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A Fundamental Perspective
on Polyelectrolyte Coagulants and Flocculants in Water Treatment

A thesis submitted in partial satisfaction of the requirements
for the degree
Master of Science in Chemical Engineering

by

Arkadeep Bhattacharya

2021

ABSTRACT OF THE THESIS

A Fundamental Perspective on

Polyelectrolyte Coagulants and Flocculants in Water Treatment

by

Arkadeep Bhattacharya

Master of Science in Chemical Engineering

University of California Los Angeles, 2021

Professor Samanvaya Srivastava, Chair

Coagulation and flocculation are important phenomena which find widespread applications in water treatment. Polyelectrolytes are charged macromolecules which have found relevance in this domain due to their proven efficiency and effectiveness. The objective of the thesis would be to review and emphasize the fundamental mechanisms on which both natural and synthetic polyelectrolyte coagulants and flocculants operate. Advances in understanding phase characteristics and structure of aggregated polyelectrolyte complexes post interaction with charged impurities are discussed. These would help elucidate the correlation between salient polyelectrolyte properties such as molecular weight, persistence length, charge density, and aggregated complex properties such as turbidity and size. This review aims to provide relevant insights that enable better coagulants and flocculants for water treatment systems through examples to ultimately correlate several concepts and develop a collective understanding.

The thesis of Arkadeep Bhattacharya is approved.

Panagiotis Christofides

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Samanvaya Srivastava, Committee Chair

University of California, Los Angeles

2021

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1. INTRODUCTION

Freshwater is an ever-dwindling resource, with 3.6 of of 7.7 billion poeple already deprived of reliable supply¹. Human water usage has compounded 40 times in the last 300 years² and six times in the last 100 years³. Moreover, the demand has increased by 1% annually, dependent on many factors, including population boom, development, and changing consumption patterns⁴. An impending crisis is inevitable as it is predicted⁵ that by 2050 global water demand will increase by 55%. As a result, a concerted effort has been initiated globally to reuse water and facilitate sustainable and industrially scalable water treatment processes to meet stricter regulatory norms, “down from 1.0 NTU in 1989 to 0.3 NTU in 2016 for processed water”⁶. Hence, research in water treatment and materials has been a subject of interest for scientists and researchers worldwide⁷⁻¹².

Materials in wastewater can be classified into several size categories ranging from coarse dispersions (10 mm), fine particulates (10^{-3} mm), colloidal (10^{-4} mm), to solution impurities ($<10^{-6}$ mm) such as ions and molecules⁶. Particles from and below the colloidal size range are stable in solution due to the combined effect of steric repulsions, van der Waals forces, and electrostatic interactions¹³. Typically, pre-treatment is necessary for removal of such stable colloidal impurities before being subjected to energy-intensive methods such as ultrafiltration and reverse osmosis in a water treatment facility. Coagulation and flocculation are methods have evolved since ages into highly effective , methods to reduce natural organic matter (NOM)¹⁴⁻¹⁶, improve color and odor¹⁷, and reduce pathogens¹⁸ along with other charged and uncharged impurities. Coagulation and flocculation have been relevant in various stages of water treatment, such as pre-treatment ¹⁹, in primary treatment^{6,11,12,20,21}, and in stages after initial treatment for reduction of non-biodegradable organic matter to de reduced²². A crucial function of coagulation and flocculation in pre-treatment stages is to significantly reduce

fouling of membranes and equipment clogging and hence improving the efficiency of energy intensive downstream processes such as reverse osmosis and ultrafiltration^{6,23-27}.

Coagulation is a step that involves overcoming all stabilizing factors of impurities in a solution^{6,20}. Generally, coagulants are materials that help decrease or destabilize the surface charge of impurities, eventually aiding in the coming together and forming aggregates or flocs, a phenomenon which is defined as flocculation⁶. Flocculation essentially strengthens or changes the size distribution of the particles via a thermally driven process known as perikinetic flocculation or an artificial orthokinetic process where external velocity gradients or flow shear are induced through device design such as baffles or mechanical agitators^{6,28}. Coagulation and flocculation is generally followed by clarification, sedimentation, filtration (RO, membrane, gravity sand) and disinfection processes downstream for better water quality output^{20,29-31}.

There remains immense scope for research in this domain. Understanding complexation physics and particle interactions would facilitate efficient methods to reduce waste and toxicity of sludge. It remains a challenge, however, to inculcate and package these insights into repeatable, feasible methods which the industry can adopt. In section 2, the fundamental principles on fundamental theory behind coagulation and flocculation, including some in-depth discussion on DLVO theory, followed by a discussion on other factors like pH, amount of coagulants, and temperature that is crucial for performance in wastewater treatment. In Chapter 3, a discussion on Polyelectrolytes (PE) is presented with a specific focus on the phase and structure of complexes formed as well as several PE characteristics are discussed. Studying various advances in protein-PE complexes demonstrated that meaningful comparisons could be drawn between protein-polymer complexes and typical colloidal-PE regimes. As this work aims to study and review better alternatives of polymer flocculants, the following sections discussed some common biopolymers such as chitosan and starch-based flocculants. Finally,

some operational and performance aspects of PEs in the industry were discussed, and shortcomings were pointed out, ending with a summary and future perspectives.

