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Polyacrylamide preparations for protection of water quality threatened by agricultural runoff contaminants

James A. Entry^{a,*}, R.E. Sojka^a, Maribeth Watwood^b, Craig Ross^c

^aUSDA Agricultural Research Service, Northwest Irrigation and Soils Research Laboratory, 3793 North 3600 East, Kimberly, ID 83443, USA

^bDepartment of Biological Sciences, Idaho State University, Campus Box 8007, Pocatello, ID 83209, USA

^cLandcare Research, Private Bag 11 052, Palmerston North, Massey University Campus, New Zealand

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"Capsule": Polyacrylamide preparations show promise in reducing flow of sediments, nutrients and microorganisms from animal production facilities.

Abstract

Waste streams associated with a variety of agricultural runoff sources are major contributors of nutrients, pesticides and enteric microorganisms to surface and ground waters. Water soluble anionic polyacrylamide (PAM) was found to be a highly effective erosion-preventing and infiltration-enhancing polymer, when applied at rates of 1–10 g m⁻³ in furrow irrigation water. Water flowing from PAM treated irrigation furrows show large reductions in sediment, nutrients and pesticides. Recently PAM and PAM+CaO and PAM+Al(SO₄)₃ mixtures have been shown to filter bacteria, fungi and nutrients from animal wastewater. Low concentrations of PAM [175–350 g PAM ha⁻¹ as PAM or as PAM+CaO and PAM+Al(SO₄) mixture] applied to the soil surface, resulted in dramatic decreases (10 fold) of total, coliform and fecal streptococci bacteria in cattle, fish and swine wastewater leachate and surface runoff. PAM treatment also filtered significant amounts of NH₄, PO₄ and total P in cattle and swine wastewater. This points to the potential of developing PAM as a water quality protection measure in combination with large-scale animal feeding operations. Potential benefits of PAM treatment of animal facility waste streams include: (1) low cost, (2) easy and quick application, (3) suitability for use with other pollution reduction techniques. Research on the efficacy of PAM for removal of protozoan parasites and viruses and more thorough assessment of PAM degradation in different soils is still needed to completely evaluate PAM treatment as an effective waste water treatment. We will present analysis and feasibility of using PAM, PAM+Al(SO₄)₃, and PAM+CaO application for specific applications. Our results demonstrate their potential efficacy in reducing sediment, nutrients and microorganisms from animal production facility effluents. Published by Elsevier Science Ltd.

Keywords: Polyacrylamide (PAM); Effluent treatment; Water pollution; Pollution reduction; Polymers

1. Introduction

Agriculture is the most wide spread source of water pollution in the United States (USEPA, 1998). For decades, most surface water quality protection from agriculture has focused on soil erosion and related non-point sources that contribute to surface water contamination. The soil erosion control literature is voluminous and links to surface water quality are well

documented. In the last decade, there has been an enormus shift in animal rearing towards large scale confined animal feeding operations (CAFOs).

CAFOs are the primary source of agricultural pollution and pose a number of risks to water quality and public health due to the large amount of manure generated. US Environmental Protection Agency (EPA) estimates that animal waste production in 1992 was 13 times greater on a dry weight basis than human production. Sources of water pollution from CAFOs include direct discharges, open feedlots, treatment and storage lagoons, manure stockpiles and land application of manure to fields. Animal waste from CAFOs are a major source of enteric microorganisms (Fraser et al., 1998; Howell et al., 1995, 1996; Mawdsley et al., 1995)

^{*} Corresponding author. Tel.: +1-208-423-6553; fax: +1-334-423-

E-mail addresses: jentry@nwisrl.ars.pn.usbr.gov (J.A. Entry), sojka@kimberly.ars.pn.usbr.gov (R.E. Sojka), watwmari@isu.edu (M. Watwood).

and nutrients such as nitrogen (N) and phosphorus (P; Hubbard et al., 1998; Snyder et al., 1998, Jordan et al., 1993) to our nation's water systems.

