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The Use of Polymers for Nitrogen Removal in Swine Wastewater: PAM and Encapsulated Nitrifier Technologies

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SUMMARY

Confined livestock production is one of the fastest growing industries in the Southeastern United States. As a consequence, many counties already are producing more manure nitrogen than available land can absorb, causing water pollution problems. We are investigating the applicability of two municipal wastewater technologies for treatment of swine wastewater.

The first technology uses polyacrylamide (PAM) flocculants to remove solids from dilute swine waste-waters typical of flushing systems. Solids and nutrient separation of swine wastes before entering lagoon treatment is an attractive approach for reducing the mass load of nutrients to be treated, while providing the farmer with more options for waste disposal. Our evaluation of PAM polymers showed that this treatment is very effective and better than alum for separating solids and nutrients from the wastewater stream. Application of 10 ppm of cationic PAM reduced 33% of the suspended solids, 38% of COD, and 82 % of the organic nitrogen.

The second technology, called Pegasus, has been recently developed and tested in municipal plants in Japan. It uses nitrifying microorganisms immobilized in polymer pellets and can remove high levels of ammonia. The nitrifiers are entrapped in 3 mm polyethylene glycol (PEG) pellets that are permeable to ammonia, oxygen and carbon dioxide, providing a very suitable environment to perform at maximum effectiveness. Since the treatment of swine lagoon effluent using constructed wetlands is limited by nitrate availability, we envision the use of encapsulated nitrifier technology as an integral part of total waste management systems that transform ammonia nitrogen into N_2. Our evaluation of CBOD and BOD in the lagoon wastewaters showed that stabilization conditions are optimum for commencement of nitrification and that high nitrification rates of ammonia may be possible using PEG pellets in aerated reactors.

INTRODUCTION

Livestock waste disposal has become a major environmental problem in the U.S. due to the rapid growth of confined animal production. Most noticeable is the case of the swine industry in North Carolina, where hog populations have increased from 2.8 million to more than 8 million in the last 5 years, and where 82 % of the production activity is concentrated in huge operations having more than 2000 pigs each (USDA, 1995). Swine waste is mostly stored and treated in large anaerobic lagoons and spread on cropland. But many counties in the region already are producing more manure-nitrogen than available cropland can absorb (Barker and Zublena, 1995). These land limitations result in undersized lagoons and overloaded land applications causing odor and water pollution problems.

Swine production systems of the future should conserve the maximum amount of nutrients that land can assimilate without causing overapplication and pollution. Assigning nutrients to nutrient deficient areas through solids separation and transport appears critical to overcome current land limitations associated with huge swine operations in the southeast region. Also critical is the exploitation of on-farm nitrification/denitrification processes to convert excess ammonia into N_2. The farmer could use this additional tool to regulate with precision the terminal amount of nitrogen applied to land.

In this paper we describe two technologies already used in municipal wastewater treatment plants, and we evaluate its applicability to treat swine wastewater. The first technology uses PAM polymers to remove solids from dilute swine wastewaters. The second technology uses PEG polymer pellets for nitrification enhancement, a critical step in any nitrogen removal system.

LIQUID/SOLIDS SEPARATION

Why solids separation?

When lagoons are used for waste treatment, the maximum area available for application of the liquid animal waste is largely limited by the pumping distance. It is also difficult for the farmer to manage liquid spraying during winter or rainy weather, when the fields are soaked and the lagoons are mostly full. Solids and nutrient separation before the waste enters the lagoon provides new alternatives for waste disposal. The high nutrient concentration and low moisture of the separated solid fraction make this fraction a valuable material: It can be temporarily stored, composted or transported miles away to nutrient deficient cropland. At the same time, the total load of nutrients to be treated is drastically reduced, increasing the life of existing lagoons, or with a more sophisticated process design, allowing the use of advanced treatment methods replacing the anaerobic lagoon.

Can solids be separated?

Modern design of swine production operations uses some type of water conveyance system to move the waste from the pig-house. Flushing systems are preferred over manure scrapping systems because of their simplicity, economy and lower ammonia emissions (Sievers, 1989). In many of these systems, wastewater is recycled from anaerobic waste lagoons to economize fresh water. Flushing is done at rates that vary from 500 to 2,000 L per 1,000 kg live mass per day. This high dilution results in wastewaters that have very low solid concentrations, often in the range of 0.2 to 2.5 % total solids content. Separation of suspended solids from diluted wastewaters is difficult with currently available screens and presses, and requires some type of chemical coagulation to bind together the small particles of solids in the water into larger clumps (Sievers et al., 1994).