2. COAGULATION AND FLOCCULATION IN WATER TREATMENT

Adapted with Permission from

Polyelectrolyte Coagulants and Flocculants in Water Treatment: A Fundamental Perspective. D. J. Iyer, A. Holkar, and S. Srivastava, In *Advances in Water Desalination Technologies*, Y. Cohen (ed.), *in press* (2021).

2.1 History

The term coagulation has been derived from the Latin term “coagulare,” which means “to clot” and flocculation from the latin term “floccus” meaning a tuft of wool³². The etymology of these phenomena is reminiscent of their ancient origins. Since the time oceans and rivers started forming, nature itself had displayed these phenomena when ocean waters destabilized colloidal clay brought in the rivers to form deltas, dating back to billions of years based on sedimentary rock data. This might have aroused the curiosity of early men combined with the desire for cleaner water (as is seen in Sanskrit Verses (2000 BC) and in the words of Hippocrates (460-377 BC)) to learn the science and invent new materials which can produce better results. Some of the earliest known coagulants and flocculants are mineral or plant-based. A mix of lime and alum was used to clarify water by Pliny as early as 77 AD^{33,34}. There is evidence that Egyptians used almonds with hand stirring to purify river water for drinking. Materials such as almonds, beans, nuts, Kataka seeds (*Strychnos potatorum*) seeds, lotus roots, pearls, rock crystal have also been mentioned in the ancient text to have coagulation properties³⁵. In the mid-18th century in England, alum was first reportedly used for clarifying and later on in municipal water facilities in Balton, England, 1881³³. Austen and Wilbert first quantified coagulation by alum by stating that “by the addition of half an ounce to 100 gallons, water can be clarified by standing, and that neither taste nor physiological properties will be impaired to it by this treatment”^{33,36,140}. In addition to several competitive studies in the USA between potash, lime, and iron perchlorate towards the end of the 19th century, alum was established as the industry

standard for pre-treatment. It was used primarily as a pre-treatment to sand filtration in conventional water treatment²⁰. Similar materials such as aluminum chloride^{37,38}, ferric chloride³⁹⁻⁴¹, and polyferric sulfate^{12,42} have also been relevant in several applications. Since the 2nd World war, coagulation and flocculation have been effective in providing drinking water by removing bacteria, pathogens, and even viruses in addition to carcinogenic inorganic substances such as asbestos fibers and arsenic²⁰.

2.2 Theory of Coagulation and Flocculation

Particle impurities in the water can be classified as inorganic materials such as minerals and metals, natural organic matter (molecules and suspended particles), and biological particles such as viruses, protozoa, bacteria. The stability of such particles in a liquid medium can be attributed primarily to functional groups which lend a surface charge density to them, resulting in electrokinetic stability. Their vast surface area to the mass ratio, which magnifies interfacial phenomena, lends additional stability. Their small size renders gravitational and hydrodynamic settling effects useless⁶. These colloidal systems, which are broadly classified as hydrophobic and hydrophilic, are predominant target impurities for coagulation and flocculation methods. In natural water, most particles have a negative surface charge primarily due to factors such as pH and readily ionizable negative functional groups⁶, which generally donate protons (H^+) and develop a negative charge. There have been instances where external ions in water react with the functional groups on these colloids via covalent or hydrogen bonding to form a coating of negative or positive charges. Lattice imperfections caused by unbalanced valencies also result in negative charges, as seen in SiO_2 and clay minerals²⁰.

The electrokinetic stability of colloids in water can be analyzed by the Gouy-Chapman and the Gouy-Chapman-Stern models^{13,43,44}. Like charges get repelled, and unlike charges get attracted towards a charged surface while being aided by thermal, kinetic, and electrostatic forces⁶. The

model for double layer originated early on with only a charged surface surrounded by ions, followed by modification by classifying a separate region that accounts for a layer of adsorbed ions by Stern.⁶ According to the Gouy-Chapman double-layer model, any charge in a solution must have surrounding counterions to balance it out. The model assumes particle surface to be flat and impervious, ions to be point sized, uniform surface charge distribution, and solvent permittivity to be independent of radial distance⁴³. Further, it was determined by^{13,45} that the counterions gravitate towards oppositely charged surfaces solely due to electrostatic repulsion and determine the concentration profile ρ_x , potential ψ_x , and field E_x . Since there has been evidence of discretization of surface charge, these assumptions are not failproof. The surface charge density of counterions on an isolated surface can be estimated by Grahame Equation¹³ as:

$$\sum_i \rho_{0i} = \sum_i \rho_{\infty i} + \frac{\sigma^2}{2\epsilon_0 \epsilon kT}$$

Here, $\rho_{\infty i}$ and ρ_{0i} are the ionic concentration (number density in m^{-3}) in bulk and on the surface. σ , ϵ_0 , k and T are the surface charge density of the particle, permittivity of medium and free space, Boltzmann constant, and temperature of the medium, respectively. From the above equation, the surface density can be calculated by expanding ionic concentration terms according to the Poisson-Boltzmann equation:

$$\rho = \rho_0 \exp\left(-\frac{ze\psi}{kT}\right)$$

Where ψ is the electric potential and ρ_0 is defined as the number density at the point of midplane or symmetry. Here, z is the valency of the ions in between the interacting surfaces. Stern made modifications to the Gouy-Chapman theory to accommodate finite ion size and specific adsorption of ions⁴³. Within the Stern layer, there was partial neutralization of charges,

followed by a diffuse layer where counterion concentration decays radially (Figure 2.1). The potentials at Stern and diffuse layers are termed Stern and Zeta potentials, respectively. The Debye length, which specifies the ionic cloud thickness near the particle, can be obtained from the Grahame equation as:

$$\kappa^{-1} = \left(\sum_i \frac{\rho_{\infty i} e^2 z_i^2}{\epsilon_0 \epsilon k T} \right)^{-0.5}$$

