperature, and consistency of the animal waste; and the degree of aeration. Higher amounts of peroxide are needed with poultry waste; waste stored for long times in storage pits or tanks; warm temperature waste; and nonaerated waste. Lower amounts of peroxide are effective with horse, cattle, goat, and swine wastes; fresh waste accumulations; cool temperature waste; and aerated waste. In general, about 5 ppm to about 500 ppm, and preferably about 50 ppm to about 200 ppm hydrogen peroxide (100% H_2O_2 basis) based on the volume of the animal waste slurry is sufficient to eliminate substantially all of the oxidizable sulfides and other sulfurous odors.

The mineral acids employed in the invention are phosphoric acid, sulfuric acid and nitric acid. The acids may be used singly or used in combination with one another. The mineral acids are added to the animal waste slurry in amounts sufficient to control the ammonia and related amine odors prominent in animal waste slurries which are not responsive to hydrogen peroxide treatment. This is accomplished by adjusting the pH of the slurry to between about 4.0 and about 8.0 with of mineral acid. Within the pH range ammonium salt formation occurs and hydrogen peroxide decomposition

is prevented. The mineral acid is phosphoric acid and the pH of the slurry is preferably adjusted to between about 4.5 and about 7.5. Within this pH range, the ammonium phosphate salts which are formed in varying amounts are monoammonium orthophosphate ($NH_4H_2PO_4$), diammonium orthophosphate ($(NH_4)_2HPO_4$), and triammonium orthophosphate ($(NH_4)_3PO_4 \cdot 3H_2O$). When the mineral acid is sulfuric acid, the pH of the slurry is preferably adjusted to between about 5.0 and about 7.0. Within this pH range, the ammonium sulfate salts which are formed in varying amounts are ammonium bisulfate (NH_4HSO_4), and ammonium sulfate ($(NH_4)_2SO_4$). When the mineral acid is nitric acid, the pH of the slurry is preferably adjusted to between about 3.5 and 5.5. Within this pH range ammonium nitrate is formed. When combinations of the mineral acids are used, combinations of the ammonium salts are formed. For example, the use of phosphoric acid and sulfuric acid will result in the formation of ammonium phosphate salts and ammonium sulfate salts.

The formation of these ammonium salts within the animal waste slurry prevents the evolution of ammonia and related amine odors from the animal waste slurry and increases the plant nutrient value of the animal waste slurry.

The aqueous hydrogen peroxide solution and mineral acid are added to the animal waste slurry either simultaneously or separately. In aqueous solutions containing hydrogen peroxide and a mineral acid which are stored for extended periods of time prior to use, phosphoric acid is the preferred mineral acid for maximum hydrogen peroxide stability. Preferably the slurry is mixed by conventional means while the slurry is being treated, with mixing continuing until the animal waste odor is no longer objectionable.

Hydrogen peroxide can be used either in the free state or combined as the peroxyhydrates of inorganic salts which break down in aqueous media to yield hydrogen peroxide. Examples of such salts are sodium metaborate peroxyhydrate and sodium carbonate peroxyhydrate. It is preferred to use the free state of hydrogen peroxide since it breaks down into water and oxygen and does not leave any foreign residue in the slurry to contaminate the environment.

The aqueous hydrogen peroxide solution may be optionally stabilized by conventional methods, such as by employing magnesium oxide or other stabilizers in the aqueous hydrogen peroxide solution. Likewise, conventional metal catalysts may also be employed to assist in the oxidation reaction. These catalysts include salts of iron, cobalt, nickel, copper, manganese, molybdenum, and vanadium with the iron salts preferred.

The following examples are given to illustrate the invention but are not deemed limiting thereof. All percentages given are based upon total weight unless otherwise indicated and parts per million (ppm) are based on total slurry volume.

EXAMPLE 1

A 4 l sample of a chicken manure slurry containing about 20% solids was removed from a 7,200 gallon slurry holding tank located outside a chicken confinement house and carefully poured into a calibrated polyethylene container to prevent aeration. The sample was then subjected to treatment with various amounts of hydrogen peroxide and phosphoric acid. After the sample was contacted with the chemical treating agent, the sample was mixed mechanically for about 15 minutes. After mixing, the atmosphere above the sample was analyzed for H_2S (hydrogen sulfide) and NH_3 (ammonia) using a gas detector test kit. The pH of the slurry was analyzed with a Bechman pH meter and the amount of solution sulfides, that is, hydrogen sulfide and dissolved sulfides was determined. Odor characteristics were evaluated subjectively by smell.

