



Technical Report: TR01.1

Polymer Coagulants and Flocculants for Stormwater Applications

INTRODUCTION - STORMWATER TREATMENT AND COAGULATION/FLOCCULATION

Many construction, highway, and other projects have traditionally relied on erosion control and passive gravitational settling methods to remove suspended material from stormwater and runoff. Today however, many projects, especially those under strict discharge permit requirements or with difficult-to-clarify water, are finding that an active treatment system using a coagulation and/or flocculation system offers significant cost, efficiency, and water quality benefits.

Polymer coagulation/flocculation systems for stormwater offer higher flow rates, reduced holding basin volume, increased sediment removal efficiency, and improved water quality. Automated control, monitoring and measurement systems assure reliable, low maintenance operation, and provide comprehensive reporting and compliance documentation.

Numerous polymer coagulants and flocculants are available, generally with unique performance, toxicity, and other characteristics. Although polymers have been used for many years in industrial and other applications, their application to stormwater is relatively new. Consequently until now there has been little quantitative data available evaluating polymers under the conditions of stormwater treatment systems.

This report presents the results of a series of tests performed to evaluate and compare performance, aquatic safety, and cost of four common polymers that are in use today. They include two synthetic polymers (aluminum chlorhydroxide and DADMAC) and two derived from “natural” materials (Mimosa tree bark and Chitosan). The report will first present an overview of coagulation and flocculation applied to stormwater treatment, followed by the test methods and results.

COAGULATION AND FLOCCULATION PRIMER

Stormwater typically contains suspended, colloidal, and dissolved materials:

- *Suspended solids* are particles which are not dissolved in water and are captured by gravimetric analysis on a 0.45 micron (μm) filter. This includes silt (2.0-50.0 μm), clay (less than 2.0 μm), and organic materials. Suspended solids are visible to the naked eye or through an ordinary microscope and contribute turbidity or “cloudiness” to the water. Such particles are large enough for removal by settling, flotation, or filtration.
- *Colloids* are dispersed particles which are not visible under ordinary microscopes (1-1000 nanometers). Colloids can include clay minerals, iron or manganese oxides, and bacteria and algae. Colloidal particles have such large surface areas relative to their mass that gravitational forces do not influence their suspension, as occurs with suspended solids. Colloidal particles are often largely responsible for the color of natural waters.

- *Dissolved solids* are those which are soluble in water and cannot be removed by processes such as filtration. Metals and chloride are typical examples of dissolved solids.

Very fine grained or colloidal materials can be difficult to remove quickly and efficiently. While dense particles such as sand and coarser materials are effectively removed by simple gravity sedimentation, finer or lower density materials are often difficult or impossible to remove by settling in a reasonable amount of time.

Sediment settling is improved when particle diameters are increased. The primary processes for increasing particle diameter to allow efficient settling are coagulation and flocculation.

Clays and most organics, which are the most common found in natural waters, are negatively-charged at a neutral pH (pH 7). This net negative charge results in stable particle suspensions due to the repulsive forces between each particle. Their effective removal requires the addition of a positively-charged coagulating or flocculating agent that neutralizes the negative charge.

Coagulation and flocculation are defined as:

Coagulation - the process by which particles are destabilized by neutralizing their electric charge, which allows particle agglomeration to occur

Flocculation - the process of physical bridging of particles, which relies primarily on the size (or molecular weight, which represents polymer chain length) of the flocculant molecule, rather than charge neutralization.

Inorganic aluminum or iron compounds have traditionally been the most widely used coagulants. However, synthetic organic polymers are also effective coagulants or flocculants because of their high density of charged sites. Synthetic organic polymers are produced by the polymerization (or chemical combination, usually by covalent bonding) of small chemical units, to form long-chain polymers of high molecular weight and variable charge.

Polymers that function primarily by charge neutralization are considered to be coagulants, whereas polymers that remove particulates by both charge neutralization and bridging are flocculants.

Water treatment polymers are predominantly water-soluble, and are classified as cationic (positively charged), anionic (negatively charged), nonionic (neutral), or amphoteric (changeable, depending on the pH of the water).

