

# Chitosan: Chemistry and Use In Water Clarification

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*Chitosan is a natural biodegradable biopolymer produced from the polysaccharide chitin, which is derived from the crustacean shells of shrimp, crab and lobster. The chemical properties of chitosan provide the necessary characteristics needed for safe and efficient clarification of recreational water. Colloidal suspensions of insoluble non-filterable particulates are responsible for the turbidity often encountered in pool and spa water. Removal of the fine particulate suspended matter is necessary in order to improve water clarity. This process is referred to as clarification, and requires the coagulation and flocculation of particulates which are subsequently removed by filtration. Metal salts serve as effective coagulating aids while polyelectrolytes are typically used as flocculents. Chitosan, a natural cationic polyelectrolyte structurally similar to cellulose, functions as an effective flocculent for a variety of both organic and inorganic substances. In addition, chitosan's chemical structure contributes to its unique ability to flocculate oil and chelate transition metal ions. This combination of properties distinguish chitosan as a unique clarifier of recreational water.*

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Pool and spa water can often exhibit various levels of clarity ranging from clear to significantly turbid. Turbidity is the result of a dispersion of suspended solids that are either filterable or non-filterable depending on the particulate size. The particles can vary in size from colloidal to coarse and consist of biological and non-biological material which may be either organic or inorganic. Clarification is the process of removing these particulates by charge neutralization, flocculation and filtration, in an effort to reduce turbidity (Kemmer and McCallion 1979).

Water clarification plays a vital role in a number of areas such as:

- Pulp and Paper Manufacture
- Industrial Wastewater Treatment
- Mining Operations
- Potable Water Treatment
- Aquaria Treatment
- Land Development
- Wine Production
- Pool, Spa, and Pond Water Treatment

Clarification is important from the standpoint of aesthetics, hygiene (removal of disease causing microbes) safety, and compliance with various regulatory requirements (Sawyer 1962).

Pool and spa water clarity is typically measured with a turbidimeter. The measurement is reported in nephelometric turbidity units (NTU) which is a measure of the light scattered by fine suspended particles present in the water. The National Sanitation Foundation recommendation for maximum water turbidity in pool and spa water is 0.5 NTU (Kowalski 1990). Routine monitoring of turbidity in both pool and spa water is useful for determining appropriate dosages and application schedules for the particular clarifier being used.

Particulate solids in recreational water vary in density, size and composition. Particles such as sand, gravel, and leaves tend to settle to the bottom of pools and do not contribute significantly to turbidity. This is in contrast to the non-settleable solids which also exist in the water as a suspension and contribute significantly to turbidity. The larger suspended solid particulates are filterable, and over time will be removed by the filtration process. The efficiency of removal is significantly dependent on the size exclusion limit of the filter being used. Particles smaller than the size exclusion limit of the filter will flow through and continue to increase in number in the filtered water resulting in increasing turbidity. It is the non-filterable suspended particulates that are primarily responsible for turbidity in pool and spa water. Non-filterable suspended particulates can in-