Polyacrylamides. PAM is a high molecular weight, long chain, water soluble polymer. Characteristics such as molecular weight (chain length) and type and density distribution of charge give these polymers varying performance characteristics and applications. For example PAM is extensively used as a settling agent for food processing and packing, paper production, mine and municipal wastewater treatment, as a clarifier for sugar extraction and potable water treatment, and as a soil conditioner to reduce irrigation water erosion. The long polymer molecule destabilize suspended charged particles by adsorbing them and building bridges between several suspended particles, resulting in newer, larger particles (or flocs) that settle out of the liquid.

PAM Experiment

Materials and Methods. We evaluated the effect of PAM on solids and nutrient separation of swine wastewater. The wastewater used (Table 1) was a flushing effluent from of a pig nursery house in Duplin Co., N.C. The system uses siphon-flush tanks activated four times a day, recirculating lagoon wastewater at a rate of about 2,100 L per 1,000 kg live mass per day. This produces a very diluted wastewater (total solids= 0.18 %), but with a very high TKN concentration. Most of this TKN is composed of ammonia from the lagoon wastewater used for flushing, while the organic N fraction in Table 1 corresponds to that contained in the fresh pig waste.

Table 1: Characteristics of the pig-house effluent.

Total Solids	1.83 g L^{-1}
Suspended Solids	335 mg L^{-1}
Chemical Oxygen Demand	1370 mg L^{-1}
pH	8.1
Total Phosphorus	60 mg L^{-1}
Organic Phosphorus	44 mg L^{-1}
Total Kjeldahl Nitrogen	374 mg L^{-1}
Organic Nitrogen	88 mg L^{-1}

PAM treatments included cationic, neutral and anionic materials (Magnifloc 494C, 985N, and 844A, respectively, Cytec Industries Inc., West Paterson, NJ)[1], which were applied at a rate of 10 mg per L of wastewater. We also included an alum treatment (1.43 g $Al_2(SO_4)_3.12H_2O$ per L of wastewater) to evaluate phosphorus removal, since alum is a standard material used to precipitate P. The flocculation experiments were performed in 1 L Imhoff cones used for standard settleable solids tests (APHA, 1992). Stock water solutions of each chemical were prepared and 10 ml aliquots containing the appropriate treatment were added to 1 L wastewater samples, mixed for ten seconds with a rod, and allowed to settle for 60 minutes before determination of solid flocculation performance was made. Flocculation performance was determined by measuring solids and nutrient concentration remaining in the supernatant and the solids settled in the bottom of the cone vessel. All experiments were repeated four times and included a control treatment consisting of 10 ml of water.

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[1] Mention of trademark, proprietary product, or vendor does not constitute a guarantee or warranty of the product by U.S. Dept. of Agriculture and does not imply its approval to the exclusion of other products or vendors that also may be suitable.

Results and Discussion. With the polyacrylamides, only the cationic PAM had a significant effect on solids and nutrient separation (Tables 2 and 3). The lack of response observed with anionic and neutral PAMs was expected because organic particles suspended in neutral and alkaline wastewaters generally have a negative charge (Stumm and O'Melia, 1968).

Table 2: Solids remaining or settled after 1-hour treatment of a pig-house effluent with various PAMs and alum. C=cationic, N=neutral, and A=anionic PAM. Mean separation by LSD at 5% level.

Treatment	Total Solids g L^{-1}	Susp. Solids mg L^{-1}	Diss. Solids g L^{-1}	Settl.. Solids ml L^{-1}
Control	1.81 b	336 a	1.47 b	< 0.5 c
PAM-C	1.70 c	227 b	1.47 b	10.2 b
PAM-N	1.81 b	384 a	1.43 b	< 0.5 c
PAM-A	1.78 b	371 a	1.41 b	< 0.5 c
Alum	2.13 a	137 c	2.00 a	139.6 a

The reaction of PAM-C with the wastewater was instanteous and produced large dark-brown flocs that rapidly settled out of the matrix wastewater, leaving a remarkable clear supernatant. Application of 10 ppm of PAM-C reduced 33% of the suspended solids, 38% of COD, and 82 % of the initial organic N concentration, while dissolved solids, pH, and ammonia concentration remained unchanged. Suspended solids concentration was linearly related to COD concentration (r=0.97), suggesting that the fraction flocculated by treatment is mostly composed of organic materials (volatile solids).

Table 3: Pig-house effluent characteristics after 1-hour treatment with various PAMs and alum. C=cationic, N=neutral, and A=anionic PAM. Mean separation by LSD at 5% level.