Dairy and other CAFOs, such as hog production operations are a major agricultural industry in the United States. In 1992, total farm gate revenues across each of the livestock and poultry industries totaled \$84.6 billion (USEPA, 1998). However, these operations are also a primary source of pollution and pose a number of risks to water quality and public health due to inability to manage and dispose of the large amount of manure generated. The number and size of animal feeding operations in the United States has been steadily increasing in the last 10 years (USEPA, 1998).

The EPA estimated that in 1992, there were about 510,000 animal production facilities in the United States which produced an estimated 2.07 trillion tons of manure. According to the EPA's 1996 National Water Quality Inventory, agricultural operations, especially animal production facilities, contribute to the impairment of at least 173,629 miles of rivers, 3,183,159 acres of lakes and 2971 square miles of estuaries. Twenty-two states reported on the impacts of specific types of agriculture on rivers and streams, attributing 20% of the agricultural impairment to animal production facilities. These findings, as well as incidents of waste spills, excessive runoff, leaking storage lagoons and odor problems, have heightened the public awareness of environmental impacts from animal production facilities. Clearly a major problem exists which constitutes a number of risks to water quality and public health.

Pollution of surface flow and groundwater from the application of animal waste to soils has been documented (Mallin et al., 1997; Mawdsley et al., 1995; Khaeel et al., 1980). Liquid-waste discharge onto soil initiates solute and microbe movement into the soil that follows natural ground water drainage patterns and contaminates adjoining surface water. These same bodies of water are often sources of drinking water and/or used for recreational activities. Human contact with recreational waters containing intestinal pathogens is an effective method of disease transmission. Therefore, it is critical to employ appropriate treatment strategies in order to maintain the quality of our lakes and streams and keep them free of intestinal pathogens and excess nutrients.

Increased N and P concentrations in water can alter the function and stability of many riparian and aquatic ecosystems. Most aquatic ecosystems develop in conditions limited by N and P. In the past few decades, intensive fertilization has contributed to the accumulation of these elements in aquatic environments (David and Gentry, 2000; Edwards et al., 2000; Sharpley et al., 2000; Vitousek et al., 1997; Koch and Reddy, 1992; Lebo and Sharp, 1993). Changes in flora and fauna have been attributed to increased input of nutrients

(Stevenson et al., 1993; Cooper and Brush, 1993; Koch and Reddy, 1992; Davis, 1991). Increased N and P in wetland ecosystems may also cause eutrophication, creating an abnormally high oxygen demand and often resulting in the death of many aquatic organisms (Cooper and Brush, 1993).

Management practices that are currently used to mitigate the input of pollutants from animal waste to surface and groundwater include control of animal numbers (Gary et al., 1985; Jawson et al., 1982), control of animal diet (Diez-Gonzalez et al., 1998), constructed wetlands, and riparian filterstrips (Coyne et al., 1995, 1998; Walker et al., 1990; Young et al., 1980). However, there are several problems with vegetative systems; (1) vegetation in wetlands or riparian areas can take from months to years to establish, (2) vegetative systems are not effective when vegetation is not growing (winter months) and can become nutrient sources rather than nutrient sinks (Hubbard et al., 1998; Snyder et al., 1998, Jordan et al., 1993), (3) riparian filterstrips or constructed wetlands are effective for only small quantities of runoff (relatively infrequent or low intensity runoff events) because continuous application can quickly overload the vegetative system's ability to withdraw nutrients (Entry et al., 2000a,b; Hubbard et al., 1998; Snyder et al., 1998; Jordan et al., 1993), and (4) vegetative systems can not be transported to the site of a waste spill or runoff area. Therefore, even when best management practices are used, animal production operations can sometimes contribute large amounts of nutrients and enteric microorganisms to watercourses.

Since the early 1990s use of polyacrylamide (PAM) has been shown to be an effective strategy for erosion control and water quality protection (Lentz and Sojka, 1994). The application of anionic polyacrylamide (PAM) to soils and/or vegetative treatments may also provide a cost-effective way to dramatically reduce bacteria and nutrient loads in animal waste effluent and thereby reduce pollution in surface and ground waters receiving these effluents. PAM application can be used alone or in conjunction with vegetative strategies, which may then operate more effectively due to reduced contaminant loads in waste streams entering the system.