Cationic polymers offer significant operational and cost benefits when used for coagulation and flocculation of runoff and stormwater, especially for water with high concentrations of colloidal materials. Those benefits include:

- Polymers can increase sedimentation rates by a factor of 10, and often much higher.
- This allows higher flow rates and reduced holding tank or basin volume.
- Improved effluent water quality – effluent typically less than 10 NTU and usually does not exceed 50 NTU during storm events
- Minimizing or reducing sludge volumes, minimizing chemically bound water

- Noncorrosive to treatment systems
- Low application dosages are normally required (on the order of a few 10's of ppm for turbidities of 1000 NTU), required compared to most other coagulants/flocculants
- There is no additional contribution to total dissolved solids concentrations and little to no effect on pH

POLYMER COAGULATION/FLOCCULATION SYSTEMS IN RUNOFF AND STORMWATER TREATMENT

ProTech has developed a simple and reliable system for incorporating a polymer coagulation/flocculation process into the temporary water treatment systems typically used at construction projects. The installation utilizes a polymer injection pump in the treatment system upstream from clarification tank. The injection pump is electronically linked to the metered influent flow rate, assuring a constant dosage as flow varies.

The polymer is added to the influent water in a metered dose, allowed to mix and react, forming a densified floc that settles out by gravity in the clarifier tanks. Proper mixing of the polymer and influent water is important, and can generally be assured by allowing an in-stream mixing time of about 10 seconds prior to discharge into the clarifier tank. However, systems must also be designed to prevent violent agitation or high speed mixing, which can decrease coagulant activity. Water from the gravity clarifier may then be routed through sand filters or cartridge filters for final polishing, if required for a specific project. Settled sediment is removed from the clarifier by vacuum truck, dewatered, and disposed of either on site or at a local landfill.

Proper polymer dosage is critical to minimize toxicity concerns as well as optimizing system efficiency and effluent water quality, regardless of the specific polymer in use. The optimum dose (determined by a series of jar tests) is proportional to the mass of suspended solids in the system, and the volume of water or flow rate. Therefore the polymer should be metered into the system proportional to the mass flux of suspended particles, which can fluctuate widely under varying storm and flow conditions. The ideal metering system includes an injection pump that is metered to flow rate according to real-time measurements of suspended sediment. The suspended sediment levels can be estimated by turbidity measurements, although a better method utilizes a streaming current detector to measure the net charge of the suspended material, which allows the polymer dose rate to be based on charge balance.

COAGULANT/FLOCCULANT POLYMER TEST PROGRAM

During the development of ProTech's polymer coagulation/flocculation systems for stormwater, it became clear that there was little data presently available regarding the toxicity and sediment/water partitioning behavior of many common water treatment polymers, particularly under the conditions of typical stormwater projects. Material Data Safety Sheets (MSDS's), for example, present the toxicity of free, dissolved polymer in clean water (water containing no suspended material), which is not representative of stormwater or runoff applications, in which the polymer is mixed into turbid water.

To investigate polymer under conditions representing typical construction site runoff and stormwater, ProTech, in conjunction with GE Betz, has conducted a research program evaluating polymer coagulant/flocculant behavior. We have evaluated the following aspects of four common polymers:

- Clarification efficiency (dose/response) - the effectiveness and efficiency of a polymer to clarify turbid water
- Aquatic toxicity – the toxicity of runoff water dosed with polymers to aquatic organisms
- Benthic toxicity – the toxicity of sediment resulting from polymer coagulation/flocculation to benthic organisms
- Cost – polymer cost per volume of stormwater treated

The four polymers evaluated were:

- Aluminum Chlorhydroxide - (Al₂Cl(OH)₅)
- Diallyldimethyl Ammonium Chloride (DADMAC)
- Mimosa bark-based - derived from the bark of the Mimosa tree
- Chitosan (1% solution) - derived from chitin, a component of shrimp and crab shells.

POLYMER COAGULANT/FLOCCULANT SUMMARY MATRIX

The following matrix presents a comparison of all test results in terms of relative rank, where 1 star is the lowest or worst and 4 stars is the highest or best. **Performance** refers to clarification efficiency including water quality and settled sediment volume. **Aquatic Safety** refers to the aquatic toxicity test data presented here. It is important to note that none of these polymers are toxic when applied in the proper dose, and conversely all are potentially toxic if overdosed. **Cost** refers to the polymer consumption to treat a unit volume of water. Note that equipment and most operating costs are essentially the same for all, since the treatment system design under consideration can utilize any polymer in liquid form. However, polymers with low clarification efficiency generally result in a greater volume of settled sediment, which incurs additional cost, as well as associated disposal considerations.

Specific data and discussions of individual tests are presented in the following sections.