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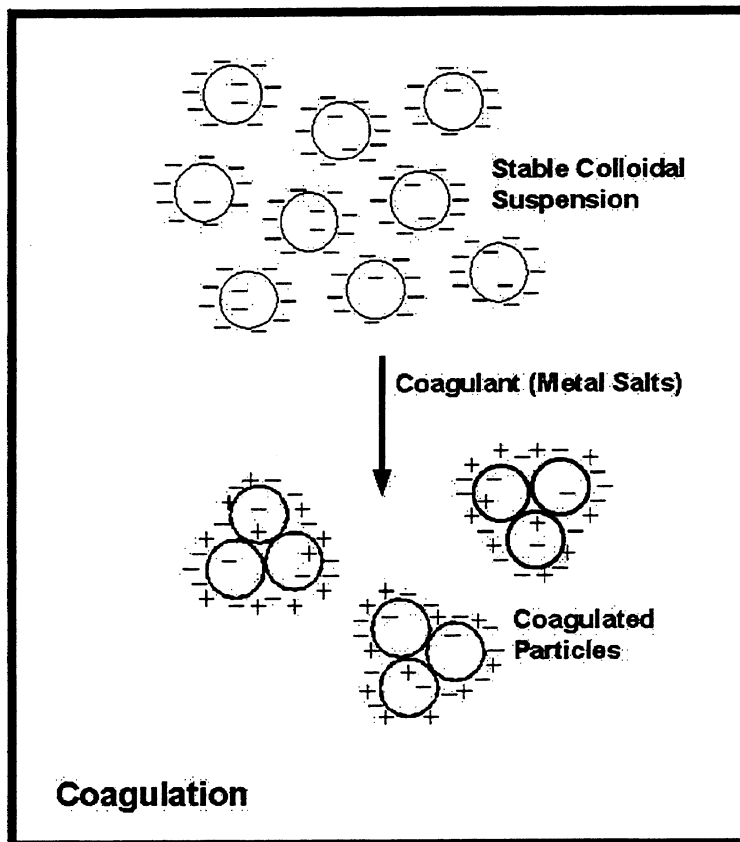
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clude silt, bacteria, viruses, organic precipitates, oil emulsions, plant-derived non-polar organic matter, particulate debris derived from sloughed off epithelial tissue, colloidal metallic and non-metallic oxides and a bewildering variety of other insoluble matter. As mentioned earlier, the size and composition of non-filtered particulates are influenced by the limits of the filter. Removal of micron size non-filterable particulates requires processes which aggregate the particles into size networks large enough to be removed by the filter. These processes are referred to as *coagulation* and *flocculation*

### Coagulation and Flocculation

Ultra-fine particulates form dispersions in water that are referred to as colloidal dispersions (Sawyer 1962, Kruyt and van Klooster 1930). Individual particles are characteristically very small and may not even be visible to the naked eye. They exhibit very large surface area to mass ratios and because of this, dispersions are greatly influenced by surface interactions in the water medium. The particles are electrically charged due to their chemical compositions and can be either negative or positive (Kemmer and McCallion 1979, Sawyer 1962, Kruyt and van Klooster 1930). For example, calcium carbonate is negatively charged and magnesium hydroxide is positive charged. The most common dispersions in water consist of negatively charged colloidal particles with masses so small that they do not settle under the effects of gravity. These negatively charged particles repel each other and are therefore prevented from coming in close contact long enough to coagulate and increase in size. Because the size of colloidal particles are larger than the wavelengths of visible light, they



**Figure 1 – Coagulation resulting from a reduction in zeta potential**

reflect and scatter light. The reflected beam of light can be seen at right angles to the beam and is known as the Tyndall effect (Sawyer 1962). This explains the light beam observed at night in a highly turbid pool.

Particle electrostatic repulsion is effective in maintaining stable colloidal dispersions with resulting turbidity. The intensity or magnitude of the particle's electrostatic charge relative to the liquid medium is referred to as the zeta potential (Kemmer and McCallion 1979, Sawyer 1962). A high electro-

Natural <i>Polysaccharides (organic)</i>	Synthetic <i>Petroleum-Derived (organic)</i>	Synthetic <i>Inorganic</i>
Cationic – <i>Chitosan</i>	Cationic – <i>copolymer of acrylamide &amp; quaternary ammonium derivatives of acrylamide</i>	Cationic – <i>Polyaluminum hydroxychloride, polyaluminum silicate sulfate</i>
Anionic – <i>Alginates</i>	Anionic – <i>copolymer of acrylic acid with acrylamide</i>	
Non-ionic – <i>Pullulan</i>	Non-ionic – <i>Polyacrylamide</i>	

