### THE PRODUCTION OF ORGANIC FERTILIZER USING TANNERY SLUDGE

by

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#### Abstract

The tanning industry is know as a potentially pollution intensive industry. The purpose of this study was the conversion of waste sludge from domestic tannery factories into useful organic fertilizer. The research team at the Tongtian Star Group in Zhejiang Province in China used an aerobic high temperature fermentation process to accomplish this aim, with warehouse-style equipment based on practicality, efficiency, and energy conservation principles. The results indicated that the organic fertilizer produced using bio-fermentation technology with integrated tannery sludge as a carrier is suitable for use in agriculture and forestry. The components of the organic fertilizer comply with the national standard. The project indicated that it is feasible to produce an organic fertilizer with tannery sludge.

#### RESUMEN

La industria del curtido es conocida como una industria potencialmente intensiva de contaminación. El propósito de este estudio fue la conversión de lodos residuales de fábricas domésticas de curtidos en un abono orgánico útil. El equipo de investigación del Tongtian Star Group en la provincia de Zhejiang en China utilizó un proceso aeróbico de alta temperatura de fermentación para lograr este objetivo, con equipos de almacenamiento basados en los principios de practicidad, eficiencia, y conservación de energía. Los resultados indicaron que el fertilizante orgánico producido utilizando tecnología de bio-fermentación con lodos de curtiembre integrados como vehículo es adecuado para su uso en la agricultura y la silvicultura. Los componentes del fertilizante orgánico cumplen con la norma nacional. El proyecto indica que es factible para producir un fertilizante orgánico con lodos de curtiembre.

#### INTRODUCTION

The final disposal of tannery sludge has been attracting government attention in recent years. Various disposal methods for tannery sludge have been adopted in different countries depending on their industrial characteristics. Survey statistics indicate that domestic (sewage) sludge is mainly used for agriculture, forestry, incineration or landfill disposal.<sup>1,2</sup> In recent years, increasing number of sludge farms have been developed by the US, UK and Japan, while the amount of sludge disposed to landfill has decreased. Because landfill disposal is not sustainable and many countries have, either unofficially or experimentally, limited the amount of sludge disposed to landfill. Such restrictions require the promotion of sludge organic matter re-use with the aim to reduce the production of methane gas in landfills.<sup>3,4</sup>

To avoid secondary pollution of soil or water from the agricultural use of sludge, that may contain toxic and hazardous compounds, Europe and the US have established technical standards for the use of municipal sewage sludge. The British standards contain methods for the determination of toxic and harmful substances in the sludge, pH measurements, index values for harmless treatment and stabilization treatment of the sludge, a determination of the type of land that can be used for sludge application, and methods for applying sludge to land.<sup>5,6</sup> In the US, a strict law, the "organic solid waste (sludge section) disposal law", limits the usage of urban sludge, and divides the sludge into two categories, A and B.7 The A-grade sludge is prepared by dehydration, high temperature composting and axenic processing, and must meet environmental standards for toxic and hazardous substances. A-grade sludge can be used for fertilizer, garden soil, landfill cover and other related uses. B-grade sludge is prepared by simple dehydration or other dehydration treatment, and sludge cannot be used to improve food crops, but only on forest soil.8 Currently, there is a big gap in the sludge disposal techniques between China and other countries. Treated but un-stabilized sludge in China can introduce secondary contamination to the environment, which may become burdensome to future city developments.

Sludge contains a lot of organic matter, and various nutrients and trace elements that can significantly change the physical and chemical properties of soil.<sup>9</sup> Sludge can increase the amount of nitrogen, phosphorus and potassium, improve soil structure and promote the formation of clusters, adjust soil pH, improve cation exchange capacity, and enhance soil porosity, permeability and water holding capacity.<sup>10</sup> Sludge can also increase the microbial community biomass and metabolic intensity in the soil rhizosphere, and inhibit rot and pathogens. When sludge is used as a fertilizer it can reduce the amount of chemical fertilizers applied, reducing the agricultural costs and pollution from chemical fertilizers. Increasing attention is being given to methods of turning waste into alternative resources. Currently, in the leather industry in China, there is no restriction on tannery sludge discharge, and the only requirement is that wastewater discharge achieves the "Integrated Wastewater Discharge Standard" (GB 16297-1996-04-12, in China). For agricultural sludge, this standard requires that the chromium concentration in dried sludge is  $\leq 1$  g/kg. However, traditional wastewater treatment processes typically lead to higher concentrations of chromium in tannery sludge, and the utilization of this sludge has caused an impact on agriculture.<sup>11</sup> From 2004, the Tongtian Star Group in Zhejiang Province in China has organized a research team to change tannery sludge into organic fertilizer.

