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Pig slurry hygienization with hydrogen peroxide – silver complex, an environmentally acceptable disinfectant

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ABSTRACT

Liquid fraction of pig slurry sampled at the site of drainage into an aerobic lagoon was treated with a hydrogen peroxide-based disinfectant with silver ions for catalytic action in order to define a hygienically acceptable substrate according to its organoleptic, physicochemical and especially microbiologic properties, intended for environmental disposal. In the *in vitro* experiment using substrate mixture with the disinfectant at a final concentration of 2%, time of action of 1 hour, and efficacy control at 24 hours, the following results were observed: the dark, turbid, green-brown, malodorous slurry samples turned light and the intensity of malodour declined substantially. The concentration of ammonium ions and nitrite decreased significantly ($P<0.01$ and $P<0.05$, respectively), whereas the nitrate concentration increase ($P<0.05$) was presumably due to oxidation. Oxidizing processes led to a significant reduction ($P<0.01$) in the biochemical oxygen demand (BOD_5). However, its value of 1992.50 ± 244.59 mgO_2/L was still ecologically unacceptable to be drained into waters. The percentage of dry matter and sedimentation decreased, ($P<0.05$), pH showed a slight increase, whereas the proportion of organic matter and electric conductivity remained unchanged. The number of mesophilic and total coliform bacteria decreased significantly ($P<0.01$). The efficacy of disinfection expressed as $\log_{10}$ reduction factor (RF) was 3.23 for mesophilic bacteria and 3.12 for total coliform bacteria, showing a >99% reduction in their number. The results obtained in the study pointed to efficient hygienization with hydrogen peroxide and silver ions, rendering pig slurry a more acceptable substrate to be disposed of into the environment.

Key words: hygienization, pig slurry, disinfectant, hydrogen peroxide - silver complex

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Introduction

The treatment and disposal of stock breeding manure always pose an ecologic problem. The organoleptic, physicochemical and epidemiologic-epizootic composition of the manure presents a hygienic risk for the atmosphere, soil and water. The atmosphere, soil and water ecosystem is modified irrespective of whether the manure is spread over arable land, used for irrigation, or drained into the waters. The related problems include emanation of malodour, detrimental gases and microorganisms, and contamination of surface and underground waters and soil.

The need for and necessity of manure hygienization in addition to its mechanical and biologic treatment have been increasingly emphasized, especially for manure microbiologic composition, which is considered to be potentially pathogenic. Manure hygienization implies a procedure of the microorganism count reduction below the infectious dose with the addition of disinfectants, i. e. chemical compounds. As not all microorganisms are thus eliminated, the term 'acceptable risk' has been introduced. On choosing chemical compounds, their efficacy should be considered; however, their degradability with ecologically acceptable degradation products (residues) is of no lesser importance.

Oxidizing agents are compounds that have been increasingly used in wastewater disinfection, whereby slurry disinfection is considered a demanding and difficult but frequently necessary procedure. The choice of the agent should primarily be based on its germicidal properties and degradability to environmentally acceptable residues.

As differentiated from solid manure, the thermic phenomena of disinfection do not occur in slurry because it assumes an environmental temperature, which makes it a favourable medium for long-term microorganism survival. Thus, slurry requires proper treatment, prolonged storage and possibly disinfection prior to its disposal into the environment (STRAUCH, 1991).

Oxidation compounds, especially peracetic acid (STRAUCH, 1988; HADŽIOSMANOVIĆ et al., 1989; ASAJ et al., 1992) and hydrogen peroxide (TAUFER, 1993), are used for slurry hygienization. However, advanced oxidizing processes based on a combination of two oxidizing compounds

have been increasingly widely employed because of their higher stability and better results (ALAM and OHGAKI, 2002; WAGNER et al., 2002). The synergistic action of metal ions (Fe^{2+}, Ag^{+}) and hydrogen peroxide has also been used for both drinking water and wastewater as well as cattle slurry disinfection (HADŽIOSMANOVIĆ et al., 1994; TOFANT et al., 2001).

The aim of the present experiment was to assess the efficacy of *in vitro* hygienization of samples of the liquid fraction of mechanically treated pig slurry using a hydrogen peroxide-based disinfectant with catalytic action of silver ions.