In the case of a spherical surface from the theory of “linear overlap superposition approximation” of electric double layers¹³, the double-layer interaction electric potential U_e , which decays exponentially with Debye length and can be defined as:

$$U_e = \frac{64\pi k T R \gamma^2}{\kappa^2} \exp -2\kappa x$$

Here the dimensionless function $\gamma = \tanh(ze\psi_0/4kT)$ where ψ_0 is the surface potential. A function of κ^{-1} , this interaction potential energy is directly related to the stability of the colloidal system and also to the electrolyte concentration, which is a different case from van der Waals forces which obey the power-law ($1/D^n$), D being the distance from the interface^{13,46}. Attractive forces of van der Waals, dipole-dipole, and dipole-induced dipole forces constitute the attractive forces that counter the electrostatic repulsion, which accounts for colloidal stability. The interparticle interaction energy (U_{vdw}) between two spherical particles of radii R_1 and R_2 depends inversely on the distance between the two spherical surfaces d as:

$$U_{vdw} = -\frac{AR_1R_2}{6(R_1 + R_2)d}$$

A here is the Hamaker constant, which is directly proportional to van der Waals interactions is in the range of 10^{-20} J. The resultant interparticle potential $U(x)$, for spherical particles with similar-sized radius, can be written as:

$$U(x) = U_e + U_{vdw} = \frac{64\pi kTR\rho_{\infty}^2\gamma^2}{\kappa^2} \exp -2\kappa x - \frac{AR}{12x}$$

It was postulated by Fuchs and later by Reerink and Overbeek in 1954^{47,48} that the aggregation rate is directly proportional to the energy barrier^{46,49}.

$$\frac{k_{fast}}{k_s} \approx \frac{1}{2\kappa r} \exp \frac{U_{max}}{kT}$$

Here r is the radius of the particle, k_{fast} and k_s represent the rate of aggregation for fast and slow regimes depending on the absence or presence of only a diffusion-controlled rate⁴³ in the solution, respectively, which has implications on the suppression of double layer due to high electrolyte concentration⁴⁶. In research and industry, electrokinetic measurements such as zeta potential measurements help extract quantitative data on the Stern potential, which can estimate the colloidal stability and get an idea about surface properties⁶.

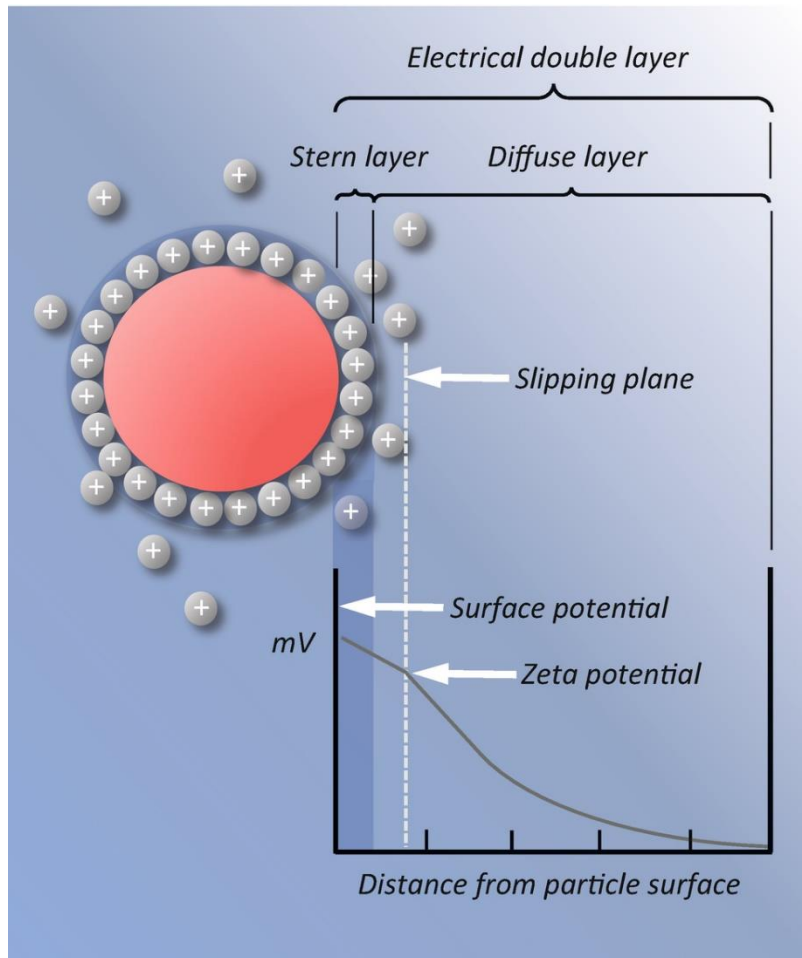


Figure 2.1 Schematic depicting the electric double layer, consisting of the surface charge, bound counterions (Stern layer), and free ions (diffuse layer) around negatively charged spherical particles. The Stern plane lies at the interface of the Stern and diffuse layers, while the interface between the latter and dispersion medium is called the slipping plane. Adapted with permission from Corbett, Mc-Neil Watson, 2018⁵⁰; Copyright (2021) Springer Nature.

