FAO European Cooperative
Research Network

Recycling of Agricultural, Municipal and Industrial Residues in Agriculture

Network Coordinator: José Martinez, Cemagref, Rennes (France)

RAMIRAN 2002

Proceedings of the 10th International Conference of the RAMIRAN Network

General Theme: Hygiene Safety

Štrbské Pleso, High Tatras, Slovak Republic
May 14 - 18, 2002

Edited by Ján Venglovský and Gertruda Gréserová

ISBN 80-88985-68-4

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CONTROL OF GASEOUS EMISSIONS FROM STORED PIG SLURRY BY MEANS OF ELECTROCHEMICAL TREATMENT

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ABSTRACT

In the frame of the FAIR5 CT97-3506 EU project, pilot scale experiments were carried out in order to test the electrochemical treatment effectiveness in the control of gaseous emissions from stored pig slurry. Different electrochemical parameters, such as electrode material and current intensity, were compared under different climatic conditions (winter and summer). The results showed a strong influence of seasons, electrode materials and current intensity. In winter period, gas concentrations in the air emitted from treated and untreated manure were very low and the electrochemical treatment, performed with copper or graphite electrodes and with current intensity of 0.2 A showed limited effects on ammonia and nitrous oxide emission reduction. The experimental trials carried out in summer period with copper electrodes and current intensity of 1.0 A, showed sensible reductions both in gas concentration in the air over manure surface and in emission rates. In particular, after sixty days of treatment, ammonia concentration in the exhaust air was 43% lower from copper-electrode treated manure than from untreated manure, whereas methane was reduced of about 60%. Furthermore, in comparison to untreated manure, the ammonia emission rate from copper treated manure was reduced of the 63%, the nitrous oxide emission rate was reduced of 50-65%, whereas the methane emission rate was reduced of 82%.

INTRODUCTION

Storage of animal manure is an important source of gaseous emissions. As a matter of fact, in fattening pig husbandry, the phase of manure storage is responsible for a considerable part, which varies from 13% (CORINAIR, 2001) to 35% (Valli et al, 2000), of the total amount of ammonia emissions.

Several techniques have been proposed in order to control gaseous emission from storage tanks, i.e. tank covering, floating layers of different materials, acidification, cooling of the manure upper layer, electrochemical treatment. Among these, the electrochemical treatment was on the market during the last years, however, in some cases it did not show a clear effectiveness in terms of gaseous emission control. In fact, not all of the 400 plants built during the 90s were really effective, and the cause of this erratic behaviour is not known.

The electrochemical treatment is performed through the immersion of couples of metal electrodes into the manure. An electronic control unit generates a low intensity direct current between each couple of electrodes, allowing the dissolution and the migration of copper ions into manure.

In order to test the effectiveness of electrochemical treatment on environmental risks reduction, the research project "Electrochemical treatment of fresh animal manure for reducing environmental and health risks - Electroproject" (FAIR5 CT97-3506) was funded by the EU from 1998 to 2001. The research project involved 3 partners (University of Udine, University of Milan, Freie Universität Berlin) with competence on the fields of agricultural engineering, environmental aspects, microbiology and chemistry. Laboratory,

pilot and full scale experiments were carried out with cattle, pig and rabbit manure.
The present paper deals with the results of the pilot scale experimental trials carried out in Italy with fattening pig manure.

MATERIALS AND METHODS

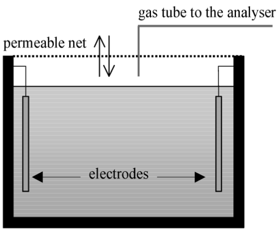
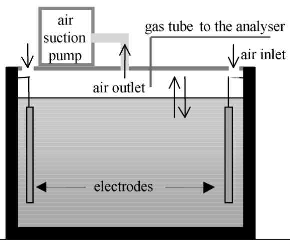
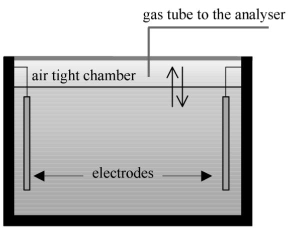
Two pilot scale experiments were carried out with different electrochemical working parameters (copper and graphite electrodes, 0.2 - 1.0 A of current intensity, Tab. 1) in order to test the effectiveness of the electrochemical treatment in the control of gaseous emissions from stored pig slurry under different climatic conditions (winter and summer). For this purpose, PVC tanks of the capacity of 0.816 m^3 were filled with 0.650 m^3 of fresh pig manure and the electrochemical treatment was applied.