Materials and methods

The liquid fraction of pig slurry, obtained by mechanical separation of the solid phase, was used as a substrate in the study. Rarefied, dark green-brown, malodorous specimens were sampled on four occasions at the site of drainage into a lagoon, wherefrom the slurry is taken for irrigation, for spreading over arable land, or is drained to nearby waters. A multi-component stabilized oxidizing hydrogen peroxide-based agent with a catalytic action of silver ions in traces was used as disinfectant.

Hygienization as a procedure of chemical treatment of the slurry was performed *in vitro* in high glass vehicles containing 500 ml of slurry. The disinfectant was added with constant mixing, which resulted in foam formation. In a preliminary experiment, three final disinfectant concentrations of 1%, 1.5% and 2% were used, the latter being chosen for the experiment. Disinfectant efficacy was tested at 1 h and 24 h by determination of organoleptic, physicochemical and bacteriologic parameters for wastewater quality assessment in accordance with standard methods (ANONYMOUS, 1975; ANONYMOUS, 1992) using titration and photometric procedures on a HACH DREL/4000 chemistry/apparatus module and HACH conductivity/TDS meter.

The following parameters were analyzed: dry matter (%), sedimentation (%), organic matter (%), pH, electric conductivity (μScm^{-1}), chloride (mg/L), biochemical oxygen demand (BOD_5; mg O_2/L), and ammonium, nitrite and nitrate (mgN/L). Bacteriologic tests included aerobic mesophilic bacteria and total coliform bacteria expressed as logarithm of total colony-

forming units per millilitre (log_{10} cfu/ml). The efficacy of disinfection was expressed as mean of the log_{10} reduction factor (RF).

Statistical analysis was performed using Statgraphics software version 4.0. Results are presented as mean ± SD (n = 4 in each group). Data were analysed using Student's *t*-test. Significance of mean differences was based on the p values of < 0.05 and < 0.01.

Table 1. Physicochemical and bacteriologic parameters determined in liquid fraction of pig slurry before and after hygienization with 2% hydrogen peroxide + Ag ions

Parameter	Before disinfection	After disinfection	
		1 hour	24 hours
Dry matter %	1.10 ± 0.04 (1.06 - 1.15)	* 0.99 ± 0.08 (0.91 - 1.10)	* 1.02 ± 0.05 (0.96 - 1.06)
Sedimentation %	4.26 ± 0.27 (3.95 - 4.60)	** 3.25 ± 0.20 (3.00 - 3.50)	** 2.81 ± 0.24 (2.50 - 3.00)
Organic matter %	55.20 ± 0.56 (54.65 - 55.98)	n.s. 54.49 ± 0.84 (53.25 - 55.05)	n.s. 54.55 ± 0.87 (53.25 - 55.02)
pH	7.4 ± 0.1 (7.3 - 7.6)	* 7.7 ± 0.1 (7.5 - 7.8)	* 7.9 ± 0.3 (7.4 - 8.2)
Electric conductivity $\mu S\,cm^{-1}$	13693 ± 360 (1323 - 14100)	n.s. 13545 ± 389 (13110 - 14040)	n.s. 13445 ± 412 (13050 - 13990)
Chloride mg/L	2125 ± 126 (1960 - 2250)	n.s. 2018 ± 113 (1920 - 2180)	n.s. 2040 ± 113 (1940 - 2200)
BOD_5 mgO_2/L	2908 ± 222 (2640 - 3110)	** 2055 ± 160 (1820 - 2180)	** 1993 ± 245 (1680 - 2220)
Ammonium NH_4-N mg/L	885 ± 97 (760 - 980)	** 338 ± 103 (240 - 480.)	** 325 ± 65 (280 - 420)
Nitrite NO_2-N mg/L	3.30 ± 0.39 (2.90 - 3.80)	n.s. 2.95 ± 0.13 (2.80 - 3.10)	* 2.70 ± 0.26 (2.40 - 3.00)
Nitrate NO_3-N mg/L	58.53 ± 1.83 (56.40 - 60.20)	* 64.38 ± 3.57 (59.90 - 68.50)	* 66.40 ± 4.39 (60.20 - 70.10)
Mesophilic bacteria log_{10} cfu/mL	4.84 ± 0.40 (4.39 - 5.18)	** 2.53 ± 0.40 (2.00 - 2.89)	** 1.61 ± 0.16 (1.47 - 1.81)
Coliform bacteria log_{10} cfu/mL	3.84 ± 0.28 (3.43 - 4.04)	** 1.00 ± 1.15 (0.00 - 2.00)	** 0.72 ± 0.83 (0.00 - 1.49)

