

new polyelectrolyte emulsion breaker improves oily wastewater cleanup at lower usage

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abstract

Optimal wastewater emulsion breaking requires understanding the conditions that promote a stable emulsion, then using the best means to enhance demulsification. Demulsification methods include addition of heat, mechanical agitation, chemical interfacial modification, continuous phase viscosity modification, “neutralization” of the emulsifying agent, or reduction of electrostatic repulsive forces.

Chemical additives are integral to most emulsion breaking activity. Petroleum refinery oily wastewater emulsion breaking is usually aided by the addition of linear polyelectrolytes. Researchers have created a novel class of polyelectrolytes that deviates from the standard linear molecular structure. The new polymeric structure maximizes charge site availability for demulsification. Laboratory and field test data show that these new polyelectrolytes promote better oil/water separation than the commonly used linear types, even at lower usage rates.

introduction

This paper reviews the concepts of emulsification and demulsification, then discusses a new polyelectrolyte structure, and finally presents laboratory data and preliminary field case study results. The data suggest that the new polyelectrolyte structure effects a performance superior to conventional technologies.

The development of what we are herein calling the “new polyelectrolyte” represents an evolution in oily wastewater polymeric treatment. The class of new

polyelectrolytes represents what could prove to be the standard of choice in the future.

petroleum refinery wastewater treatment

Wastewater treatment is normally classified as primary, secondary, and tertiary. Most petroleum refineries in the United States will have facilities for primary and secondary treatment. Some have tertiary treatment facilities.

Primary wastewater treatment includes those facilities which are designed to remove easily separable solids and oils from the wastewater. Gravity separation by use of primary clarifiers or API separators followed by enhanced oil and particulate removal by use of induced air flotation (IAF) or dissolved air flotation (DAF) facilities is a common arrangement. The effluent from primary treatment facilities should contain less than 20 ppm (mg/L) of (insoluble) oil & grease. Most of the soluble organic matter normally remains with the effluent.

Secondary treatment refers to the removal of soluble biodegradable organic matter, typically by use of aerated tanks or ponds containing an activated sludge microorganism population. The aerated activated sludge unit will often have an associated clarifier (referred to as a secondary clarifier) for concentrating and reintroducing the activated sludge population to the aeration unit while producing a clear product effluent. Often the effluent from the secondary clarifier is sufficiently pollutant-free that it can be safely discharged to a receiving estuary.

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Tertiary treatment refers to any treatment which occurs downstream of the secondary treatment plant and may include such processes as sand or activated carbon filtration, oxidation, reverse osmosis, or other treatments which will remove recalcitrant pollutants to make the effluent suitable for discharge or reuse.

In this paper, application of a new polyelectrolyte will be discussed in the context of primary wastewater treatment, specifically in application to air flotation units. Air flotation units work on the concept of adding buoyancy to oil droplets and solids by addition of small air bubbles into the substrate. The bubbles attach to the oil and solids, adding buoyancy for faster separation by flotation. Skimmers remove the floating froth or sludge, leaving a refined underflow effluent. Polyelectrolyte addition to air flotation units is normally used to free emulsified oils and build floc for enhanced separation and improvement of effluent quality.

oil-in-water emulsions

Oil/water mixtures may involve two distinct phases, or they may be present in an emulsified form. In general, emulsions are stable mixtures of two immiscible liquids consisting of a discrete phase that is dispersed in a continuous phase in the form of microscopic droplets. Emulsions are further classified as either oil-in-water emulsions (i.e., oil is the discrete phase dispersed in water, the continuous phase) or as water-in-oil emulsions (i.e., water dispersed in oil). This paper discusses oil-in-water emulsions only.

The typical droplet size for emulsified oil is 0.1 to 5.0 microns. Above 5.0 microns, droplets coalesce into free oil. Below 0.1 micron, oil droplets tend to be solubilized in water and means for removal include ultrafiltration, carbon adsorption, or activated sludge biological treatment.

The stability of an emulsion is dependent upon the free energy of coalescence, which is a function of oil droplet surface area. The total surface area of oil will decrease when two drops coalesce into one larger drop. This is thermodynamically favored, as there is a resultant negative free energy. Under these conditions, demulsification is a spontaneous process. Pure two-component systems normally do not form emulsions.