**Table 1 – Examples of Synthetic and Natural Polyelectrolyte Polymers**

static charge denotes a high zeta potential and a low electrostatic charge is characterized by a low zeta potential. Reducing the stability of the colloidal dispersion is necessary in order to reduce the turbidity. This is accomplished by reducing the particle's electrostatic charge or zeta potential. Reduction of the colloidal particle's zeta potential allows the particles to come sufficiently close together because the attractive Van der Waals forces exceed the repulsive electrostatic forces. The particles are then able to coagulate and form aggregates of increasing size. As shown in Figure 1, particle charge reduction is typically accomplished by adding a *coagulant* and/or *polyelectrolyte* to the water. Coagulants typically are chemicals that form ions of opposite charge to that of the particles when dissolved in the water. Other types of coagulant aids that exist as insoluble negatively charged particles such as bentonite clay minerals have been described (Murcott and Harleman 1996). The most commonly used coagulants are metal salts such as aluminum sulfate and ferric chloride which form the highly charged cations,  $Al^{+3}$  and  $Fe^{+3}$  respectively (Kemmer and McCallion 1979). These ions are very effective in reducing negative charges on colloidal particles and function optimally between pH 6–7. The use of metal salts is highly dependent on pH and dosage. The coagulated particles formed with metal salts may tend to be gelatinous and negatively affect filter performance.

In many cases, particularly when using metal salts, the coagulated colloids may still be too small to remove by filtration thus necessitating the use of a *polyelectrolyte* also known as a *flocculant*. Polyelectrolytes are water soluble or water dispersible high molecular weight long chain *polymers* composed of repeating monomeric units (Kemmer and McCallion 1979, Sawyer 1962, Gutcho 1977). As shown in Table 1, polyelectrolyte polymers can be categorized into inorganic or organic compounds. The inorganic polyelectrolytes are polymerized metal salts which exist as positively charged polymers in solution. These include polyaluminum hydroxychloride (aluminum chlorohydrate), polyaluminum silicate sulfate (aluminum hydroxide sulfate) and polyaluminum sulfate (Ash and Ash 1996). Organic polyelectrolytes can be either *synthetic* (petroleum-derived) or *natural*. Their monomeric units consist of chemical sites which are ionic and impart polymeric charge to the linear chains. These charges can be either positive or negative depending on the nature of the chemical sites. Positively charged polymers are referred to as cationic and negatively

charged polymers as anionic. Some organic polyelectrolytes do not contain ionic sites and are therefore uncharged or non-ionic polymers. The majority of *synthetic* organic polyelectrolytes are composed of polyacrylamide and its derivatives. The *natural* organic polyelectrolytes are commonly polysaccharides and are derived from either plants, microbes, animals or shellfish. These polysaccharides can be either anionic, cationic or non-ionic as shown in the examples provided in Table 1.

When added to water containing colloidal and/or coagulated particulates of opposite charge, polyelectrolytes are able to bind and gather the particles into larger aggregates that are easily filterable. The aggregates are often called flocs and the process is referred to as *flocculation*. This process is depicted in Figure 2. Due to the polyelectrolyte's high molecular weight, many particles can bind to each linear polymer chain resulting in a highly bridged network. Since most suspended particles in water tend to be negatively charged, cationic polyelectrolytes are preferred polymer types.

An example of *cationic flocculation* is shown in Figure 3. The jar in panel A contains a filtered colloidal suspension of soil in water exhibiting a turbidity