The tannery sludge from the Tongtian Star Group contained organic compounds (31.2%), chromium (183 mg/kg), copper (45 mg/kg), lead (102 mg/kg), cadmium (0.62 mg/kg) and arsenic (2.3 mg/kg), with average concentrations determined by relevant standard analysis methods. These pollutant concentrations are below the levels specified in the "agricultural control standards for pollutants in sewage sludge", GB4284-1984. From these data, the comprehensive re-use of tannery sludge began to look more feasible. In 2007, the "Comprehensive Utilization of tannery sludge technology research" plan from the Tongtian Star Group received approval from Science and Technology Bureau, Quzhou City, and project teams began to research techniques for producing organic fertilizer from tannery sludge.

#### DEVELOPMENT OF ORGANIC FERTILIZER PRODUCTION FROM TANNERY SLUDGE

In this research project, in order to avoid the toxicity and disposal problems associated with chrome tanning, an iron-THPS (Tetrakis(hydroxymethyl) phosphonium sulfate) combination tanning system has been used.<sup>12</sup> The tannery sludge was collected from Liannianfeng Biotechnology Co., Ltd. Quzhou, Zhejiang, China and stored at 4 °C until use. Since 2007, the technology for organic fertilizer production from tannery sludge has been revised twice, and a trial production run has been completed at Liannianfeng Biotechnology Co., Ltd. Quzhou.

#### **Process of Organic Fertilizer Production**

The following scheme (Figure 1) shows the technical process for organic fertilizer production.

#### Selection of Fermentation Type

Currently, biological sludge fermentation processes can be classified as aerobic or anaerobic fermentation depending on the different oxygen demands of the micro-organisms. Fermentation methods include composting fermentation, tanktype fermentation, tower fermentation, barrel fermentation and others. The research project at the Tongtian Star Group used

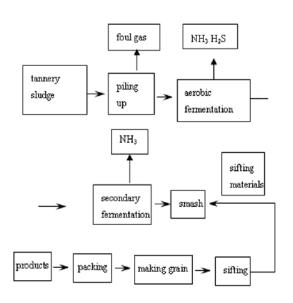


Figure 1. Technique process of organic fertilizer.



Figure 2. Fermentation warehouse.

an aerobic high temperature fermentation process with warehouse-style equipment based on practicality, efficiency, and energy conservation principles. The warehouse body was 4m long, 3m wide, 1.5m high, had a volume of 18 m<sup>3</sup>, and supplied oxygen using blast equipment (Figure 2).

#### **Strain Selection and Growth Conditions**

Microbial strains evolve digesting particular materials, and will only work efficiently on sludge containing similar components, so fermentation with exogenous microbes will introduce regional differences. Therefore, research into an appropriate fermentation strain for the treated sludge is necessary. The temperature of manure fermentation, speed of fermentation and degree of harmlessness of the strain were correlated with the quality of the selected strains. To ensure high-temperature and rapid fermentation, a strain with good decomposing ability, wide adaptability, and resistance to high temperatures were required. The Tongtian Star research team collected local strains in Quzhou, and prepared a bacterial complex, AM111. The AM111 complex not only includes bacteria and fungi with good composting ability, but also contains actinomycetes, lactic acid bacteria and yeast. The results indicated that AM111 can provide satisfactory fermentation of tannery sludge.