2. Polyacrylamide

Polyacrylamide (PAM) is a generic chemistry term, referring to a broad class of compounds. There are hundreds of specific PAM formulations that vary in polymer chain length and number and kinds of functional group substitutions. In some chain segments PAM amide functional groups are substituted with groups containing sodium ions or protons. They freely dissociate in water, providing negative charge sites (Fig. 1). In PAM formulations used for erosion control,

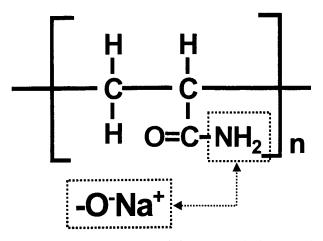


Fig. 1. Diagram of a repeating unit in a polyacrylamide molecule, showing potential substitution of a sodium formate functional unit to allow aqueous dissociation of Na⁺ to provide a net negative charge site on the polymer macro molecule.

typically one in five chain segments provide a charged site in this manner. These formulations are water soluble (linear, not gel-forming, not cross-linked, not super water-absorbent) anionic polymers with typical molecular weights of 12–15 Mg mol⁻¹ (more than 150,000 monomer units per molecule). They are commercially available as industrial flocculent polymers that accelerate separation of solids from aqueous suspensions in sewage sludge dewatering, mining, paper manufacture, clarification of refined sugar and fruit juices and as a thickening agent in animal feed preparations.

Large anionic PAM molecules are used for erosion control mainly for environmental and safety considerations. Commercial, anionic, moderate molecular-weight PAM products for erosion control are usually of two types. The most commonly used PAM products are fine granular forms. The second most common product formulations are concentrated liquid emulsions of PAM and mineral spirits. The latter category includes "inverse emulsions" that contain a surfactant to help disperse the PAM when mixed with water. Emulsions are more commonly used with sprinkler PAM application than in furrow irrigation. Both granular materials and emulsified concentrates require substantial turbulence or agitation and high flow rate at the point of addition to water in order to dissolve PAM.

2.1. Polyacrylamide use for erosion control

Soil stabilizing polymers were used to aid road and runway construction in World War II (Wilson and Crisp, 1975). Uses were adapted for agriculture in the early 1950s (Weeks and Colter, 1952). PAM and other conditioners improved plant growth by reducing soil physical problems by stabilizing aggregates in the entire 30-40 cm tilled soil depth. In this approach hundreds of

kilograms per hectare of PAM were applied over the course of several spray and tillage operations. Material and application costs limited PAM-use to high value crops, nursery operations, etc. By the 1980s polymer costs, formulations and purity improved. Paganyas (1975) and Mitchell (1986) noticed reduced sediment in runoff when irrigating furrows after pretreatment with PAM. Malik et al. (1991b) found that PAM, applied via infiltrating water, is irreversibly adsorbed in the top few millimeters of soil once dry.

In the 1990s, water soluble anionic PAM was found to be a highly effective erosion-preventing and infiltration-enhancing polymer, when applied at rates of 1-10 g m^{-3}) in furrow irrigation water (Lentz et al., 1992; Lentz and Sojka, 1994; McCutchan et al., 1994; Trout et al., 1995; Sojka and Lentz, 1997; Sojka et al., 1998a, c). Coulombic and Van der Waals forces attract soil particles to PAM (Orts et al., 1999, 2000). These surface attractions stabilize soil structure by enhancing particle cohesion, thus increasing resistance to shear-induced detachment and preventing transport in runoff. The few particles that detach are quickly flocculated by PAM, settling them out of the transport stream. Modest amounts of Ca++ in the water shrink the electrical double layer surrounding soil particles and bridge the anionic surfaces of soil particles and PAM molecules, enabling flocculation (Fig. 2; Orts et al., 2001; Wallace and Wallace, 1996).