Figure 2.2 depicts the interaction potentials between two flat surfaces as a function of normalized inter-surface distance with varying surface charge density. Interparticle interaction potentials between two spherical particles also follow a similar evolution with surface charge density¹³. Substantial repulsive energy barriers between particles with high surface charge density inhibit their agglomeration, while weakly charged particles present long-range interparticle attraction and agglomerate readily in suspension. For typically charged colloids,

the repulsive energy barrier is often too high for the particles to overcome readily; the particles either remain at distances corresponding to the secondary minimum or farther away. They are entirely dispersed, thereby forming a stable system¹³.

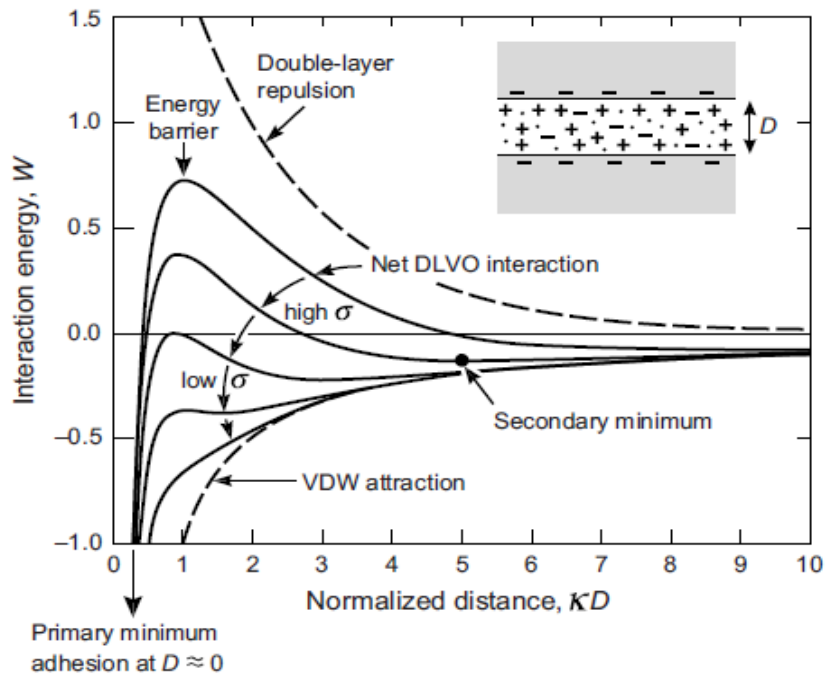


Figure 2.2 A representation of the change in interaction energy (W) with the distance between the species (D) at varying surface charge density (σ). The double-layer curve represents a stable system that approaches instability due to change in σ , ultimately leading to an unstable system, involving only van der Waals (VDW) attraction. The secondary minimum represents a kinetically stable system. Adapted with permission from Ch. 14, “Intermolecular and Surface Forces” Jacob N. Israelachvili, 2011⁵¹. Copyright (2011) Elsevier Books.

2.3 Mechanisms for Coagulation and Flocculation

The primary reason for coagulation is the weakening of repulsive interactions or through additional external factors which accentuate attractive interactions among the colloidal impurities in solution. The former can be brought about by reducing the surface charge density of particles or restricting the length scales over which the repulsive interactions are effective,

i.e., increasing the solution ionic strength to reduce the Debye length. The latter is mediated by multivalent macro-ions or polyelectrolytes that can bridge particles^{18,38,52-54}. The double-layer thickness can be decreased by oppositely charged ions³³, which can aid coagulation by suppressing the zeta and stern potential levels. It has been established that van der Waals forces are insensitive to ionic concentrations of the solution. However, repulsive interactions are affected strongly due to a change in pH levels. When the ionic strength of the solution increases, the surface charges are screened better, and Debye length is consequently reduced. Thus, reducing the Debye length and weakening electrostatic repulsion, thereby promoting particle aggregation. There are several primary mechanisms established and understood for coagulation and flocculation:

(1) **Charge Neutralization:** As the name suggests, after the addition of specific coagulants, hydrated species are created, which are generally cationic and get readily adsorbed⁵⁴ to commonly negatively charged impurities in wastewater, and subsequently either reduce or neutralize their charges, resulting in reduced electrostatic repulsion and compression of the double layer, effectively promoting coagulation^{6,20}. Cationic polyelectrolyte flocculants with high charge density display a strong affinity for adsorption with anionic impurities resulting in destabilization or even charge reversal leading to eventual flocculation at dosages to neutralize the charge and nullify the zeta potential⁵².