Tab. 1: Experimental design and managing parameters of the pilot scale trials

	Trial 1 - winter			**Trial 2 - summer**		
	Untreated	30 days treated + 30 days stored	30 days treated + 30 days stored	Untreated	60 days treated	60 days treated
Electrodes	-	Graphite	Copper	-	Graphite	Copper
Current intensity (A)	-	0.2	0.2	-	1.0	1.0
Polarity inversion time (s)	-	60	60	-	240	240

The concentration of gases (ammonia, carbon dioxide, methane and nitrous oxide) was measured by the use of a gas monitor which worked on the spectrum photo-acoustic principle (Bruel & Kjiaer 1302). Three different methodologies for gas monitoring were adopted (Tab. 2). The first methodology was used to measure the gas concentration over manure surface ("permeable net" methodology), whereas the second ("ventilated chamber" methodology) and the third ("air-tight chamber" methodology) were adopted for evaluating gas emission rates.

Tab 2: Different methodologies adopted for gas monitoring

Gas concentration $mg\ m^{-3}$	**Gas emission $mg\ h^{-1}\ m^{-2}$**	
"PERMEABLE NET"	**"VENTILATED CHAMBER"**	**"AIR-TIGHT CHAMBER"**
		

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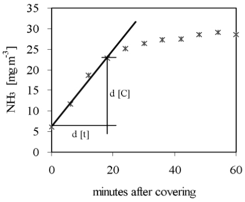
<tr><th>Gas concentration
mg m^{-3}</th><th colspan="2">Gas emission
mg h^{-1} m^{-2}</th></tr>
<tr><td>“PERMEABLE NET”</td><td>“VENTILATED CHAMBER”</td><td>“AIR-TIGHT CHAMBER”</td></tr>
<tr><td>In order to avoid the wind influence on the manure surface, the pilot tanks were covered with a gas-permeable plastic net. The gas concentrations were continuously monitored during the trial period in exhaust air between manure surface and the covering net.</td>
<td>During different days of the trial (day 15, 25 and 45), the pilot tanks were covered with completely air-tight covers. In the air between the manure and the cover a constant airflow was maintained by means of an air suction pump. Gas emission was calculated as:

$$Eg = (Cg_{in} - Cg_{out}) * Q$$
Eg: Gas emission (mg h^{-1})
Cg$_{in}$: Gas concentration into the ventilated chamber (mg m^{-3})
Cg$_{out}$: Gas concentration in the introduced air (mg m^{-3})
Q: Airflow rate (m^3 h^{-1})</td>
<td>During different days of the trial (day 15 and 20), the pilot tanks were covered without applying any airflow with completely air-tight covers for short time periods (2 hours). Gas emission was calculated as

$$Eg = \{d[C]/d[t]\}*\{V/A\}$$
Eg: Gas emission (mg h^{-1} m^{-2})
d[C]/d[t]: Concentration gradient (mg m^{-3}h^{-1})
V: volume of the air tight chamber (m^3)
A: free surface of the manure (m^2)

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RESULTS

Trial 1 - winter

Gas concentrations determined by the above described "permeable net" methodology, were very low in winter conditions, when manure temperature ranged from 0 to 15°C. Ammonia concentration ranged from about 2.3 to 8.4 mg m^{-3}, carbon dioxide ranged from 660 to 760 mg m^{-3}, whereas nitrous oxide concentration was always below the instrumental detection limit (0.05 mg N_2O m^{-3}).

Gas emission determination by the "ventilated chamber" methodology showed slightly higher differences among the theses.

As a matter of fact, in comparison to the untreated manure, ammonia and carbon dioxide emission rate were more reduced in graphite-treated manure than from copper-treated manure (Tab. 3). In particular, ammonia emission reduction ranged from 17 to 27% and carbon dioxide emission reduction ranged from 27 to 30%.

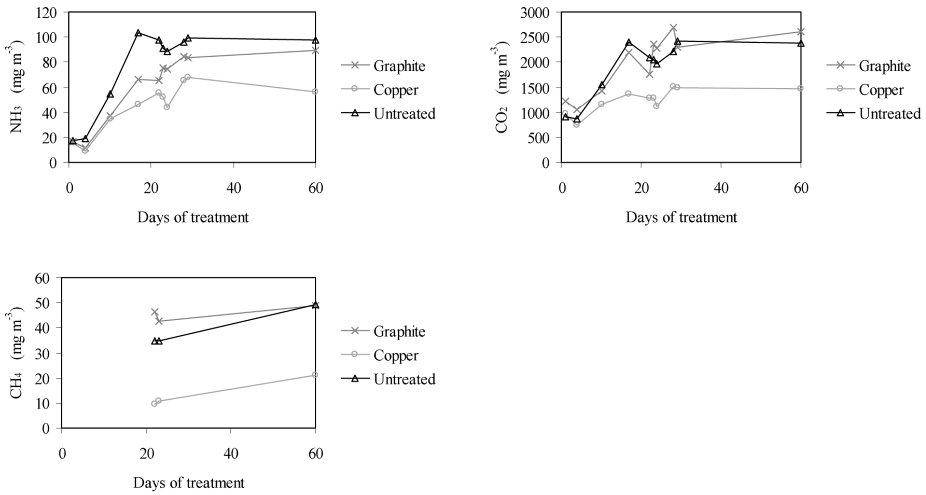
Tab. 3: Emissions of gases and % reduction in comparison with untreated manure (trial 1)