Treatment	pH	COD (ppm)	Org. N (ppm)	NH4-N (ppm)
Control	8.3 a	1330 a	67 a	296 a
PAM-C	8.2 a	850 b	16 c	300 a
PAM-N	8.4 a	1260 a	74 a	302 a
PAM-A	8.3 a	1250 a	60 ab	293 a
Alum	7.1 b	580 b	37 ab	306 a

Alum was more effective than PAM-C in reducing suspended solids and COD levels (Tables 2 and 3). Its phosphorus removal efficiency was also good (data not shown). For example, alum treatment reduced 89 % of the initial organic P and 94 % of inorganic soluble P concentration. In comparison, PAM-C affected only the organic P fraction, which was reduced 77% relative to initial levels. Even though the flocculation performance of alum is good, it has many disadvantages relative to PAM for livestock wastewater treatment. The most important disadvantage is the quantity of solids generated for ultimate disposal. For example, addition of alum typically produce a 0.5-1.0 g L^{-1} solids increase per g L^{-1} of chemical used (EPA, 1973). The alum rate applied in this experiment (1.43 g L^{-1}) is that recommended for wastewaters containing 100 mgP L^{-1}. Our data shows a significant increase of 0.5 g L^{-1} in the dissolved solids fraction alone and possibly a much larger increase in the precipitated fraction. This is represented by the large amounts of light-grey sludge comprising the settleable solids fraction. Also noticeable in Table 3 is the lower pH associated with alum treatment, which may affect nitrification processes. In summary, the large chemical demand, the sludge production and additional costs make this material inappropriate for animal wastewater treatment. In contrast, PAM was very effective for solids and nutrient separation, while it is used at very low concentrations (1-20 mg L^{-1}) and therefore does not produce additional solids.

Equipment considerations

The basic requirement is a tank where mixing and settling can take place, and a holding tank to store the separated solids. Voermans and Kleijn (1990) designed a sedimentation silo having a conic bottom used for solids separation and drains on the walls for final liquid separation. In this system, chemicals are injected in the slurry stream and recirculation is used for mixing. Similar flocculator/reactor vessels with no moving parts are currently sold in the USA for industrial and food wastewater treatment. Once the flocs are formed, it is also possible to use standard screw or reciprocating presses and screens for final separation and further dewatering.

We observed that when the PAM treated wastewater was left on the bench overnight, the separated flocs raised to the surface and floated. This was likely due to biological production of gas bubbles like CO_2 and CH_4. Voermans and Kleijn (1990) also observed solids flotation after polymer treatment, specially at high temperatures when biological activity was high. It may be possible then to take advantage of this flotation property and use dissolved

air flotation technology right after the flocculation vessel. In this technology, microscopic air bubbles attach to the floc particles and carry them to the surface where the solidified waste is skimmed off. We think that the dissolved air flotation process in combination with PAM application should produce a swine wastewater substantially free of suspended solids, but experimental data is needed to support this thought.

NITRIFICATION ENHANCEMENT

Why nitrification is important?

Nitrification is becoming an increasingly important component in total farm management systems, to the point that the effectiveness of any biological nitrogen removal treatment depends on the ability of nitrifying organisms to oxidize ammonia to nitrate. Nitrifiers oxidize ammonium nitrogen to nitrite, then to nitrate nitrogen. Nitrification is a very limiting process in waste animal treatment, but a necessary condition to be able to remove nitrogen from the farm in the form N_2, as in municipal plants. The farmer could use this nitrification/denitrification mechanism to regulate with precision the terminal amount of nitrogen applied to land. This is a very valuable tool because it can remove N during periods of low crop uptake requirements or heavy rains when the probability of nutrient loss by leaching is high.