Table 1: Emulsifying Agent Mechanisms

Type	Action	Results
Liquids	Surface-Activity	The agent reduces surface/interfacial tension between droplet and continuous phase.
Liquids	Chain Intertwinement	The agent adsorbs to the droplet as extended chain to increase steric hindrance to particle contact.
Solids	Particle/Particle Contact	The agent increases the electrostatic repulsion between particles.

The formation of a stable emulsion requires sufficient mixing energy in the presence of a third component which acts as an emulsifying agent. An emulsifying agent is a surface active agent that alters the characteristics of the oil/water interface. When interfacial tension between two immiscible fluids is significantly reduced, an emulsion is formed. Normally an emulsifying agent that is soluble in a particular phase will tend to make that the continuous phase. Polar, hydrophillic emulsifying agents will allow generation of oil-in-water emulsions. Examples of specific emulsifying agents found in refinery wastewaters include, surfactants, fatty acids, organic acids, metallic salts, sulfides, clay, and silt.

Emulsifying agents can be solids or liquids that operate through one or more of the generally recognized mechanisms shown in Table 1. Other factors affecting emulsion stability include pH, viscosity, density, temperature, amount of water in the emulsion, mechanical shear, agitation, and retention time.

oil-in-water demulsification

Demulsification is the process by which an emulsion is destabilized. Demulsification is a two-step process, flocculation followed by coalescence.

Coagulation/flocculation neutralizes repulsive forces that stabilize the emulsion, creating discrete droplets. The droplets coalesce, increasing in size so that they can no longer be dispersed in the continuous phase. The process is governed by Stokes' law:

$$\text{Terminal Velocity } V = 2 G r^2 (\rho_1 - \rho_2)$$

where:

- V = rate the droplet will settle or rise
 D = effective droplet diameter
 h = medium (continuous phase) viscosity
 ρ_1 = droplet density
 ρ_2 = medium (continuous phase) density
 G = gravitational constant

The rate of flocculation is influenced by the droplet size and the viscosity of the continuous phase. The density difference between the discrete phase droplets and the continuous phase medium ($\rho_1 - \rho_2$) will determine whether sedimentation or “creaming” occurs.

- For ($\rho_1 - \rho_2$) = negative; creaming occurs (i.e., droplets rise to the surface)
- For ($\rho_1 - \rho_2$) = positive; sedimentation occurs (i.e., droplets settle to the bottom)

Coalescence is the process where two or more droplets come together to form a larger, less stable droplet. Breaking of an emulsion occurs when several droplets coalesce and give rise to a bulk, free oil phase. Coalescence will increase if one or more of the following happens:

- Diffusivity increases
- Droplet size increases
- Viscosity of the continuous phase decreases
- The concentration of the discrete phase increases

The traditional methods used to enhance demulsification are based on improving the rates of flocculation or coalescence. This can be accomplished by:

- Addition of heat
- Mechanical agitation
- Chemical modification of the droplet / liquid interface
- Chemical modification of the continuous phase viscosity
- Displacement / destruction of the emulsifying agent
- Reduction of electrostatic / steric repulsive forces

Chemical demulsifiers are used to affect the last four methods list above.

demulsifier applications for breaking oil-in-water emulsions

Treatment requirements for oil-in-water emulsion breaking include chemical addition to break the emulsions and mechanical equipment to improve the oil/water separation. Various chemical agents are used to destabilize emulsions. Emulsion breakers must be capable of dispersing evenly throughout the emulsion, migrating to the interface quickly, and effectively countering the stabilizing effects of the emulsion. Mechanisms include balancing or reversing the interfacial surface tension on each side of the interfacial film, neutralizing the stabilizing electrical charges or precipitating the emulsifying agents as is done with the reactive cations H^+ , Al^{+3} , Fe^{+3} , or Ca^{+2} . Acid, aluminum and ferric and calcium salts are the main commodity chemicals used for demulsification. Emulsion breakers can be commodity or specialty chemicals. In many cases the specialty chemicals will promote superior demulsification or be more cost-effective for oil-in-water demulsification.

Table 2 (next page) lists oil-in-water demulsification techniques, along with advantages and disadvantages.

conventional polyelectrolytes

In many wastewater applications a highly charged cationic coagulant is employed to neutralize the natural negative charges of dispersed particles or oil. The charge-neutralized particles are then more readily coagulated with mixing. Addition of a small amount of a long chain linear polyelectrolyte may be employed to effect bridging of coagulated particle groups, increasing floc size and thereby improving settling characteristics (or floating — in the case of an air flotation unit). This is a two-step process, employing a high charge density inorganic or organic coagulant, followed by a long chain polymeric flocculant.