Calcium electrolytes are needed in irrigation water when using anionic PAM for infiltration and erosion control (Orts et al., 2001; Wallace and Wallace, 1996). Calcium ions act as a bridge between anionic soil surfaces and the anionic PAM macromolecule. Calcium has a double charge and small hydrated radius which favors flocculation. By contrast, sodium ions have a large hydrated radius which impairs ion bridging, generally leading to dispersion rather than flocculation of solids. Lentz and Sojka (1996) noted that when irrigation water sodium adsorption ratio (SAR) was increased from 0.7 to 9.0 [m mol_c l⁻¹]^{0.5} that PAM's infiltration enhancement over control water was greatly diminished. Water low in electrolytes or with high SAR can be easily amended through addition of gypsum (calcium sulfate) or calcium nitrate fertilizer. PAM has been used in conjunction with gypsum to accelerate leaching of sodic soils, by reducing surface sealing (Malik et al., 1991a).

PAM delivery via irrigation water is very efficient, because it needs only stabilize the thin veneer of soil directly active in the erosion process. In furrow irrigation, PAM treats only about 25% of the field surface area to a few millimeters depth, thus only 1–2 kg ha⁻¹ of PAM per irrigation is required to halt erosion and improve infiltration (Fig. 3). PAM achieves its result by stabilizing soil surface structure and pore continuity (Fig. 4).

In 1995, the United States Natural Resource Conservation Service (NRCS) published a PAM-use conservation practice standard (Anonymous, 1995) which was revised in 2000. PAMs were first sold for erosion control in the United States in 1995, and by 1999 about 400,000 ha were PAM-treated in the United

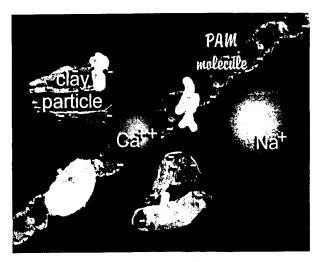


Fig. 2. Conceptual diagram of a polyacrylamide molecule adhering to soil particles, a calcium ion with relatively small hydrated radius, a sodium ion with a relatively large hydrated radius and microorganisms. The diagram is not to scale.

States. The United States' market is expected to continue to grow as water quality improvements are mandated by new Federal legislation and court action, and since PAM use is one of the most effective, economical and least intrusive management approaches recently identified that can meet the needed water quality improvement. With continued research, PAM-use has also been found effective for soil stabilization of construction sites and road cuts. Statewide standards for these uses having been formalized in Wisconsin and is being considered in other states.

PAM reduced sediment in furrow irrigation runoff 94% in 3 years of studies in Idaho (Lentz and Sojka, 1994). The original 1995 NRCS PAM application method called for dissolving 10 g m⁻³ PAM in furrow inflow water as it first crosses a field (water advance—typically the first 10–25% of an irrigation duration). Using this method PAM dosing is halted when runoff begins. The PAM applied during water advance generally prevents erosion throughout a 24 h irrigation. Application amounts dissolved in the advancing stream, usually total 1–2 kg ha⁻¹ per irrigation. For freshly formed furrows, Lentz and Sojka (1999) reported that on 1–2% slopes, the effectiveness of applying PAM at a uniformly dosed inflow concentration varied with inflow-rate, PAM concentration, duration of furrow





Fig. 3. Photo of water flowing in irrigation furrows without polyacrylamide treatment of the water (left) and after polyacrylamide treatment of the water (right).

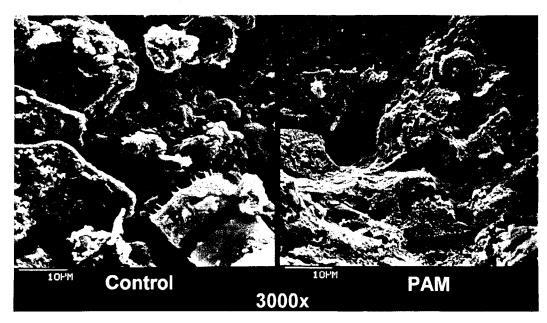


Fig. 4. Scanning electron photographs of soil without polyacrylamide added to the irrigation water (left) and after polyacrylamide treatment of the water (right). Note the matting of the polyacrylamide residue, which is thought to increase soil structural stability and increase force needed to induce the particle detachment that causes erosion.

exposure, and total amount of PAM applied. Erosion control with PAM was similar for three application methods: (1) application of 10 kg ml⁻¹ dissolved in the advance, (2) application of 5 kg ml⁻¹ during advance, followed by 5–10 min of 5 kg ml⁻¹ re-application every few hours, or (3) continuous application of 1–2 kg ml⁻¹. Continuous application of 0.25 kg ml⁻¹ controlled erosion about one third less effectively.