Values are expressed as mean (x) ± standard deviation (SD) and range in parentheses (min - max); n = 4 *per* measurement; *P<0.05; **P<0.01; n.s. nonsignificant

Results

Results of pig slurry liquid fraction treatment with the oxidizing agent, hydrogen peroxide with silver ions, are presented in Table 1 and Fig. 1 and 2. Table 1 shows data obtained by comparison of the physicochemical and bacteriologic parameters before and after the addition of disinfectant.In comparison with control sample, the values of organic matter content, electric conductivity, and chloride and nitrite concentrations did not change

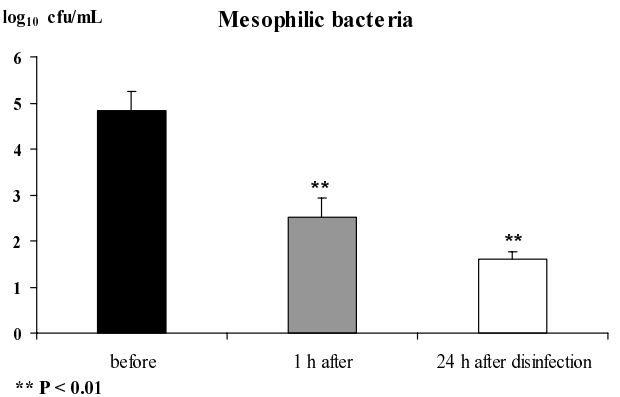

Fig. 1. Aerobic mesophilic bacteria before and after hygienization with H_2O_2 + Ag ions

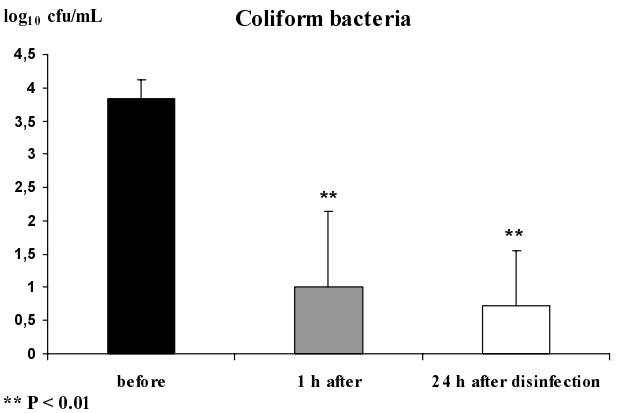

Fig. 2. Total coliform bacteria before and after hygienization with H_2O_2 + Ag ions

significantly at 1 h of treatment. At 24 h, nitrite concentration showed a significant change from control sample ($P<0.05$), and it was the only parameter the value of which was found to modify only 24 h from treatment. At 1 h, the percentage of dry matter decreased, while those of pH and nitrate increased ($P<0.05$), without any significant changes recorded at 24 h. Sedimentation percentage, BOD_5, and number of mesophilic bacteria and total coliform bacteria showed significant reduction ($P<0.01$) at both 1 h and 24 h of treatment. Sedimentation percentage and total mesophilic bacterial count underwent significant reduction between 1 h and 24 h of disinfectant reaction ($P<0.05$ and $P<0.01$, respectively).

Mean values of the microbiologic parameters of mesophilic bacteria and total coliform bacteria are presented in Fig. 1 and 2. Their total count decreased significantly ($P<0.01$), which is a key indicator of hygienization efficacy.

Discussion

Safe slurry disposal by either draining to waters or spread over arable land poses the dual requirements of reducing the risk of pathogenic microorganism transmission to the environment. When the risk of the presence of pathogenic microorganisms is low, i.e. in the case of clinically healthy animals, a set of guidelines proposed by the Expert Group of the European Communities Commission are applied. These guidelines mostly recommend slurry spread over arable land after slurry storage in an aerobic lagoon for at least 60 days in summer or 90 days in winter. In case of a notifiable disease outbreak, chemical treatment according to given recommendations is required. Liquid slurry should be mixed before, during and after the addition of disinfectant. Upon treatment, the slurry should be left to stand for at least 4 days or, even better, for 7 days, and then ploughed into arable land. The addition of chemicals, i.e. oxidizing agents, causes foaming; therefore, storage tanks should not be overfilled. In practice, procedures for small volumes of liquid slurry are used (HASS et al., 1995).