(2) **Sweep Flocculation:** When coagulants and flocculants (mainly aluminum and ferric-based) dosed in pH ranges or higher than their solubility limits, hydroxide precipitates form, they act as traps for impurities⁵⁴. This method is also sometimes referred to as entrapment or enmeshment. Since the impurities are electrostatically attached to the precipitates, sweep flocculation can be considered a form of charge neutralization⁵⁵. In the case of aluminum and iron salts, the multivalent cations get adsorbed to neutralize the surface charges. However, at ample dosage, encapsulation and precipitation of dispersed particles

dominate³⁰. Interestingly in a system with kaolin impurities, at a pH of 7, a reduction in suspension turbidity at 15 μ M aluminum sulfate dosage was attributed to charge neutralization, while sweep flocculation was said to play a role beyond 60 μ M dosage, due to hydrolysis and precipitation of metal coagulant species⁵⁴.

(3) **Bridging and Patch Flocculation:** These mechanisms are primarily displayed for polymer-based coagulants and flocculants. In the case of patch flocculation, particles with low molecular weights and high charge densities are preferred. This was primarily discovered to differentiate the previous process from bridging when the polyelectrolyte and the impurities are oppositely charged, eventually leading to complete coverage. Bridging is generally observed for the situation of high molecular weight polymers with lower charge densities wherein adsorption with similar⁵⁶ or oppositely charged impurities are possible, followed by latching of particles in the vicinity of the adsorbed particle by the pendant loops of the polymer with charged centers, eventually leading to the formation of aggregates or flocs^{52,57}. It has been established that due to successive adsorption of polymer chains with time, the ones below are compressed to the surface, resulting in eventual relaxation to flatter “inactive” configurations, thus reducing the number of available “active” loops^{57,58}. Polymer materials following the bridging mechanism are classified as “flocculants” as opposed to “coagulants” since they do not follow charge neutralization^{32,52}. The bridging mechanism in polyelectrolyte systems has also shown to form stronger flocs as compared to metal coagulants²⁸.

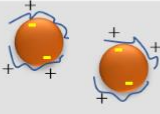

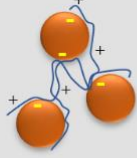
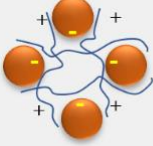
MECHANISM	DESCRIPTION	ILLUSTRATION
Simple Charge Neutralization	Reduction of Double Layer thickness and charge neutralization	
Charge Packing	Unevenly Distributed surface charges are neutralized	
Bridging	Primary flocs are adsorbed and connected via large MW flocculants	
Sweeping	Small colloidal pollutants are trapped in the mesh of polymeric precipitates	

Figure 2.3 Different mechanisms of coagulation and flocculation. Adapted with permission from “A review on chitosan-based flocculants and their applications in water treatment,” Yang et al., ⁵⁹, 2016, Water Research. Copyright (2016) Elsevier.

2.4 Factors Affecting Coagulation and Flocculation

2.4.1 Coagulant Dosage

Dosage is a critical parameter since it impacts both the cost and toxicity of the waste generated in water treatment. Attaining that perfect level for coagulant or flocculant dosage is crucial since low levels would put more pressure on downstream filtration processes. In contrast, the excess dosage can have implications such as restabilization of colloidal impurities due to steric repulsion and charge reversal while having the apparent problem of residual chemical loading in the effluents^{60,61}. Hence, the concept of Critical Coagulant Concentration (CCC) for hydrophobic colloids was devised to optimize the coagulation and flocculation processes. In

charge neutralization due to double-layer repression, CCC depends only on counterion concentration enough to compress the diffuse layer independent of the particle concentration⁶². Restabilisation may also occur in some suspensions where multiple peaks and troughs in residual turbidity are seen. In Figure 2.4 (a), coagulants concentration increases along the x-axis, and $S_4 > S_3 > S_2 > S_1$ depict colloidal silica concentrations. As the colloidal concentration increases from top to bottom, we see that stabilization zones vary with the same increase in coagulant. The shaded areas depict coagulated zones and the solid white area depicts stable suspensions. Hence, at a constant pH, we see that there is subsequent destabilization and restabilization zones at certain intermediate colloidal concentrations, which can be attributed to charge reversal. In Figure 2.4 (b), the same data is plotted with showing the relationship between coagulant dosage and colloid concentration.⁶³