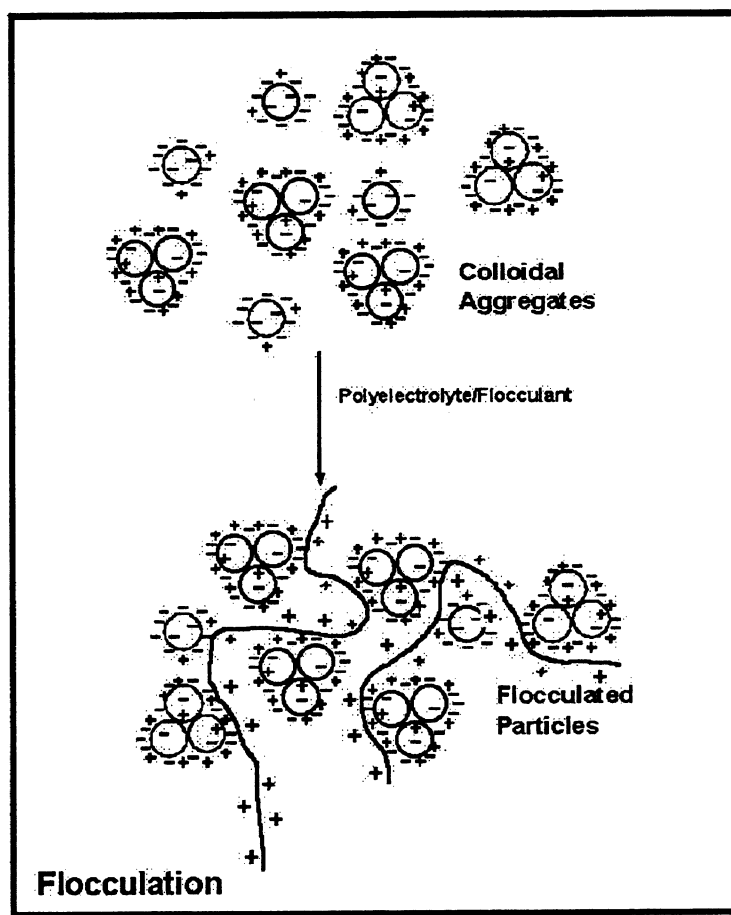
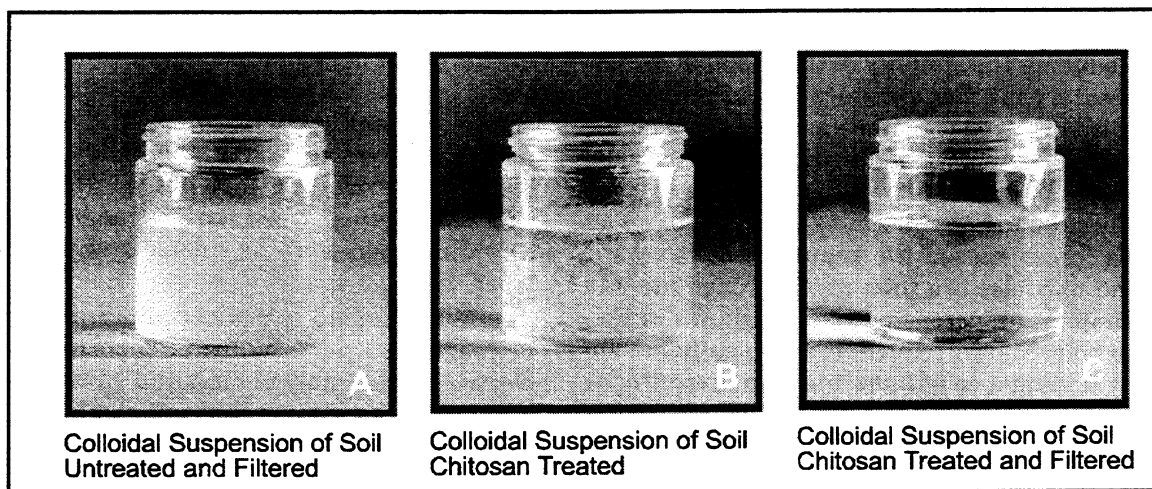


Figure 2 – Flocculation by Polyelectrolyte



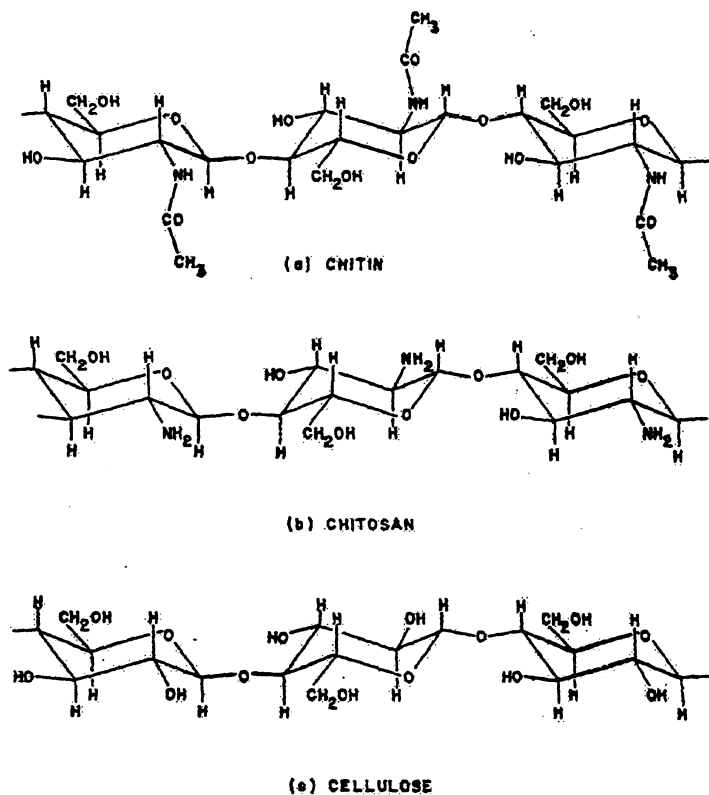
**Figure 3 – Clarification of a Colloidal Dirt Suspension Using Chitosan**