The AM111 complex can be stored in a cool dry place for a maximum of 6 months. Following practical trials, it has been determined that 1-2 kg of AM111, produced by a solid medium, should be used for each 1 t of organic fertilizer produced. At the inoculation stage, the AM111 should be included in a mixture of dried rice bran and ground phosphate rock, and then added to the piled materials, to ensure uniformity and growth space for strain. The experimental data indicate that AM111 has a strong resistance to heat, a high fermentation temperature and a rapid fermentation speed. The fermentation temperature inside the warehouse can reach 55°C within 10 hours and above 70°C (or even 80°C) within 20 hours. The fermented tannery sludge can reach maturation in only 7 to 10 days. After the organic fertilizer has reached maturation it is taken out of the warehouse, and the heat energy from the bio-fermentation can be used continuously for the next 7-10 days as the moisture ratio decreases to 20% or less. The fertilizer can then be packaged without further drying, thus saving energy and money.

#### **Optimized Materials**

The mixture of materials listed below is optimal for high quality organic fertilizer production with high temperature and rapid speed. This optimal mixture was obtained from several trials. The mixture can supply the growth requirements of most microorganisms, providing good nutrients and raw materials. The mixture is shown in Table 1.

#### Preparation and Storage of Samples

During composting, samples were taken from fermentation warehouse each day, and were dried and ground depending on the requirements of the analytical method. The sampling method is described in "sampling of city life litter and physical analysis methods" (CT Ting 303 Township-95).

- 1. Sampling method. A triangular cloth bag was used to sample the fertilizer during fermentation. During the sampling, to maintain the true representativeness of the samples, samples were taken from different layers and were fully mixed.
- 2. Preparation of samples. Samples were homogenized on plastic film placed over or pavement, and were divided into four sub-samples before analysis.
- 3. Analysis of organic fertilizer. Samples from the pilot trials were sent to the Ministry of Agriculture Fertilizer Quality Supervision for analysis. The results were compared with the bio-organic fertilizer standard of the Ministry of Agriculture to determine if the samples meet the requirements or specifications of the standards.

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Materials* Proportions (%)		Source				
Tannery sludge	20	Tongtian Star Group				
Pig manure	55	Local piggery				
Rice bran	5	Local farmer				
Sawdust, straw	5	Local farmer				
Tea seed cake	5	Local farmer				
Zeolite	5	Local chemical supplier				
Ground phosphate rock	5	Local chemical supplier				
	Tannery sludge         Pig manure         Rice bran         Sawdust, straw         Tea seed cake         Zeolite	Tannery sludge20Pig manure55Rice bran5Sawdust, straw5Tea seed cake5Zeolite5				

## TABLE IRaw subsidiary materials.

\*Materials comprising the overall tannery sludge; the water content of pig manure is about 70%; 1–2 kg of AM111 complex for each 1 t organic fertilizer.

#### BEHAVIOR OF THE ORGANIC FERTILIZER

#### **Characteristics of the Organic Fertilizer**

Organic fertilizers are produced from animal wastes such as animal manure and waste from animal processing, and plant residues such as compressed cakes of plant waste, straw, dead leaves, and grass clippings. These materials are treated by physical, chemical and biological methods to remove potentially harmful materials including pathogenic bacteria, parasitic eggs, and weed seeds, to meet appropriate standards (the Chinese standard is NY 525-2002). The material can then be described as organic fertilizer. The organic fertilizer produced in these trials was analyzed for a range of parameters with some results shown in Table 2. It can be seen that the heavy metal levels meet the GB 8172-87 standard for controlling urban wastes for agriculture. The death rates for intestinal parasites and bacteria are also acceptable (not shown).

#### Maturity of the Organic Fertilizer

Generally, the production of organic fertilizer includes pretreatment, compost fermentation, mixing and granulating. The key process in the production of organic fertilizer is composting, which typically requires a large area and does not completely decompose the waste. Although the equipment required for composting is freely available, it can cause environmental pollution and requires a great deal of labor. The research project team at the Tongtian Star Group researched composting methods for more than two years, selecting tannery sludge as the carrier, and using AM111 as the fermentation agent. The selection of these materials meant that the organic fertilizer could be produced using a high temperature fermentation process where the tannery sludge made use of aerobic microbes to decompose the material and generate high temperatures which can kill harmful miscroorganisms and eliminate harmful materials.