Comparative Runs A and B

In Run A, the slurry was mixed for 15 minutes in the absence of hydrogen peroxide and phosphoric acid.

In Run B, the slurry of Run A was contacted with 55.8 ml of a 1% H_2O_2 solution (100 ppm).

Process of the Invention — Runs 1 to 5

In Run 1, the slurry of Run B containing 100 ppm H_2O_2 was contacted with 55.8 ml of a 1% H_3PO_4 solution (100 ppm).

In Runs 2 and 3 additional amounts of a 1% H_3PO_4 solution were added to the slurry of Run 1 to increase the acid concentration in the slurry to 500 ppm and 1,033 ppm respectively.

In Run 4, the slurry of Run 3 containing 100 ppm H_2O_2 and 1,033 ppm H_3PO_4 was contacted with an

additional amount of H_2O_2 (1% solution) to increase the hydrogen peroxide concentration to 200 ppm.

In Run 5, a 4 l sample of a chicken manure slurry was contacted with 500 ppm H_2O_2 (1% solution) and 1,063 ppm H_3PO_4 (1% solution).

In each of the runs, the slurry was mixed for 15 minutes after addition of the treating agent and then analyzed as described above. The results are set forth in Table I.

Prior to hydrogen peroxide addition (Run A) the slurry sulfide concentration was 5mg/l and the atmosphere above the slurry had a strong hydrogen sulfide, ammonia and skatole odor. After the initial hydrogen peroxide addition (Run B) the slurry sulfide concentration dropped very sharply to 0.1 mg/l but the atmosphere above the slurry had a strong ammonia and skatole odor indicating incomplete oxidation of skatole and the amine compounds. The slurries treated with both hydrogen peroxide and phosphoric acid (Runs 1 to 5) showed a complete absence of slurry sulfides. The atmosphere above the slurries also showed a complete absence of hydrogen sulfide, a slight ammonia odor, and a skatole odor. The slurries recovered from Runs 1 to 5 had an increased ammonium and phosphate content resulting from the formation of ammonium phosphate salts.

EXAMPLE 2

The procedure set forth in Example 1 was repeated in the following runs.

Comparative Run C

In Run C, a 4 l sample of a chicken manure slurry was contacted with 200 ppm H_2O_2 (1% solution), and 200 ppm Fe ion (ferrous sulfate solution).

Process of the Invention — Runs 6 to 9

In Run 6, a 4 l sample of a chicken manure slurry was contacted with 200 ppm H_2O_2 (1% solution), and 3,613 ppm H_3PO_4 (1% solution).

In Run 7, a 4 l sample of a chicken manure slurry was contacted with 200 ppm H_2O_2 (1% solution) and 1,467 ppm H_2SO_4 (1% solution).

In Run 8, a 4 l sample of a chicken manure slurry was contacted with 200 ppm H_2O_2 (1% solution), 1,490 ppm H_2SO_4 (1% solution) and 200 ppm Fe ion (ferrous sulfate solution).

In Run 9, a 4 l sample of a chicken manure slurry was contacted with 200 ppm H_2O_2 (1% solution), 1,488 ppm H_3PO_4 (1% solution), and 200 ppm Fe ion (ferrous sulfate solution).

In each of the runs, the slurry was mixed for 15 minutes after addition of the treating agent and then analyzed as described in Example 1. The results are set forth in Table II.

Comparative Run C demonstrates that a slurry treated with hydrogen peroxide and a catalytic amount of iron salt for 15 minutes is completely absent of slurry sulfides and atmospheric hydrogen sulfide odors. This treatment alone, however, is not sufficient to eliminate the ammonia and skatole odors. Inventive Run 6 demonstrates that a slurry treated for only 15 minutes with hydrogen peroxide and phosphoric acid is completely absent of slurry sulfides, and atmospheric hydrogen sulfide, ammonia and skatole odors. Inventive Run 7 demonstrates that a slurry treated for only 15 minutes with hydrogen peroxide and sulfuric acid is completely absent of slurry sulfides and atmospheric hydrogen