of 53 NTU. Following the addition of *chitosan* (cationic polyelectrolyte), flocculation of colloids and aggregation into larger particles is clearly observed in panel B. Filtration of the chitosan-treated suspension removed the large aggregated flocs resulting in clear water with a turbidity of 0.2 NTU as shown in panel C.

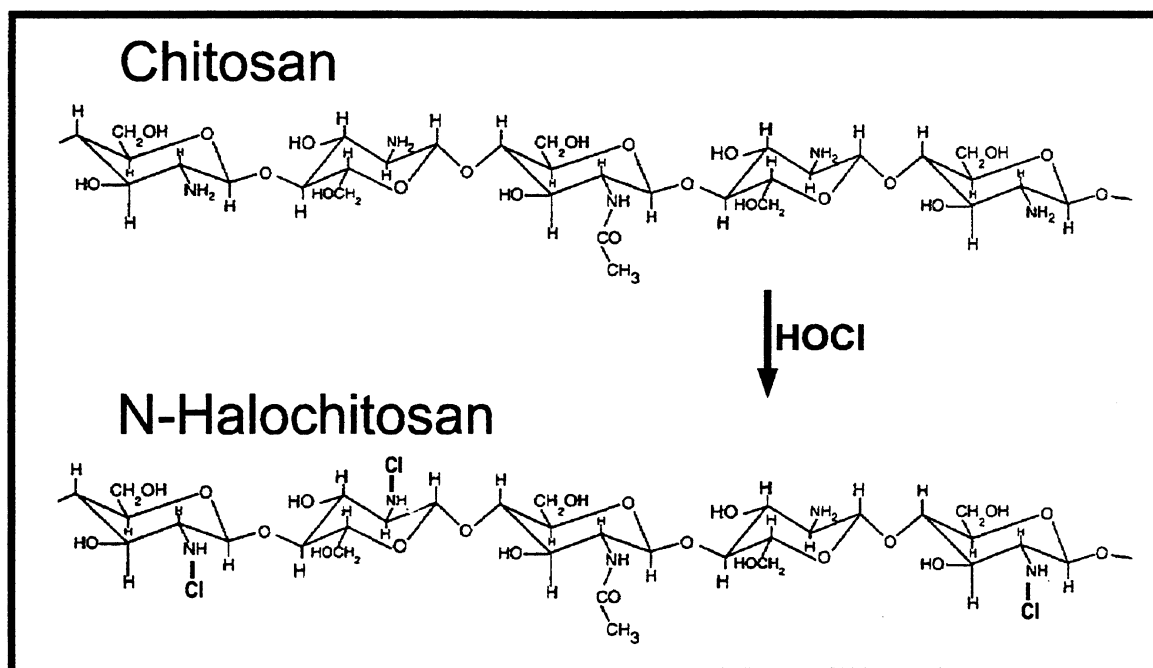
### Chitosan

Chitosan is a natural biodegradable polysaccharide biopolymer derived from chitin, the major component which makes up the shells of crustaceans (Muzzarelli 1977). Chitosan is structurally similar to the polysaccharide cellulose as seen in Figure 4.