The final biological indicator of the fertilizer quality was the seed germination rate, in which the effect of the fertilizer maturity on seed germination was considered (Table 3.) If the seed germination rate is more than 80% of the control germination rate this indicates that the fertilizer quality is acceptable. In the germination experiments, the germination rate of pilot fertilizer was 79% compared with the control of 95%, which means that the germination rate is 83% of the control. The quality of the fertilizer is acceptable.

#### Efficacy of the Organic Fertilizer Osmanthus Fragrans Experiments

In May 2007, two plots of *Osmathus fragrans* in Qujiangfeng Village, were selected to test the efficacy of the organic fertilizer. Plot 1 was a control plot which did not receive fertilizer, while Plot 2 had organic fertilizer added at a rate of 50 kg per Mu (a Mu is one fifteenth of a hectare). On June 24 2009, the diameter at breast height (DBH) for each *O. fragrans* tree was measured 0.6 m from the ground. Figure 3 shows Plot 1 at the start and end of the trial period.

Figure 4 shows the effect of the fertilizer after two years. The organic fertilizer promoted the growth of *Osmanthus fragrans* with increased stem lengths and leaf growth. In the control experiment, the average stem length was only 1.15m, while the average stem length was 2.0 m to those with the addition of

Index	Standard Values (%)	Experimental Values (%)	Test Methods	
Total nutrients (N+P <sub>2</sub> O <sub>5</sub> +K <sub>2</sub> O)	≥ 4.0	7.5	NY 525-2002	
Ν		1.92 NY 525-2002		
P <sub>2</sub> O <sub>5</sub>	4.42 NY		NY 525-2002	
K <sub>2</sub> O		0.63	NY 525-2002	
Organic matter	≥ 30	50	NY 525-2002	
Moisture content	≤ 20	6	G 178576-2002	
рН	5.5-8.0	7.9	NY 525-2002	
Cd	≤ 3.0	ND (Not detected)	GB 18877-2002	
Hg	≤5.0	0.00001	GB 18877-2002	
Pd	≤1.0	ND	GB 18877-2002	
Cr	≤3.0	0.0091 GB 18877-2002		
As		0.0014	GB 18877-2002	

 TABLE II

 Elemental concentrations in the organic fertilizer (dry weight basis.)

# TABLE IIISeed germination rates.

Treatment Method	Total Number of Seeds	# of Seeds Germinated	Germination Rate* (%)	Average Germination (%)	
Distilled water	60	58	97		
	60	57	95	95	
	60	56	93		
Organic fertilizer filtered juice	60	47	78		
	60	48	80	79	
	60	48	80		

\*germination rate (%) = number of seeds germinated in 3 days/ total number of seeds  $\times 100\%$ .

organic fertilizer. The addition of fertilizer improved the growth by 73.9% compared to the control trial, and the size and height of the leaves were also better in the fertilized treatment compared with the control.

#### Panicum Virgatum Experiments

In 11 2008, Panicum virgatum (energy grass) was planted in two plots in Qujiang Hualong County. One plot was a control without added fertilizer, while organic fertilizer was added to the other plot at a rate of 80 kg per Mu?. On June 24, 2009, photographs and samples were taken of the plots. The photographs are shown in Figure 5.



before fertilization

after fertilization

Figure 3. Comparison before and after fertilization of *O. fragrans* tree.

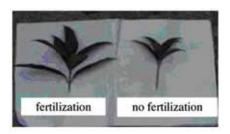


Figure 4. Comparison fertilization and no fertilization.



Figure 5. Influence of organic fertilizer on the growth of Panicum virgatum.

Qujiang Huanong County predominantly has red soil with low organic mater contents. The average height of energy grass is about 0.5 m in the control trial, but about 2.0 m with the addition of organic fertilizer, a four-fold increase. This shows clearly the efficacy of the organic fertilizer.