Polymer Test Summary and Ranking				
Polymer type	Performance	Aquatic Safety	Cost	Overall
Aluminum Chlorhydroxide	☆☆☆	☆☆☆☆	☆☆	Good performance Moderate cost Toxic only if overdosed >2X
DADMAC	☆☆☆☆	☆☆☆☆	☆☆☆☆	Best performance Lowest cost Toxic only if overdosed >2X
Mimosa bark	☆☆	☆☆☆☆	☆☆☆	Moderate performance Moderate cost Toxic only if overdosed >2X
Chitosan	☆	☆☆☆☆	☆	Poorest performance Highest cost Toxic only if overdosed >2X

INDIVIDUAL TEST RESULTS

CLARIFICATION EFFICIENCY - DOSE/RESPONSE

Each polymer was tested to evaluate and compare their effectiveness and efficiency to clarify turbid water. The water for the tests was collected from a ProTech project site in the Sacramento area. The water, collected from a holding basin, contained high levels of colloidal material and iron oxides which was essentially impossible to remove by gravitational settling. Turbidity was measured at >1000 NTU. Note that although this water contained significant colloidal material and iron oxides, making it more difficult to treat than some other stormwaters, it is typical of many construction projects (particularly in the central/northern California region).

Polymer dosage was determined by a series of standardized jar tests conducted for each polymer. The first dose of each pair of data points for each polymer is considered here as the “optimum”, as it was based on the visual jar test results (i.e., the dose where the test water becomes visually clear) to determine the proper dosage. This is a standard method for determining dosage at a project, although more rigorous methods can be used, such as continuous turbidity measurements or TSS measurements.

The dose of the second of each pair of data points is double the “optimum” dose, to represent a 2X overdose (i.e., overdosed by 100%). Note that Chitosan is supplied in a 1% chitosan solution, so for example, 1000 ppm of the 1% solution is equal to 10 ppm pure Chitosan.

Polymer Clarification Efficiency Summary				
Polymer	Dosage (ppm)	Turbidity (NTU)	Conductivity (mmhos)	pH
Control	0	>1000	59	7.15
Al ₂ Cl(OH) ₅	75	38	74	7
	150	29	83	7
DADMAC	25	2	63	7.3
	50	5	61	7.3
Mimosa Bark	50	66	67	7.2
	100	41	76	7.2
Chitosan 1%	380	330	60	7.3
	600	78	81	7.0
	800	41	85	7.0
	1000	30	95	7.0
	1100*	53		
	2200*	25		

*The 1100 and 2200 ppm doses were conducted on a different water sample from the same site, because the original sample was exhausted before the 2X test could be completed

Clarification Efficiency Summary

On a dose/response basis, the DADMAC polymer is clearly the most efficient, reducing turbidity to 2 NTU at a dose of 25 ppm.

The aluminum chlorhydroxide and mimosa bark polymers yield approximately equal results, reducing turbidity to about 30-40 NTU with doses of 75-100 ppm.

Chitosan (1% solution) reduced turbidity to approximately 30 NTU at a dose of 1000 ppm, equivalent to 10 ppm pure chitosan.

AQUATIC TOXICITY

The aquatic toxicity of each polymer was determined according to EPA “Methods for Measuring Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms” (EPA/821/R-02/012, 5th edition). 96 hour static survival tests were conducted on rainbow trout and fathead minnow, and 48 hour static survival tests were conducted on daphnia magna. Water for the test was the same as that used in the clarification efficiency tests presented above, which was collected from a job site in the Sacramento Valley, with a turbidity of >1000 NTU with high levels of iron oxides and colloidal materials.

The following samples were tested:

- Untreated water was tested as a control
- Water treated with each polymer at the optimum dosage, as determined by the dose/response testing
- Water treated with each polymer at 2X the optimum dosage (overdosed by 100%)

Aquatic Toxicity Test Summary					
Polymer	Dosage (ppm)	Turbidity (NTU)	% survival		
			Daphnia Magna (48 hour)	Rainbow Trout (96 hour)	Fathead Minnow (96 hour)
Control	0	>1000	95	100	90
Al ₂ Cl(OH) ₅	75	38	95	100	95
	150	29	95	100	100
DADMAC	25	2	95	100	100
	50	5	95	100	100
Mimosa Bark	50	66	95	100	95
	100	41	100	100	100
Chitosan 1%	1100	53	100	100	100
	2200	25	100	100	100

Survival rate results below are discussed in terms of Daphnia Magna, Rainbow Trout, and Fathead Minnow, respectively, unless indicated otherwise.

Control sample results give survival rates of 95, 100 and 90%. Therefore polymer test results with the same survival rates are interpreted as indicating no toxic effects (although the small number of samples does not allow a rigorous statistical analysis, it is reasonable to assume that test results within 5% of the control results indicate no toxic effects.)