The cellulose polymer is composed of repeating monomeric units of glucose linked together into a long polymeric chain while chitosan is composed of repeating monomeric units of glucosamine. The only difference between glucose and glucosamine is the nitrogen in glucosamine which replaces the oxygen at the second carbon in glucose. This nitrogen can be protonated on all of the non-acetylated monomeric units resulting in a long chain polymer of positive charge. It is this unique property of chitosan which makes it the only naturally occurring cationic biopolymer known. Its parent polymer chitin contains glucosamine residues that are acetylated on the nitrogens, rendering the chitin molecule insoluble. This insolubility, combined with mineral matter, contributes to the tough hard shells of crustaceans such as crab and lobster. Chitosan is biodegradable and proven safe for human consumption. Chitosan is currently being used as a dietary supplement to prevent fat uptake and reduce serum cholesterol. It is used to clarify wine and treat wastewater from food processing plants. Intra-chain positive charges on chitosan polymers repel each other causing the polymer chains to extend into long rod-like shapes which allows more binding interaction of nega-



**Figure 4 – Molecular Structure Comparison**



**Figure 5 – Molecular Structure of N-Halochitosan**

tively charged colloidal aggregates. This property increases chitosan's effectiveness as a flocculating agent.

### Chitosan as an Oil Flocculant

Chitosan exhibits the unique property of binding and flocculating non-polar hydrocarbons such as oil. This is due to formation of a patented N-halo derivative of chitosan which is formed in the presence of a halogen such as chlorine or bromine (Heinsohn and Dilgillian 1994). The polymeric halo derivatives of chitosan will typically contain approximately 8–98% of 2-deoxy-2-haloaminoglucose monomeric units with the halogen being chlorine or bromine. This type

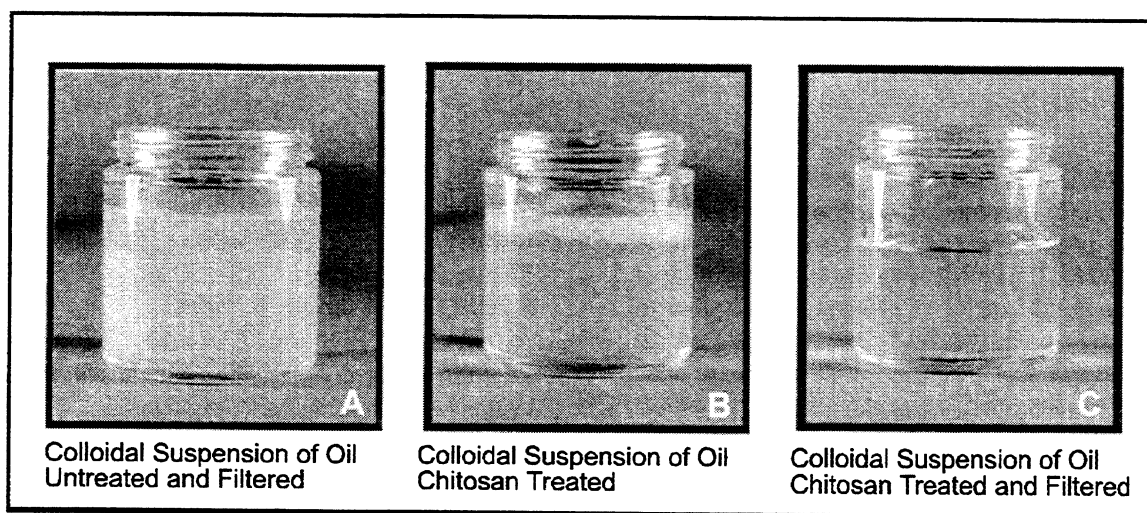
lotions.

As shown in Figure 6, chitosan, in the presence of chlorine, effectively flocculates a filtered colloidal suspension of moisturizing cream in water (see panel B). Filtration of this flocculated solution results in clear water as shown in panel C. This figure demonstrates the importance of utilizing an oil-removing polyelectrolyte to maintain highly clarified water. The colloidal suspension of moisturizing cream shown in panel A is highly turbid even after filtration.