In the present study, disinfection efficacy of a multi-component oxidizing hydrogen peroxide-based agent with monovalent silver ions in traces for catalytic action was assessed. The addition of the disinfectant to

the liquid fraction of pig slurry immediately resulted in foaming and observable organoleptic changes. The substrate turned light, and malodour emanation was greatly reduced. This could be ascribed to the oxidation of sulphur compounds, sulphides, sulphites and mercaptans (TAUFER, 1993) as well as to the reduction in the rate of malodorous metabolites phenol, p-cresol, p-ethylphenol and skatole (WU et al., 2002). The oxidation-induced decrease in the concentration of ammonium ions ($P<0.01$) may have also reduced ammonium emanation from the slurry, because pH showed only a minimal increase from 7.43 to 7.88, and the ability of ammonium release is low in a poor alkaline area due to less pronounced urolytic processes. The ability of hydrogen peroxide to oxidize organic matter in the slurry manifested as BOD_5 reduction by about 32%; however, its mean value of 1993 ± 145 still was a 100-fold allowed value for draining to the waters.

Microbicidal efficacy was expressed as a mean $\log_{10}$ RF of sanitation indicator bacteria, mesophilic bacteria and total coliform bacteria. The results obtained for mesophilic bacteria and total coliform bacteria (RF 3.23 and 3.12, respectively) were satisfactory, indicating a 99.9% reduction in the microorganisms. However, due to the high initial microorganism count and their residual count upon hygienization, their number may have risen again. The final disinfectant concentration of 2% was chosen as being most efficacious. Although relatively high, the use of this concentration has been reported in the treatment of municipal sewage (POFFE et al., 1978). Studies of the *in vitro* efficacy of the same oxidizing agent, hydrogen peroxide with silver ions, according to the DGHM (Deutschen Gesellschaft für Hygiene und Mikrobiologie) suspension method for test *Bacillus subtilis* have shown that growth is halted after only a 30-min action of its 2% concentration, postulating a conclusion that the disinfectant may have the same effect on the sporogenic *Bacillus anthracis* (ANONYMOUS, 1998).

It is concluded that treatment of the liquid fraction of pig slurry with the oxidizing agent, a mixture of hydrogen peroxide and silver ions, at a final concentration of 2%, results in efficacious hygienization in terms of improved organoleptic and environmentally relevant physicochemical and microbiologic parameters.

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SAŽETAK

Uzorci tekuće frakcije svinjskog tekućeg gnoja uzeti na mjestu utoka u aerobnu lagunu bili su obrađeni dezinfekcijskim pripravkom na osnovi vodikova peroksida uz katalitičko djelovanje srebrnih iona. To je učinjeno radi dobivanja higijenski prihvatljivijeg supstrata za ispuštanje u okoliš glede organoleptičkih, fizikalno-kemijskih te osobito mikrobioloških svojstava. U pokusu *in vitro* mješanjem supstrata s dezinficijensom u koncentraciji 2% i djelovanju od jednog sata te provjerom učinkovitosti nakon 24 sata dobiveni su sljedeći rezultati: tamni, mutni, zelenosmeđi uzorci tekućeg gnoja neugodnog mirisa postali su svjetliji, a jačina neugodna mirisa bitno se smanjila. Koncentracija amonijevih iona značajno se snizila ($P<0,01$), također i koncentracija nitrita ($P<0,05$), a može se pretpostaviti da se zbog oksidacije povećala koncentracija nitrata ($P<0,05$). Oksidacijskim procesima u gnoju značajno ($P<0,01$) je smanjena biokemijska potrošnja kisika (BPK_5), ali vrijednost $1992,50 \pm 244,59$ mg O_2/L još je uvijek ekološki neprihvatljiva za utok u vodotoke. Smanjio se postotak suhe tvari i sedimentacije ($P<0,05$), a pH se neznatno povećao, dok su sadržaj organske tvari i elektroprovodljivost ostali u istim granicama. Značajno je smanjen ($P<0,01$) broj mezofilnih i ukupnih koliformnih bakterija. Uspješnost dezinfekcije iskazana kao $\log_{10}$ faktor redukcije (RF) iznosila je za mezofile 3,23, a za ukupne koliforme 3,12 što predstavlja redukciju njihova broja veću od 99%. Dobiveni rezultati upućuju na učinkovitu higijenizaciju vodikovim peroksidom i srebrnim ionima nakon koje tekući gnoj postaje prihvatljiviji supstrat za ispuštanje u okoliš.

Ključne riječi: higijenizacija, svinjski tekući gnoj, dezinficijens, vodikov peroksid-srebro kompleks