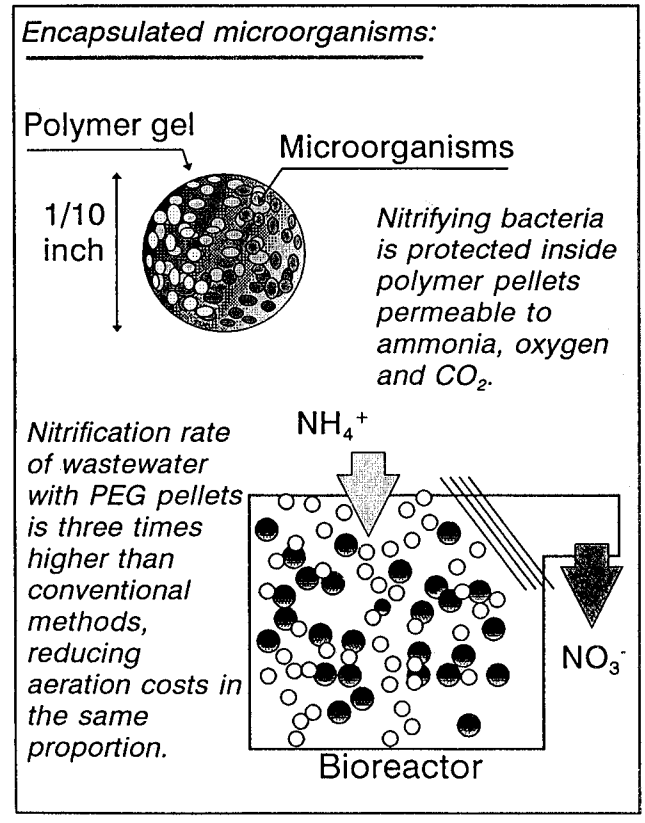
Once nitrification is initiated, the transformation into N_2, or denitrificaton process, is a relatively easy step. It needs an anaerobic environment and a source of carbon to feed the denitrifying microorganisms, similar to conditions typically found in wetlands or anaerobic lagoons. In fact, our research with constructed wetlands for swine wastewater treatment have shown that these specialized wetland systems have the potential to remove large amounts of nitrogen through denitrification, but their performance is limited by nitrate availability (Hunt et al., 1996).

What is the problem with nitrification?

With wastes rich in carbonaceous materials, such as swine wastewater, the nitrifying bacteria have a very slow growth rate relative to other microorganisms. These heterotrophic microorganisms compete successfully for limited oxygen, having a growth rate five times higher than that of nitrifiers (Figueroa and Silverstein, 1992). Even when oxygen is supplied, the nitrifying population needs an adaptation period to reach a minimum concentration before oxidation to nitrate begin. These concepts are illustrated in the nitrification experiments of Blouin and coworkers (1989). They first tried to nitrify stabilized swine waste through aerobic treatment. Stabilized waste is that found after primary treatment, such as in anaerobic lagoons. This type of wastewater contains very low concentrations of nitrifying bacteria: e.g. less than 0.09 most probable number (MPN) per milliliter of nitrosomonas and 2.3 MPN/mL of nitrobacteria (Blouin et al., 1989). Ammonia nitrogen, which was in high concentration (~1000 mg L^{-1}), was not oxidized after 49 days of incubation. However, when the same waste was first inoculated with both enriched nitrifying populations (10^6-10^7 MPN/mL), only 5 days were needed to obtain complete nitrification.

Encapsulated Nitrifiers

The immobilization of microorganisms in polymer resins is a widely applied technique in drug manufacturing and food processing. The application for wastewater treatment has been recently developed and tested in Japan and there are currently several full-scale municipal wastewater treatment plants using this technology (Pegasus process).



Through the immobilization process the nitrifying microorganisms are provided with a very suitable environment to perform at maximum effectiveness. The nitrifiers are entrapped in 2 to 3 mm pellets made of

polymers that are permeable to ammonia, oxygen and carbon dioxide needed by these microorganisms, resulting is a fast and efficient removal of ammonia-nitrogen (Takeshima et al., 1993). Typical materials are polyethylene glycol (PEG) and polyvinyl alcohol (PVA) polymers. These pellets are functional for more than 10 years (Y. Nakayama, pers. comm.) and can remove high amounts of ammonia. Wastewater is treated in a nitrification tank equipped with a wedge-wire screen to retain the pellets inside, and a whole-floor aeration system to ensure high oxygen transfer and appropriate fluidization of the pellets. Pellet volume is about 5 to 10 % of the total reactor volume. Tanaka and coworkers (1991) found that the nitrification rate with this technology can be three times higher than those of the conventional activated sludge processes. This shorter retention time results in smaller reactors. This is important when assessing the application of nitrification technologies for animal systems because aeration cost can be a limiting factor.

Application to Swine Wastewater Treatment.

The rate of nitrification with PEG pellets is about 250 mg of ammonia-N per L per day at a 7.5 % pellet to total volume ratio (Tanaka et al., 1991). On the other hand, an operation with 1000 pigs (avg. pig weight = 120 lb) needs to dispose about 3.2 kg N per day after lagoon treatment (Barker and Zublena, 1995). Thus, a small reactor with 12.8 m^3 volume (~ 1.8 x 2.2 x 3.3 m) is required to nitrify this effluent. Of course, the size may be smaller if the nitrifying bioreactor is used to complement land application. Our measurement of oxygen demand in lagoon effuent from the Duplin Co. farm showed a BOD_5 of 97.4 ± 0.7 and a carbonaceous BOD of 46.4 ± 2.2. This means that waste stabilization conditions are adequate to use PEG technology. We are currently doing research to evaluate the use of this technology for swine wastewater.

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