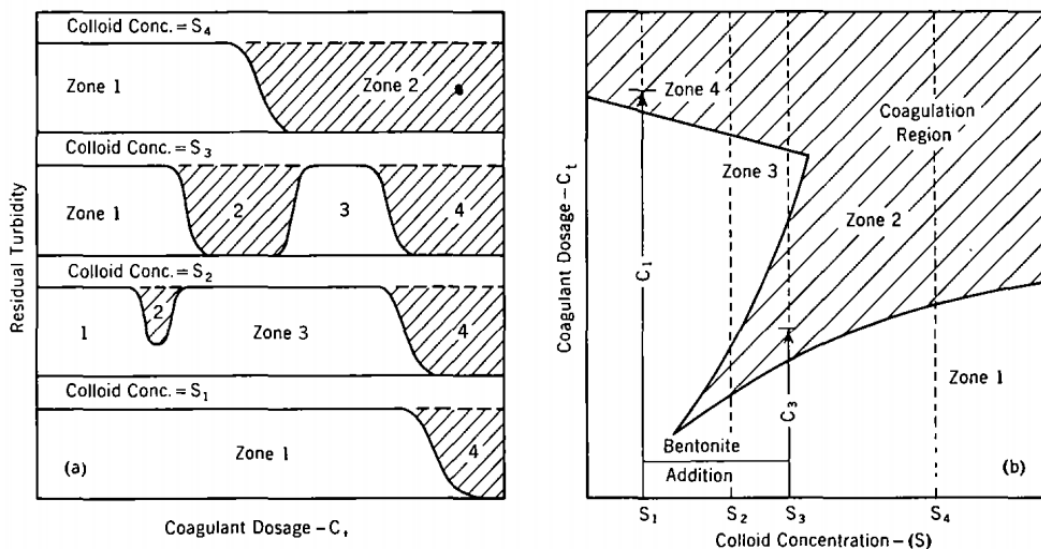


Figure 2.4 (a) Depiction of multiple stabilization zones for coagulation of colloidal suspensions by aluminum and iron (III) coagulants at constant pH. Colloid concentration increases from top to bottom. **(b)** Relationship between colloid concentration and dosage for the same dataset. Adapted with permission from “Stoichiometry of Coagulation,” Stumm and O’Melia, 1968, AWWA; Copyright (1968) John Wiley and Sons⁶³

Blankert et al.⁶⁴ reported that using an in-line coagulation system functioning through real-time dosage adjustment in dead-end ultrafiltration (UF) systems has been done. This was achieved by empirically correlating the UF filtration resistance post backwash (UF PB) to the filtered volume based on pilot tests. The difference between the observed and empirically determined UF PB resistance values was then fed to a proportional-integral controller to enable dosage adjustment. However, because this approach was largely empirical, obtaining optimal dosage values remained a challenge. This drawback was allayed by the self-adaptive approach demonstrated by Gao et al.⁶⁵, wherein optimum coagulant dosage was determined based on real-time tracking of UF PB resistance post every cycle of dosage adjustment (Figure 2.5).

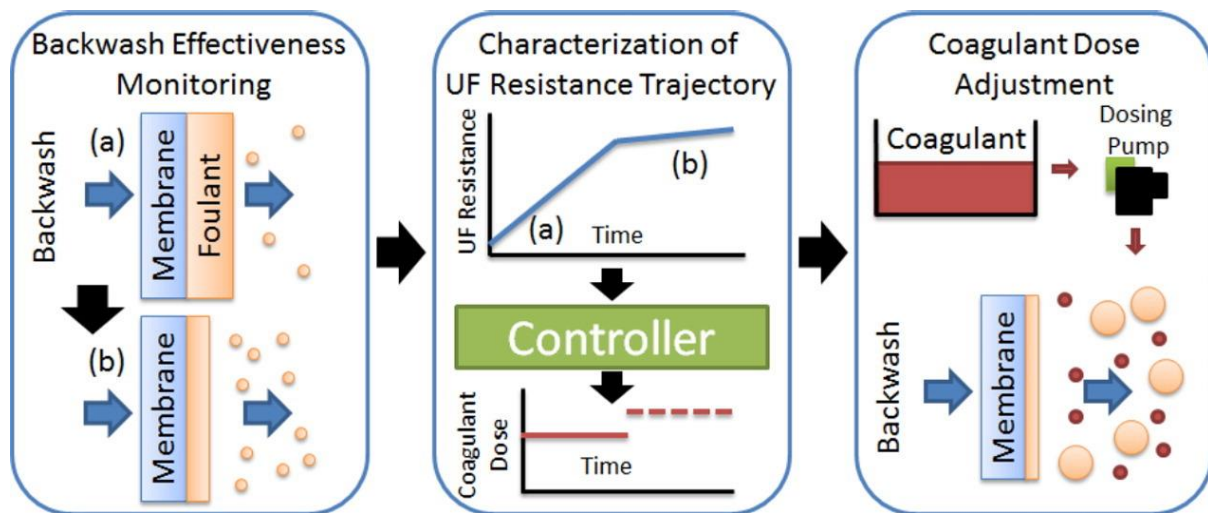


Figure 2.5 Quantification of the backwash effectiveness and membrane fouling by tracking the ultrafiltration resistance trajectory in real-time, is optimal to adapt and control coagulant dosage. Adapted with permission from “Self-adaptive cycle-to-cycle control of in-line coagulant dosing in ultrafiltration for pre-treatment of reverse osmosis feed water”, Gao et.al, Cohen⁶⁶, 2017, Desalination; Copyright (2017) Elsevier.