Certain types of oils or fatty acids such as those found in cellular membranes, consist of both a hydrophilic (water compatible) and a hydrophobic (water-

of derivative is referred to as an N-halochitosan whose structure is represented in Figure 5.

N-halochitosans are very effective in flocculating colloidal dispersions of crude oil and a variety of non-polar hydrocarbons such as those present in skin creams, moisturizers and suntan



**Figure 6 – Clarification of a Colloidal Oil Suspension Using Chitosan**

Run No.	ml chitosan Solution	ml NaOCl Solution	Turbidity, NTU
1	2	0	6.0
2	3	0	6.0
3	2	2	1.0
4	2	3	1.8

Data from United States Patent 5,362,717

**Table 2 – Effect of N-Halochitosan on Algae Flocculation**

incompatible) portion. These types of oils would have a tendency to form a layer on the surface of pool water with the hydrophobic portions sticking above the water surface and the hydrophilic portions submerged. Interaction of these molecules with pool and spa surfaces can lead to a buildup of hydrophobic scum which acts to attract more hydrophobic material along the water's edge. The so-called scum line can be prevented by using an oil flocculating polyelectrolyte such as chitosan which brings the material to the filter. Chitosan-oil complexes tend to be more particulate than oily. This property can be beneficial to filter performance as oily filter deposits typically result in high filter backpressures and therefore short backwash cycles.

N-halochitosan has also been demonstrated more effective than chitosan in flocculating algae (US. Patent 5,362,717). Data from this patent appears in Table 2.

An algae suspension was measured by turbidimetry before and after chitosan addition, with or without added sodium hypochlorite. In the presence of sodium hypochlorite, essentially all the algae sedimented to the bottom of the vessel resulting in a solution exhibiting a significantly lower turbidity. Algae suspensions containing chitosan without sodium hypochlorite remained suspended and exhibited a higher turbidity.

### Chitosan as Chelator of Heavy Metals

Another useful property of chitosan is its ability to bind and precipitate transition metal ions (Muzzarelli 1973). The chitosan metal interactions likely involve a combination of chelation and adsorption of metal ions with the hydroxyl groups and nitrogen electrons of the polymer. Chitosan will also flocculate the oxides, sulfites and sulfates of cobalt, chromium, aluminum, iron, zinc, cadmium manganese and selenium. At pH 7.0–7.5, up to 86% of cadmium and 77% of lead was collected from the original starting solutions of 10 µg/ml of these particular heavy metals (Muzzarelli 1973). Interestingly, N-halochitosan has been demonstrated to be more effective

than chitosan in removing polyvalent metal impurities such as aluminum and vanadium from aqueous streams (Deans 1994).

### Summary

Clarification of recreational water is a necessary process which removes both large and fine suspended particles that contribute to turbidity. Filtration has limitations based primarily on the size of particulates. Effective clarification of water requires the use of coagulants and/or flocculants to increase particulate size such that removal by filtration is possible. Coagulants are typically low molecular weight metal salts while flocculants are high molecular weight polymers. The polymers are either chemically synthesized or naturally derived and are typically polyelectrolytes carrying either positive or negative charges. Colloidal particulates in water tend to carry negative charges and can be bridged into large filterable aggregates through binding interactions with cationic (positively charged) polyelectrolytes such as chitosan.

Chitosan is naturally derived from the shells of crustaceans, is biodegradable and exhibits unique properties particularly suited to water clarification. It binds and flocculates oils and other non-polar hydrocarbons in the presence of chlorine or bromine as well as aggregating algae. Chitosan also possesses the unique property of binding and chelating soluble heavy metal ions effectively allowing their removal from water. The many combined properties of this unique polyelectrolyte place it at the forefront in water clarification.

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## About the Author

**Everett J. Nichols, Ph.D.** is the Director of Research and Development for Vanson, Inc. He received his undergraduate degree (BSPH – Bacteriology and Public Health) from Washington State University and graduate degrees (MSPH – Pathobiology and Public Health and Ph.D.) from the University of Washington. He has over 19 years of research experience in the structural and functional properties of carbohydrate biopolymers.

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