$$4000 \text{ mL} = 55.8 \text{ mL } H_2O_2$$

$$400 \text{ mL} = 5.58 \text{ mL } H_2O_2 = 558 \text{ } H_3PO_4$$

$$1\% H_2O_2 = 100 \text{ ppm} = \frac{100}{1000 \text{ oz}}$$

$$10\% H_2O_2 = 1000 \text{ ppm}$$

$$10\% = 1000 \text{ ppm}$$

4L + 58.8
(sample) 5 (chem) 3,966,450

sulfide odor. The atmosphere also had a sharply dropped ammonia concentration. Inventive Run 8 demonstrates that a slurry treated for only 15 minutes with hydrogen peroxide, sulfuric acid and a catalytic amount of iron salt is completely absent of slurry sulfides and atmospheric hydrogen sulfide, ammonia and skatole odors. Inventive Run 9 demonstrates that a slurry treated for only 15 minutes with hydrogen peroxide, phosphoric acid and a catalytic amount of iron salt is completely absent of slurry sulfides and atmospheric hydrogen sulfide. The atmosphere also had a sharply decreased ammonia concentration.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the scope and the spirit of the invention, and all such modifications are intended to be included within the scope of the following claims.

TABLE I

Example 1	Treating Agent (ppm)		pH	Slurry Sulfides (mg/l)	Atmosphere (ppm)		Odor
	H ₂ O ₂	H ₃ PO ₄			H ₂ S	NH ₃	
Comparative Run A	0	0	7.15	5	410	15	Strong H ₂ S, NH ₃ , skatole
Run B	100	0	7.15	0.1	6	8	Strong NH ₃ , skatole
Inventive Run 1	100	100	7.10	0	0	2.5	Strong skatole
Run 2	100	500	7.00	0	0	1	Strong skatole
Run 3	100	1033	6.50	0	0	0	Skatole
Run 4	200	1033	6.50	0	0	0	Slight skatole, animal
Run 5	500	1063	6.50	0	0	0	Slight skatole

TABLE II

Example 2	Treating Agent (ppm)				pH	Slurry Sulfides (mg/l)	Atmosphere (ppm)		Odor
	H ₂ O ₂	H ₃ PO ₄	H ₂ SO ₄	Fe			H ₂ S	NH ₃	
Comparative Run C	200	0	0	200	7.20	0	0	16	Strong NH ₃ , skatole
Inventive Run 6	200	3613	0	0	6.25	0	0	0	Slight animal, musty
Run 7	200	0	1467	0	6.50	0	0	2	NH ₃ , skatole
Run 8	200	0	1490	200	6.50	0	0	<1	Silage, animal
Run 9	200	1488	0	200	6.50	0	0	1	NH ₃ , skatole

<means "less than"

What is claimed is:

1. A process for simultaneously controlling the odor of an animal waste slurry and increasing the plant nutrient values in said animal waste slurry, which comprises: contacting an animal waste slurry with about 5 ppm to about 500 ppm hydrogen peroxide as an aqueous hydrogen peroxide solution based on 100% hydrogen peroxide; adjusting the pH of the slurry to between about 4.0 and about 8.0 with a mineral acid selected from the

group consisting of phosphoric acid, sulfuric acid, and nitric acid;

mixing the slurry until the animal waste odor is no longer objectionable whereby ammonia and related amine odors are converted into ammonium salts; and

recovering a treated animal waste slurry containing increased amounts of ammonium salts selected from the group consisting of ammonium phosphate salts, ammonium sulfate salts, and ammonium nitrate.

2. The process of claim 1 wherein the pH of the slurry is adjusted to between about 4.5 and about 7.5 with phosphoric acid and the ammonium phosphate salt values are increased in said slurry.

3. The process of claim 1 wherein the pH of the slurry is adjusted to between about 5.0 and about 7.0 with sulfuric acid and the ammonium sulfate salt values are

increased in said slurry.

4. The process of claim 1 wherein the pH of the slurry is adjusted to between about 3.5 and about 5.5 with nitric acid and the ammonium nitrate values are increased in said slurry.

5. The process of claim 1 wherein the slurry is contacted with about 50 ppm to about 200 ppm hydrogen peroxide as an aqueous hydrogen peroxide solution.

* * * * *

1 mg - 1 L
100 mg/L H₂O₂ < density = 1.11 g/mL
pH = 3.1

1000 mg/L H₂O₂

H₃PO₄ =

1 mL : 1 mm slurry

H₃PO₄

nu. 9.8 g/mol
density 1.885 g/mL

1000 mL H₃PO₄

1000 mL

2000 mL