Table 2: Demulsification techniques

Technique	Method of Breaking	Advantages	Disadvantages
Simple Electrolyte Addition	Increases ionic strength which decreases emulsifier solubility; reduces charge repulsion	Simple, inexpensive	Toxic to bacteria; not effective for complex organic or solid agents
Metal Ions Addition	Changes emulsifier into insoluble metal salt if simple soap	Simple, inexpensive	Toxic to bacteria; not effective for complex organic or solid agents
Agitation	Promotes droplet contact enhancing coalescence	Simple, no chemicals needed	Energy intensive; may create more stable emulsion
pH Increase	Increasing pH will precipitate emulsifier if simple soap	Simple, inexpensive	Relatively toxic to bacteria; only works if simple soaps; can generate more complex agents; corrosive
pH Decrease	Decreasing pH will neutralize negative charges that stabilize emulsion	Simple, inexpensive	Relatively toxic to bacteria; corrosive
Inorganic Coagulants	Charge neutralization and adsorption of oil dispersed phase	Relatively low cost per pound	Relatively high sludge volume; corrosive; pH sensitive
Organic Polyelectrolytes	Charge neutralization and bridging to increase contact and settling rate; can displace/destroy emulsifier	Low sludge volumes; multi-functional; pH tolerant; lower dosages needed than with inorganics; improved separation; more easily dewaterable sludge	Relatively high cost per pound for specialty chemicals

recent advances in polyelectrolyte technology - the new polyelectrolyte

A new polyelectrolyte, the subject of this paper, was designed to accomplish both functions with a single multifunctional molecular structure. This product consists of an array of block copolymers, each block being either hydrophilic or hydrophobic. Block copolymers exhibit unique properties and as a result, are more desirable than random copolymers or a blend of homopolymers. By synthetic manipulation of the functional groups in the block copolymer, a much more effective polymer has been designed. The main advantage over the two-product coagulant/flocculant conventional treatment is that both functions are provided by a single product.

The main advantages over linear flocculants are as follows.

- Whereas linear polymers can coil and fold upon themselves, rendering some of the charged

monomers unreachable or unusable for particle neutralization, the block polymer design includes purposeful placement of charged monomers towards the outermost ends of the radially protruding branches. This configuration maximizes charged monomer utility for particle charge neutralization. Charged monomeric units are thus not wasted at unavailable sites.

- The new polyelectrolyte configuration maximizes multi-particle contact, resulting in bridging activity that is theoretically superior to that of a conventional linear polyelectrolyte.

Researchers have designed this product in accordance with the goals of achieving improved product or pollutant recovery from wastewaters, with the use of less polyelectrolyte.

benchtop testing

To evaluate the performance of the new polyelectrolyte, oily wastewater from an induced air flotation (IAF) application at a western refinery was chosen as a test substrate. A Wemco laboratory flotation machine was used to generate data for comparing the performance of the new polyelectrolyte with a conventional linear cationic polyacrylamide of equivalent charge density and molecular weight. The properties of the substrate were: 6.6 pH, 1000 ppm (mg/L) total solids, 87.5 NTU turbidity.

Test conditions employed for the Wemco cell evaluation were 15 seconds of agitation at 900 rpm without air addition, followed by 30 seconds of air injection, followed by froth collection. Subnatant samples were collected 60 seconds after mixing was terminated. Turbidities were measured on the subnatant samples using a Hach Ratio Turbidimeter.

The data, shown in Figure 1, indicate that the new polyelectrolyte achieved optimum performance as measured by minimum turbidity at a dosage that was 30% lower than that for the conventional linear polymer. Each data point in Figure 1 represents an average of multiple tests under those conditions.

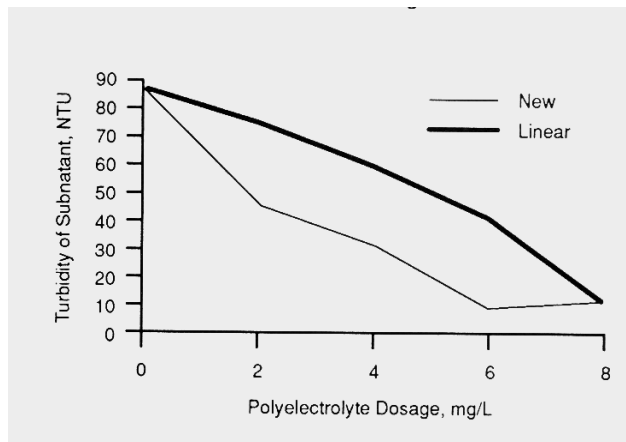


Figure 1: Laboratory IAF performance comparison of linear vs. new polyelectrolyte efficacy

chemical plant trial

To evaluate the performance of the new polyelectrolyte, an oily wastewater influent to a dissolved air flotation (DAF) unit at a southeastern chemical plant, was identified as a field test substrate.