Furrow irrigators often use a simple application strategy which they call the "patch method". This involves spreading dry PAM granules along the first 1 to 2 m of furrow below the inflow point. The amount of granules to apply can be estimated on an area-equivalent basis—furrow spacing×length at a 1-2 kg ha⁻¹ field application rate. Typical patch doses are 15-30 g/furrow (approximately half ounce to an ounce or teaspoon to tablespoon amounts). When water flows over this "patch" of dry granules, a thin slimy PAM mat forms that slowly dissolves during the irrigation. Advantages and disadvantages of each application method depend on field conditions and system requirements (Sojka et al., 1998b).

In medium- to fine-textured soils (loams and clays) furrow irrigation stream advance is usually slower when using PAM, especially for the first irrigation on newly formed or cultivated furrows (Sojka et al., 1998a, c). The infiltration rate of PAM-treated furrows on medium- to fine-textured soil is usually greater than on untreated furrows. Without PAM, surface seals form on untreated furrow bottoms, due to the destruction of soil aggregates with rapid wetting and the detachment, transport and redeposition of fine sediments in the furrow stream. Surface seals block most of the pores at the

soil surface, reducing the infiltration rate. Pore continuity is maintained when aggregates are stabilized by PAM. For equal inflows, net infiltration on freshly formed PAM-treated furrows in silt loam soils is typically 15% more, compared to untreated water. On clay, infiltration can increase 50% compared with untreated water (Sojka et al., 1998c). Sojka et al. (1998c) reported that infiltration at 40 mm tension varied among irrigations over the range 12.9–31.8 mm h⁻¹ for controls and 26.7–52.2 mm h⁻¹ for PAM-treated furrows and that infiltration at 100 mm tension varied from 12.3 to 29.1 mm h⁻¹ for controls and 22.3–42.4 mm h⁻¹ for PAM-treated furrows.

3. Environmental and safety concerns

Environmental and safety considerations of anionic PAMs have been reviewed (Barvenik, 1994; Bologna et al., 1999; Seybold, 1994). The most significant environmental effect of PAM use is its erosion reduction, protecting surface waters from sediment and other contaminants washed from eroding fields. PAM greatly reduces nutrients, pesticides, and biological oxygen demand (BOD) of irrigation return flows (Agassi et al., 1995; Lentz et al., 1998, 2001). In Australian tests of PAM, sediment, nutrient, and pesticide reductions exceeded levels achieved by traditional conservation farming methods (Waters et al., 1999a, b). There are some specific environmental issues related to PAM charge type and purity.

One important environmental and applicator safety consideration is the need to use PAMs that contain

<0.05% acrylamide monomer (AMD). AMD is a neurotoxin, but PAMs below these AMD contents are safe, when used as directed at low concentrations (Barvenik, 1994). In soil, PAM degrades at rates of at least 10% per year as a result of physical, chemical, biological and photochemical processes and reactions (Tolstikh et al., 1992; Wallace et al., 1986; Azzam et al., 1983). Because PAM is highly susceptible to UV degradation, its breakdown rate when applied at the soil surface for erosion control may be faster than the earlier-cited 10% per year reported rate, which was for biological degradation of PAM mixed into a large soil volume. PAM does not revert to AMD upon degradation (MacWilliams, 1978). Furthermore, AMD is easily metabolized by microorganisms in soil and biologically active waters, with a half life in tens of hours (Lande et al., 1979; Shanker et al., 1990). Bologna et al. (1999) showed that AMD is not absorbed by plant tissues, and apparently breaks down rapidly even when injected directly into living plant tissue.