2.4.2 Solution pH

Necessary adjustment of pH to achieve optimum coagulation is probably the most crucial parameter to consider while improving the effectiveness of treatment methods^{15,20,37,60,67-72}. This is because the formation of surface groups on particulate impurities depends on the pH, which can affect the stability of the suspension. For a case of silica dispersion with Fe (III) coagulant, different pH ranges have shown different characteristics.⁶³ In low pH ranges of around one and at low colloidal concentrations, destabilization of the colloidal solution is not observed, which may be primarily attributed to the low potency of de-hydrolyzed aquo-metal ion species existing in this region and also a scarcity of available contact sites for perikinetic destabilization⁶². Upon increasing the pH to 2, stronger adsorption of hydrolyzed species is observed, with charge reversal and restabilization observed at high dosage. In the pH range of 3-5, adsorption is the dominant mechanism that becomes stronger from 3 to 5. At pH 3.0, restabilization is due to charge reversal as more positive ions are present; however, at pH 5.0, restabilization can be attributed to excessive site coverage and bridging. At pH of 6.0 to 9.0, restabilization is not seen as everything settles down due to bridging followed by entrapment or sweep flocculation by hydrolyzed species as the dosage increases. For ferric-based coagulants (poly ferric sulfate), it was seen that pH also affects the process of flocculation, particularly the size and regrowth capacity of flocs on applying shear force with optimum pH in the range of 5.5-6.5⁴². Similarly, in the use of poly ferric chloride (PFC) to treat water from the Yellow River with a dissolved organic carbon level of 1.86-3.71 mg/L, and high alkalinity 245.1-262.7 mg CaCO₃/L in the pH range of 8.15-8.4, it was observed that adjusting the pH to 5.5-6 yielded excellent turbidity reduction. Polyferric chloride dosage of 0.15 mmol/L was found to give the shortest time to reach a steady-state with maximum floc sizes and growth rates. On increasing the pH levels from 4 to 6.25, a decrease in the residual turbidity was observed, which eventually started slightly increasing at pH 9. In acidic conditions, hydrolysis

was limited, and charge neutralization was the dominant mechanism, whereas, for higher pH values, better removal was seen due to sweep flocculation^{15,41}. In a study of removal of humic acid by cationic PEs, there was a substantial reduction in polymer dosage needed by 375% when pH was reduced from 6.0 to 2.8, essentially due to a reduction in the degree of ionization of humic acid⁷³. The removal of dissolved organic carbon depends on a mix of mechanisms such as charge neutralization, coagulant and organic matter speciation, and adsorption and sweep flocculation^{14,41}. In the case of alum, a pH range of 6-8 has proven to be very effective^{41,60,71,74}. It has been demonstrated by Black and Chen^{62,75} that the restabilization zones can be eliminated by raising the pH levels in kaolinite systems with aluminum sulfate as the coagulant. It is also crucial to clean the probes used to monitor pH in treatment systems which would help in accurate estimation of corrosion and scaling²⁰.

2.4.3 Temperature

Temperature is a crucial parameter in coagulation chemistry. It affects the solubility of hydroxide species, which increases with decreasing temperature⁵⁷. The size and strength of flocs and stability of impurities, coagulants, and flocculants are all affected by temperature⁷⁶. Turbidity was found to be inversely related to temperature, with impurity removal with alum coagulants worsening on lowering temperatures from 20 °C to 1 °C⁷⁷. It was hypothesized that enmeshment was severely affected at low temperatures and that flocs formed were smaller. It was determined that ferric coagulants performed better than alum at low temperatures⁷⁸ because it shifted the optimal pH for sweep coagulation⁷⁸. Hence, a pH adjustment could be employed as a corrective measure to compensate for adverse temperature effects. It is further shown that alum had a significant variation of floc size with temperature with small sizes at low temperatures out of alum, ferric sulfate, and polyaluminum chloride (PACl)⁷⁹. Polymerized coagulants such as PACl have been identified to perform best at low temperatures as they produce the biggest flocs. For removal of suspended particulates from palm oil mill effluents,

performance decreased significantly at temperatures greater than 20 °C due to increased kinetic energy of particles at higher temperatures impeding floc formation⁸⁰. Furthermore, it was suggested that convection currents due to heating could also prevent the settling of particles^{81,82}.

3. POLYELECTROLYTE COAGULANTS AND FLOCCULANTS

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Polyelectrolyte Coagulants and Flocculants in Water Treatment: A Fundamental Perspective. D. J. Iyer, A. Holkar, and S. Srivastava, In *Advances in Water Desalination Technologies*, Y. Cohen (ed.), *in press* (2021).⁸³

For centuries, cost-effective and biodegradable natural polyelectrolyte coagulants such as *Moringa oleifera* (drumstick), *Strychnos potatorum* (Kataka seeds), tannin, opuntia³⁸, chitin, and sago⁷¹ have been used for water purification. Today, polyelectrolytes find widespread usage in various stages of wastewater treatment; as primary coagulants for removing turbidity, pathogens, algae, and organics, as a flocculant and filter aids, and also for thickening of sludge. However, in alignment with the theme of the thesis, the discussion is kept restricted to applications of coagulants and flocculants. As discussed in chapter 2, polyelectrolytes mainly follow bridging or patch flocculation mechanisms. However, various other mechanisms have been reported involving the coagulating action of natural coagulants due to the adsorption of polyelectrolytes and charged proteins on colloid surfaces to induce flocculation^{38,84,85}. Some natural and synthetic coagulants still suffer from drawbacks such as low availability, difficulties in scalability, short shelf life, low resistance at oxidizing temperatures, and lack of suitability for industrial wastewater treatment⁶². Whereas natural coagulants require many purification steps to achieve consistency for industrial use⁸⁵⁻⁸⁸, synthetic polyelectrolytes are highly customizable to cater to specific operating industrial conditions, allowing tunability of molecular weight to surface characteristics and polydispersity, providing effective coagulation and flocculation even in extreme temperature and pH conditions.