#### **ENVIRONMENTAL IMPACT**

With the development of industrial processes, there is a great deal of organic sludge produced that cannot be used safely or effectively, and thus ends up in landfills, wasting land resources, and potentially creating secondary pollution. If this project was put into operation, it could result in the production of 50000 t of organic fertilizer, with the collection and treatment of 50000 t of pig manure (moisture content 80%), and the treatment of tannery waste and city sludge. Assuming the total nitrogen content was 3.3%, and then total phosphorus content was 1.29% in the organic fertilizer, this would reduce annual emissions of nitrogen and phosphorus by 8000 t and 3000 t, respectively.

Sludge and organic waste contain large amounts of organic matter, and various nutrients and trace elements, and thus can improve the physical and chemical properties of soil. The use of organic fertilizers produced from sludge can increase the nitrogen, phosphorus and potassium levels, improve soil structure and promote the formation of a granular structure, and adjust soil pH and cation exchange capacity.

Quzhou City is located in a red soil area in the south of China with poor quality, acid soil which requires a great deal of fertilizer to consolidate and improve the quality of the land. An area of approximately 20 million Mu requires treatment each year. Organic fertilizer produced from tannery sludge can modify red soil, reducing the amount of chemical fertilizers required, which would reduce both cost and potential environment pollution. This treatment method for tannery sludge could allow further development of organic crop planting.

#### **INDUSTRIAL APPLICATION**

The organic fertilizer produced using bio-fermentation technology with integrated tannery sludge as a carrier has been widely used in the tanneries in the south of China. The system was conducted in Ningbo Shunfan Leather Production Company and Tongtian Start Group in Zhejiang Province. Since March of 2007, 3000 sheep skins were processed to leather every day for each company. 3000 t sludge can be collected every year in every company. The main different influence on growth of plants by organic fertilizer between the traditional and the novel system are displayed in Table IV. It is obvious that through the comparison of organic fertilizer by

Rate of Bud Emergence	Chlororphyll Content /(mg.g <sup>-1</sup> )	Average Stem Length /cm	Root Length /cm
86.1%	2.48	42.83	11.37
75.7%	2.51	40.00	12.53
82.5%	3.03	52.33	14.29
80.4%	2.84	55.50	14.14
	Emergence           86.1%           75.7%           82.5%	Emergence         Content /(mg.g <sup>-1</sup> )           86.1%         2.48           75.7%         2.51           82.5%         3.03	Emergence         Content /(mg.g <sup>1</sup> )         Length /cm           86.1%         2.48         42.83           75.7%         2.51         40.00           82.5%         3.03         52.33

TABLE IVEffect of application of organic fertilizer on plants growth of rice seeding.

tannery sludge and control, chlororphyll content, average stem length and root length increased 18.15%, 20.06% and 25.68%, respectively. The same trend can be obtained by comparison of organic fertilizer by tannery sludge, raw tannery sludge and commodity organic fertilizer. It indicated that organic fertilizer by tannery sludge can bring helpful influence on the growth of biology. On the other hand, rate of bud emergence of organic fertilizer sludge is superior to the raw tannery sludge, and the possible reason was the toxic of tannery sludge without treatment. In the industrial production, the cost of an aerobic high temperature fermentation process with warehouse-style equipment is lower than that of traditional treatment method. And the organic fertilizer can bring some profit, so the total cost of the novel pickling is lower than traditional system.

#### CONCLUSIONS

The research team at the Zhejiang Tongtian Star Group Limited Company used oxidation ditch biotechnology to treat waste water and improve the tannery process. After composting, the concentration of potential pollutants within the tannery sludge were below the "agricultural control standards for pollutants in sewage sludge" specified in GB 4282-1984. This indicates that the organic fertilizer produced using bio-fermentation technology with integrated tannery sludge as a carrier is suitable for use in agriculture and forestry. The components of the organic fertilizer comply with the national standard. The project indicated that it is feasible to produce an organic fertilizer with tannery sludge.

#### **ACKNOWLEDGEMENTS**

The authors would like to thank Specialized Research Fund for the Doctoral Program of Higher Education (NO.200806101041), National Science Foundation of China (NO:50903055) for financial support, and support by National 973 specialized Fund(NO.2007CB616900.)

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