Used at prescribed rates, anionic PAMs are environmentally safe. Cationic and neutral PAMs have toxicities warranting caution or preclusion from sensitive environmental uses. The US Department of Agriculture, NRCS specifies anionic PAMs for controlling irrigation-induced erosion. Negative impacts have not been documented for aquatic macrofauna, edaphic microorganisms, or crop species for the anionic PAMs used for erosion control when applied at recommended concentrations and rates Kay-Shoemake (1998a, b). Nitrification of added urea appears to be somewhat accelerated (approximately 10% over 2 weeks) in PAMtreated microcosm soils (Kay-Shoemake et al., 2000b), but no other significant impacts of PAM-application on fertilizer fate have been noted. Sorptive dynamics of the common pesticides, 2,4-D and atrazine, are not dramatically altered by PAM treatment of field soil samples, although some slight changes in desorption and degradation rates have been reported (Watwood and Kay-Shoemake, 2000). Even at very high concentrations, when PAMs are introduced into waters containing sediments, humic acids or other impurities, PAM effects on biota are greatly buffered due to adsorption and deactivation associated with the suspended impurities (Buchholz, 1992; Goodrich et al., 1991). Watwood and Smith (unpublished data) have found that although PAM additions to field soils do correlate with discernable changes in microbial carbon utilization patterns, these effects are totally masked by impacts of other field variables, such as crop cover type or nutrient status.

Lentz et al. (1996) studied loss of PAM into runoff and irrigation return flows. They determined that, because of PAM's high affinity for suspended sediments and soil in waste ditch streams, only 1-3% of the PAM applied left fields in runoff. Furthermore, lost PAM only traveled 100-500 m in waste ditches before being

completely adsorbed on sediments in the flow or onto ditch surfaces (Lentz and Sojka, 1996). Ferguson (1997) reported on a watershed scale test of PAM, where over 1600 ha were irrigated using PAM-treated water for a 2-week period. On any given day, about half of the 40 farms in the study were contributing runoff to the watershed's drainage, which collected in Conway Gulch, a tributary of the Boise River. Water from the fields and the drain was analyzed for P, sediment, and PAM. About half of the water in the drain was field runoff. PAM was not found detrimental to the water quality, and was detected in drain water samples only twice (<0.8 µg l⁻¹) during monitoring.

4. Polyacrylamide degradation in soil and water

PAM degradation rates in soil are estimated to be approximately 10% year⁻¹ (Barvenik, 1994). Degradation of the acryamide monomer (AMD) is fairly rapid (Kay-Shoemake et al., 1998a; Shanker et al., 1990; Lande et al., 1979). AMD was completely degraded within 5 days after applying 500 mg PAM kg⁻¹ garden soil (Shanker et al., 1990). Lande et al. (1979) applied 25 mg PAM kg⁻¹ soil and reported that half life of an AMD in agricultural soils was 18–45 h.

There have been mixed, and sometimes conflicting, reports regarding the effects of PAM application on bacterial biomass levels in soils and waters (Nadler and Steinberger, 1993; Steinberger et al., 1993; Kay-Shoemake et al., 1998a, b). Kay-Shoemake et al. (1998a) found higher culturable heterotrophic bacteria in PAM-treated soils planted to potatoes, but not in those planted to beans. These observations, along with other studies showing either increases or decreases in bacterial numbers for PAM-treated soils, indicate that these effects are likely site- specific and may interact with other important variables, such as nutrient levels, crop cover type or herbicide regimes.

Bacterial enrichment cultures, derived from PAM-treated field soils, were capable of growth with PAM as a sole source of N, but could not grow with PAM as sole C source, whereas AMD served as a sole source of both N and C for bacterial growth (Kay-Shoemake et al., 1998b). A unique PAM-specific amidase has been described (Kay-Shoemake et al., 1998a, b). This enzyme, which is apparently induced by the presence of PAM in soils, breaks amide linkages found in PAM, releasing NH₄⁺, which is rapidly taken up by bacteria during growth. In laboratory incubations, 20% N was removed from added PAM preparations over a period of 120 h (Kay-Shoemake et al., 1998b).