Aluminum Chlorhydroxide results were 95, 100, and 95% survival at the optimum dose of 75 ppm. This is equivalent to the Control results and indicates no increased risk or toxicity for any species. At the 2X overdose rate of 150 ppm survival rates were 95, 100, and 100%, also indicating no increased risk or toxicity.

DADMAC results were 95, 100, and 100% survival at both the optimum dose of 25 ppm and 2X overdose rate of 50 ppm, indicating no increased risk or toxicity.

Results for the Mimosa polymer were 95, 100, and 95% survival at the optimum dose of 50 ppm. This is equivalent to the Control results and indicates no increased risk or toxicity to any species. At the 2X overdose rate of 100 ppm survival rates were 100, 100, and 100%, which again indicates that the Mimosa polymer is non-toxic.

Chitosan results were 100, 100, and 100% survival at the optimum dose of 1100 ppm. This is equivalent to the Control results and indicates no increased risk or toxicity to any species. At the overdose dose rate of 2200 ppm survival rates were 100, 100, and 100%, again indicating no increased toxicity.

Treated Effluent Toxicity Summary

All four tested polymers showed no toxicity towards daphnia magna, rainbow trout or fathead minnow. This demonstrates that, when properly applied, any or all of the polymers can be safely used in a stormwater treatment system.

LC50 Values

LC50 values (i.e., 50% lethal concentration, or the concentration at which 50% of test organisms are killed) of the free polymer in clean water (i.e., not treated effluent) are presented here. Note that free polymer is essentially not present in treated effluent, as the data above indicate (otherwise toxic effects would almost certainly be observed in the treated effluent tests). In a stormwater treatment scenario, the LC50 data is relevant to a worst-case system upset, in which a volume of free polymer is somehow released to receiving waters.

More importantly however, the comparison of LC50 values points out important differences between polymers, and should clarify some popular misconceptions of natural versus synthetic polymers.

Polymer LC50 values (mg/L)			
Polymer	Daphnia Magna 48 hour	Rainbow Trout 96 hour	Fathead Minnow 96 hour
Al ₂ Cl(OH) ₅	>5000	390	517
DADMAC	17.5	0.49	1.65
Mimosa Bark	258	Not Available	1.3
Chitosan (pure solution)	13.7	1.1	6.4

Note that the $Al_2Cl(OH)_5$, a synthetic polymer, is by far the least toxic, and is in fact less toxic than many household cleaners. Chitosan is approximately equal in toxicity to DADMAC with regard to rainbow trout, which is generally considered a sensitive species. Note also, for example, that Chitosan is considered a hazardous substance according to federal Resource Conservation and Recovery Act (RCRA) standards (due to acidity, at a pH of about 4), while many synthetic polymers such as DADMAC are not RCRA hazardous.

BENTHIC TOXICITY

A series of tests was also conducted to determine the toxicity of treated sediment to benthic organisms, or the organisms that normally inhabit sediment in stream and lakebeds. The benthic toxicity of settled sediment, from water treatment with a DADMAC polymer was determined according to EPA “Methods for Measuring Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates” (EPA/600/R-99/064). Ten day whole sediment toxicity tests were conducted on the amphipod *Hyalella azteca* and the midge *Chironomus tentans*. Survival and growth of the organisms was measured on treated sediment and a control sediment, and the results compared to determine toxicity.

Tests were conducted on both the control sediment and a test sediment from a working water treatment system. The test sediment was collected from a ProTech job site in the Sacramento Valley, and was a dense, fine-grained clay-like material.