The chemical plant generates about 111 cubic meters/hr (488 gpm) of wastewater from chemical

operations, boiler and cooling system blowdown and storm water. Treatment includes the use of chemical emulsion breakers at the DAF unit to remove oil and grease from the waste stream prior to discharge to an activated sludge biological treatment process.

The goal of this investigation was to compare the efficacy of the new polyelectrolyte treatment program with the historical treatment which employed a ferric inorganic coagulant along with a linear organic flocculant. Benefits of organic polyelectrolyte treatment include pH stability, less sludge generation, elimination of difficulties associated with ferric usage, and production of a more easily dewaterable sludge.

Standard jar tests were performed on samples of the test substrate. Inorganic and organic coagulants, conventional linear polyelectrolytes, and the new polyelectrolyte were evaluated for treatment performance. Treatment efficacies were determined on the basis of the resultant subnatant water clarity. Turbidities were measured on the subnatant samples using a Hach turbidimeter.

Figure 2 shows that cleanup of this oily waste-water was enhanced by use of an organic coagulant in conjunction with the new polyelectrolyte. The ferric/linear flocculant treatment at the DAF reduced the turbidity from an average of 20 NTU to 15.6 NTU. The dotted lines on the left portion of the graph show these averages. Root mean square deviation of the inlet and outlet turbidity before the test was calculated as 7.0 and 9.9 NTU, respectively.

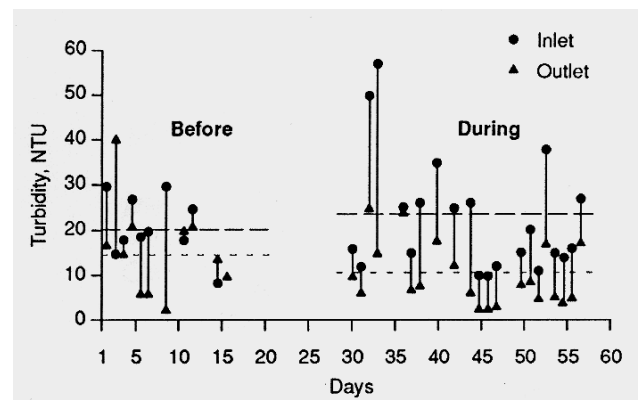


Figure 2: DAF inlet and outlet turbidity measurements before and after during new polyelectrolyte/coagulant test

The coagulant/new polyelectrolyte treatment at the DAF improved effluent clarity by reducing turbidity from an average of 22.8 NTU to an average of 10.2 NTU. The dotted lines on the right portion of the graph show these averages. Root mean square deviation of the inlet and outlet turbidity during the test was calculated as 12.5 and 6.7 NTU, respectively.

Figure 3 shows unit cost of treatment chemicals prior to and during the new polyelectrolyte treatment test. The average dosages were reduced so that the average unit cost of treatment dropped approximately 40 percent.

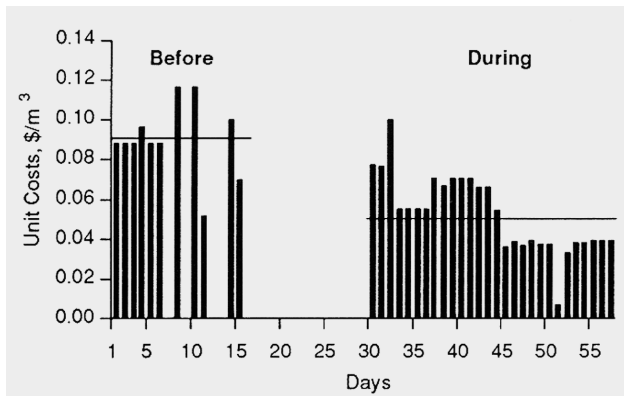


Figure 3: DAF chemical treatment units costs before and during polyelectrolyte testing

The new treatment improved effluent clarity and did so at lower dosages and use costs.

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