PAM-specific amidase activity has been documented in laboratory cultures, as well as in field soil samples, following exposure to PAM (Kay-Shoemake et al., 1998b) The enzyme appears to have a broad substrate range, exhibiting activity against formamide and propionamide, but does not dramatically impact degradation rates of carbaryl, diphenamid or naphthalene acetamide in PAM-treated soils (Kay-Shoemake et al., 2000a). Both intracellular and extracellular activity have been noted, and production and secretion of the enzyme appears to be dependent on C availability, as cells cannot derive C directly from PAM.

Taken together, these results indicate that the most likely mechanisms of PAM degradation in soils and water include removal of N by microbial activity and breakage of the linear chain via UV and shear forces in the field. This combination of effects likely leads to the production of polyacrylates of various chain lengths. Kawai (1993) documented that polyacrylate with molecular weight $\leq 10,000$ is subject to complete mineralization, leading to the ultimate production of CO_2 and H_2O .

5. Polyacrylamide use for removal of enteric bacteria and nutrients from wastewater

Sojka and Entry (2000) found that after water traveled 1 m at 7.5 and 15.5 l min-1, PAM-treatment reduced algae, total bacterial and microbial biomass and total fungal biomass relative to the control treatment. After water traveled 40 m at 7.5, 15.5, and 22.5 l min⁻¹, PAM-treatment reduced algae, the numbers of active and total bacteria, active and total fungal length, total bacterial biomass, total fungal and microbial biomass relative to the control treatment. In a study to determine the efficacy of PAM to remove enteric bacteria and nutrients from animal wastewater, Entry and Sojka (2000) found that PAM+Al(SO₄)₃, and PAM + CaO mixtures reduced populations of total and fecal coliform bacteria and fecal streptococci in cattle, fish, and swine wastewater leachate and surface runoff by approximately 100-1000 fold compared with no treatment.

Entry et al. (2002) found that PAM reduced populations of total coliform and fecal coliform bacteria in swine manure leachate from columns containing four different soil types, ranging from sand to clay, by at least 10 fold compared with soil columns without PAM (Entry et al., 2002). In the same study, $PAM + Al(SO_4)_3$, and PAM + CaO treatments reduced populations of total coliform and fecal coliform bacteria in the same leachate from 10 to 100 fold in all three manure sources compared with the control treatment and from 100 to 1000 fold compared with the source manure. Since PAM, $PAM + Al(SO_4)_3$, and PAM + CaO seem to be indiscriminate to the type and species of microorganisms removed from water, one might speculate that these mixtures could effectively remove a large range of pathogenic bacteria and fungi as well as parasitic protozoa including Cryptosporidum parvum and Giardia lamblia from flowing water. The PAM mixtures should not be expected to sterilize water, but they should be able to substantially reduced the numbers of pathogenic bacteria in runoff prior to entering public water systems. Water treatment with lower concentrations of pathogenic microorganisms, should entail reductions in energy, disinfectant and filtration associated with the purification process.

PAM + Al(SO₄)₃, and PAM + CaO compounds also removed significant amounts of NH₄⁺, PO₄⁻³ and total P in cattle and swine wastewater leachate and surface runoff (Entry and Sojka, 2000). These compounds should be able to reduce these pollutants from wasteflowing from animal confinement areas. PAM + Al(SO₄)₃, and PAM + CaO compounds did not remove significant amounts of NH₄, PO₄ and total P from fish wastewater leachate or surface runoff. However, there were substantially lower concentrations of NO₃, NH₄⁺, PO₄⁻³, total P, K, Ca and Mg in fish waste than cattle or swine wastewater. If nutrient concentrations in wastewater are low, there is less chance that they will contact binding sites on the PAM molecule or Al^{+3} and Ca^{+2} . Therefore $PAM + Al(SO_4)_3$, and PAM + CaO may be unable to further remove nutrients from wastewater when nutrient concentrations are already extremely low.