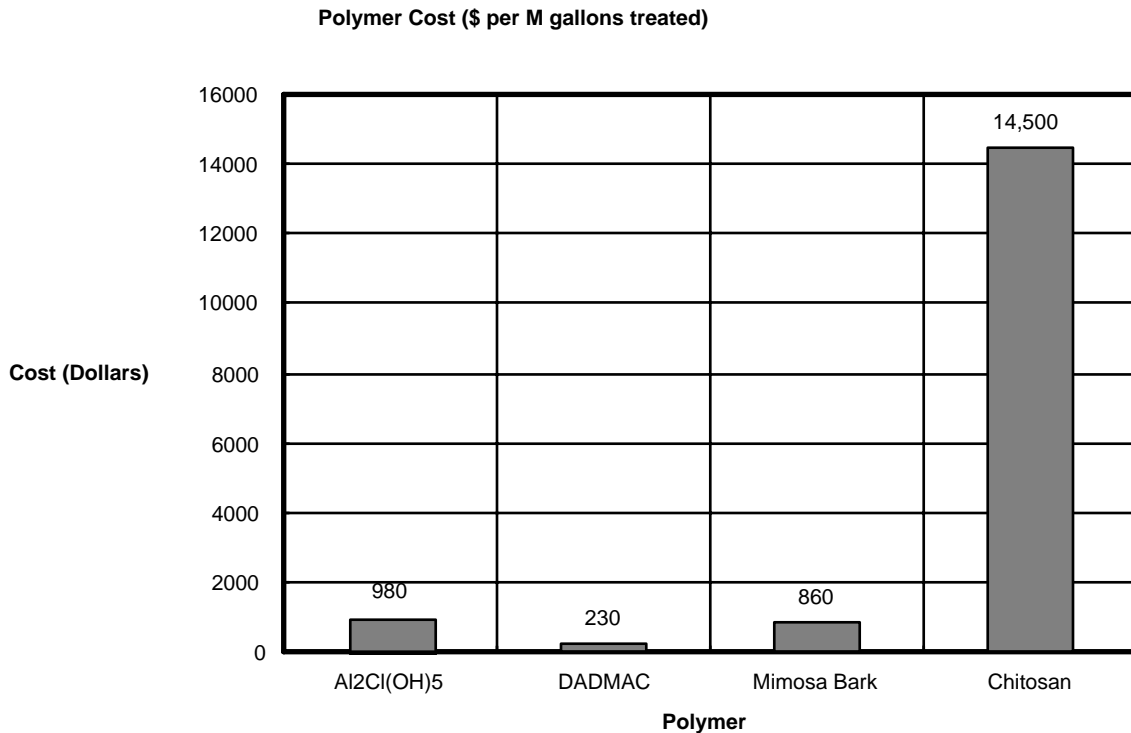
Benthic Toxicity Summary				
	H. azteca		C. tentans	
	% survival	growth	% survival	growth
Control sediment	100%	Not measured	70%	Not measured
Treated sediment	95%	0.04 to 0.14mg	68%	0.10 to 0.34mg

The results indicate that there is no statistically significant reduction in survival or growth for the treated sediment with respect to the control sediment. According to the test laboratory, the results from the control tests are typical of in-house sensitivities, and indicate that the organisms were in good condition.

The data therefore indicates that the polymer-treated sediment is effectively non-toxic. This could be for two reasons - either because the polymer is not bioavailable to benthic organisms, or because it is inherently non-toxic to the organisms. In either case, the results indicate that there would be no harmful effects to benthic organisms in the unlikely event that treated sediment was discharged to a stream or lake bed.

POLYMER COST

The following chart presents a cost comparison based on the consumption rates from the clarification efficiency study presented above, for the >1000 NTU influent water of this study. Note that this water contained significant colloidal material and iron oxides, making it more difficult to treat than some other stormwaters. However, it is typical of many construction projects (particularly in the central/northern California region). In a flow-through treatment system, equipment and most operating costs are essentially the same for all polymers, since the system can utilize any polymer in liquid form. However, polymers with low clarification efficiency generally result in a greater volume of settled sediment, which incurs additional cost, as well as associated disposal considerations. These costs are given as example only, as costs vary considerably based on region, manufacturer, and quantity.



The DADMAC polymer is clearly the least expensive, as well as the most efficient. The Aluminum Chlorhydroxide and the Mimosa Bark polymers are approximately equal in cost. Chitosan is the most expensive by a significant margin.

CONCLUSIONS

This study leads to the following conclusions:

- Polymer coagulation/flocculation is a very effective means of treating stormwater, with the ability to rapidly reduce the turbidity of difficult-to-treat waters from >1000 NTU to <50 NTU.
- Proper polymer dosage is critical in order to optimize clarification efficiency and minimize toxicity. Because the suspended solids level of stormwater varies with flow and storm events, polymer dose must be precisely metered in proportion to suspended solids levels.
- The four polymers tested here exhibit no aquatic toxicity when correctly dosed. However all polymers are potentially toxic when overdosed. This study demonstrates no toxic effects at the 2X overdose, which was the limit of the study. Therefore toxic effects are only likely to occur at >2X overdose. It is also important to note that in the event of overdosing excess polymer would quickly react with background sediments, greatly reducing potential toxic effects.
- Toxicity testing points to the necessity of an accurate and reliable polymer metering system. The metering system is the critical link in a stormwater treatment system. Any polymer can be safely applied just as any polymer can be toxic if not properly used.
- The DADMAC polymer is the most economical, not only in terms of direct polymer cost but also for settled sediment handling and disposal costs. The mimosa bark and aluminum chlorhydroxide and polymer are 3-4X as expensive, while Chitosan is by far the most expensive, with direct polymer cost at least 50X that of DADMAC.