	Days of treatment	*Copper*		*Graphite*		*Untreated*
		mg h^{-1} m^{-2}	*Reduction(%)*	*mg h^{-1} m^{-2}*	*Reduction(%)*	*mg h^{-1} m^{-2}*
NH_3	**15**	6.2	1	4.6	27	6.2
	45	7.5	4	6.5	17	7.8
CO_2	**15**	523.8	24	477.0	30	685.8
	45	756.6	13	638.4	27	862.8

Trial 2 - summer

The experimental trial carried out in summer conditions showed sensible reductions both in gas concentration in air over manure surface and in emission rates, due to the electrochemical treatment performed with copper electrodes and current intensity of 1.0 As resumed in the graphs of Fig. 1, concentration of ammonia and carbon dioxide increased during the first 20 days. Successively, gas concentration was stable or slightly decreasing until the end of the trial. Exhaust air from copper treated tank showed the lowest concentration of ammonia, carbon dioxide and methane. Exhaust air from graphite treated tank showed an intermediate concentration of ammonia, whereas the concentrations of carbon dioxide and methane were similar to those in exhaust air from untreated tank.

Fig. 1: Gas concentrations over manure during the trial 2



As concerns gas emissions, copper-treated manure showed the best performances in the reduction of carbon dioxide, methane and nitrous oxide in comparison to the untreated manure (Tab. 4). Both copper- and graphite-treated manure showed significant reduction of ammonia emission, ranging from 28 to 63% in comparison to the untreated manure.

Tab. 4: Emissions of gases and % reduction in comparison with untreated manure (trial 2)

	Days of treatment	*Copper* mg h^{-1} m^{-2}	*Copper* Reduction(%)	*Graphite* mg h^{-1} m^{-2}	*Graphite* Reduction(%)	*Untreated* mg h^{-1} m^{-2}
NH_3	**15**	28.2	63	52.2	31	75.6
	20	96.0	28	73.2	45	132.6
CO_2	**15**	1699.0	55	4277.0	+ 14	3754.0
	20	1798.0	56	3612.0	11	4060.0
CH_4	**15**	33.6	n.r.	n.r.	n.r.	n.r.
	20	25.2	82	119.4	13	137.4
N_2O	**15**	0.6	50	3.6	+ 200	1.2
	20	0.4	65	1.8	+ 50	1.2

CONCLUSIONS

Gas concentrations and emissions from manure were low in winter, due to a low microbial activity and to an higher gas solubility in manure. For these reasons, the treatment effectiveness resulted lower in winter than in summer.

As a matter of fact, the best results in terms of gas emission reduction were found in summer, treating the manure with copper electrodes and a current intensity of 1.0 A. Ammonia emission was reduced of the 28 to 63%, carbon dioxide and nitrous oxide were reduced of the 55% and 50-65% respectively and methane was reduced of the 82% in comparison to untreated manure.

The present results fit with the conclusions debated by Ranalli et al. (1996), which supposed a reduction of gas emissions due to different microbiological actions, i.e. the reduction of the microbial cell activity by alteration of ATP synthesis and the interaction of sulphydrilic groups of some enzymes with copper ions. Furthermore, Müller (2001) remarked that the ammonia emission reduction could be also explained by the formation of copper-ammonia complexes. Moreover, also physical modifications in the floating layer due to the electric current (i.e. thin crusts in the interface) could cause gas emission reduction.

In the frame of the same research project, experimental trials in full scale pig manure storage tanks were also carried out. Results obtained from these full scale trials did not allow to find significant effects in terms of gas emission reduction, probably due both to the less accuracy of the gas measurement methods applied at large scale and/or to an under sizing of the specific electrical power applied in comparison to the pilot scale plants.

In conclusion, electrochemical treatment showed potential effects in terms of ammonia and methane emission reduction at pilot scale. However, in order to correctly scale up the technology, some other aspects should be more deeply considered:

- the treatment homogeneity in large volume tanks,
- the requirement of specific electrical power higher than that normally adopted as standard design.

These last aspects have not been adequately considered in some of the existing commercial electrochemical treatment plants and they could have negatively influenced the treatment effectiveness.

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