Columns containing sandy soils PAM + Al(SO₄)₃ or PAM + CaO application to soil surface reduced NH₄ concentrations in leachate (Entry and Sojka, 2000). The PAM + Al(SO_4)₃, and PAM + CaO treatments reduced NH₄ concentrations in leachate compared with the source wastewater and control treatment. The PAM+CaO treatment reduced NO₃+ concentrations in leachate compared with the source wastewater and control treatment. Columns containing sandy loam soils without PAM + Al(SO₄)₃ or PAM + CaO reduced PO₄⁻³ concentrations in leachate compared with source wastewater. The PAM + Al(SO₄)₃ and PAM + CaO treatments applied to sandy loam soils reduced PO₄⁻³, concentrations in leachate compared to the source wastewater and control treatment. Columns containing sandy loam soils without PAM + Al(SO₄)₃ or PAM + CaO reduced total P concentrations in leachate compared with source wastewater. $PAM + Al(SO_4)_3$ and PAM + CaO treatments reduced total P concentrations in leachate compared with the source wastewater and control treatment.

The efficacy of PAM compounds to remove total and fecal coliform bacteria water in field soils (Entry et al., submitted for publication) was much lower than the values reported in the manure study (Entry and Sojka, 2000). The main difference between the two studies was that water was flowing at 8.6 l min⁻¹ when manure types were varied and at 60 l min⁻¹ when soil types were varied. When water was flowing over PAM + Al(SO₄)₃

or PAM + CaO patches at 60 l min⁻¹, the PAM granules most likely did not throughly mix throughout the water column. Sojka and Entry (2000) showed that bacteria were effectively removed from water flowing in furrows at rates from 7.5 to 22.5 l min⁻¹. As flow rates increased, PAM removed a smaller percentage of bacteria from water. PAM + Al(SO₄)₃ or PAM + CaO patches are increasingly effective at lower flow rates. When PAM molecules are dissolved in water and adhere to microorganisms or nutrients they may stay dissolved until the molecule adheres to an object that is heavy enough to settle out of the flow. This would explain why PAM, PAM + Al(SO_4)₃ and PAM + CaO in faster flowing water is not as effective as the same treatments in slower flowing water. The effectiveness of these compounds may be increased if sand or silt size particles are present in the water flow. Various PAM formulations are routinely used in municipal water treatment facilities for sewage sludge dewatering and for finish treatment of potable drinking water. The ability of PAM to flocculate microorganisms and remove them from water treatment facilities has been understood for some time (Barvenik, 1994).

6. Future research

Future research may be directed toward efficacy of PAM-related compounds to remove specific bacterial species from waste water. We have not found reports investigating the ability of PAM compounds to remove specific species of disease causing bacteria or fungi. These tests may require the release of specific bacteria such as Escherichia coli O157H7 or Salmonella typhi in controlled water environments. We have not found investigating the efficacy reports $PAM + Al(SO_4)_3$, and PAM + CaO to remove protozoan parasites such as Giardia lamblia, Cryptosporidum sp. including C. parvum, Entamobea histoltica in a free living and cyst form. Since PAM compounds remove larger organisms like fungi and algae from waste water, we speculate that they might remove protozoans with similar efficiency.

Diseases due to viral infections that can be transmitted by water range from dermatitis caused by Schitsoma sp. to the fatal illness Meningoecephalitis caused by Nageleria fowleri. PAM related compounds may remove viruses from waste water less efficiently than bacteria because of the viruses smaller size. However, if viruses are preferentially attached to soil particles or larger organisms they may be removed from water more efficiently than free floating virus particles or some bacteria.

We have tested the efficacy of PAM, PAM + $Al(SO_4)_3$, and PAM + CaO to remove algae, total and active bacteria and total and active fungi and total and fecal

coliform bacteria in fresh water in Southern Idaho (Sojka and Entry, 1999; Entry and Sojka, 2000) and total and fecal coliform bacteria in fresh water in Queensland, Australia (Entry et al., 2002). The efficacy of PAM, PAM + Al(SO₄)₃, and PAM + CaO to remove disease causing organisms from marine or brackish water has not been tested. If PAM can remove microorganisms from marine or brackish waters the compound may become a new tool to protect coastal areas from microbiological pollution.

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