Typical impurities in natural water systems have an anionic surface charge⁸⁹ and hence cationic polyelectrolytes (PEs), or polycations are used in the removal of such materials, such as poly(diallyl dimethyl ammonium chloride) (PDADMAC) and poly(dimethylamino)ethyl

methacrylate (PDMAEMA). Polycations possess several advantages over conventional coagulants and flocculants (like alum) denser sludges are formed, lower dosing is required and reduced levels of mineral residue left in the purified water, leading to an overall treatment cost reduction by 25-30%⁵². Similarly, anionic PEs such as anionic polyacrylamides (APAM) are used for the treatment of water with cationic impurities such as clay, and as scale inhibitors^{52,90}. They are also utilized as polymer aids to cationic salts to form larger aggregate flocs that settle faster⁵². Moreover, a substantial reduction in dosage requirements (40-60%) of alum is seen when APAM is used as a polymer aid⁹¹. Non-ionic polymers such as polyethylene oxide are also used as polymer aids and are generally less toxic compared to polycations and are preferred in cases when biodegradability is a priority. Figure 3.1 summarizes the different polymers used for water treatment³⁰.

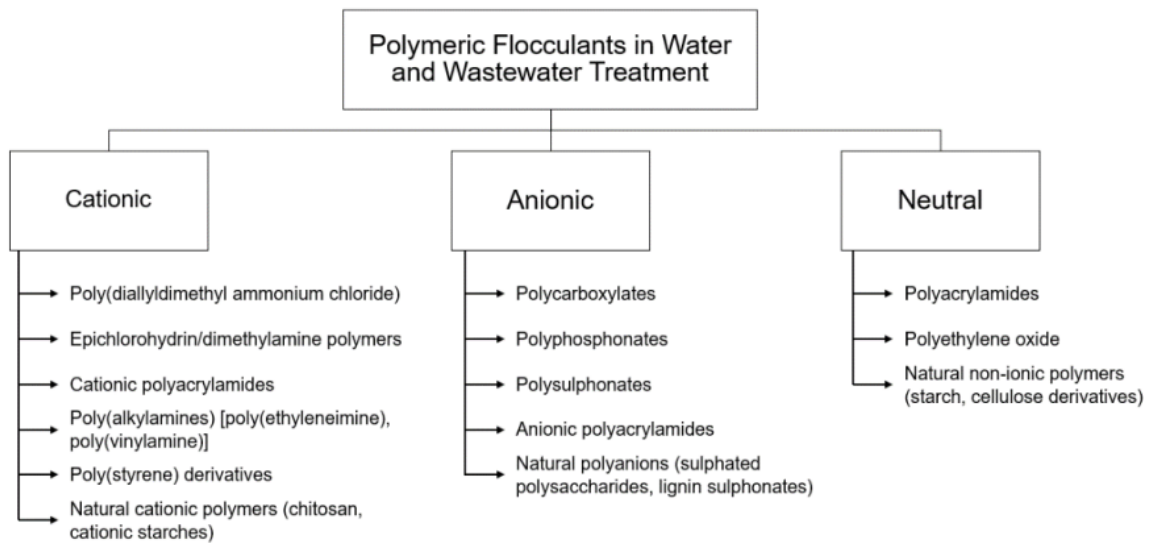


Figure 3.1 Classification of some polymeric flocculants used in wastewater treatment. Adapted with permission from “Chitosan for coagulation/flocculation processes – An eco-friendly approach”, Renault et al. 2009³⁰, European Polymer Journal; copyright Elsevier.

3.1 Polyelectrolyte-Colloid Interactions: A Fundamental Perspective

Polyelectrolyte (PE) characteristics such as charge density, degree of ionization, size, and persistence length significantly affect coagulation and flocculation. In the following sections, the effect of these parameters on both the phase behavior and structure of polyelectrolyte-colloidal systems have been discussed. This would facilitate in better design of such macromolecules targeted towards destabilizing various colloidal systems. Various natural and synthetic PEs currently being used in the industry and in research stages have been discussed in the forthcoming sections. The DLVO theory⁹² has failed to predict flocculation results even qualitatively since it neglects the role of the adsorption mechanism of these PEs on the surface of impurities⁹³. Hence recent experimental and simulation work has shed light on such interactions for improved coagulants and flocculants design.

3.2 Structure of Polyelectrolyte-Colloid Mixtures

Surface adsorption of PEs is the first step in their interaction, accompanied by a gain in free energy from the electrostatic interaction between the colloid surface and PE monomers. It is known that oppositely charged ions surround charged bodies in aqueous solutions known as counterions. As soon as a PE monomer attaches itself to the surface of an oppositely charged colloid and their counterions are replaced, there is an exchange of entropy where the PE loses entropy, and the counterions gain entropy freedom. This energy exchange^{94,95} dictates PE-colloidal interactions. PE chains can form “trains, loops, and tails”⁸³ where some PE is entirely collapsed on the colloid surface, whereas some have extended tails into the medium, as shown in Figure 3.2a⁹⁶. Such configurations of PE-colloid complexes have various structures such as “U-shaped, solenoidal and rosette-like PE-colloid complexes” (Figure 3.2b)^{83,97}, which eventually floc together to settle down via common mechanisms of bridging or charge neutralization.

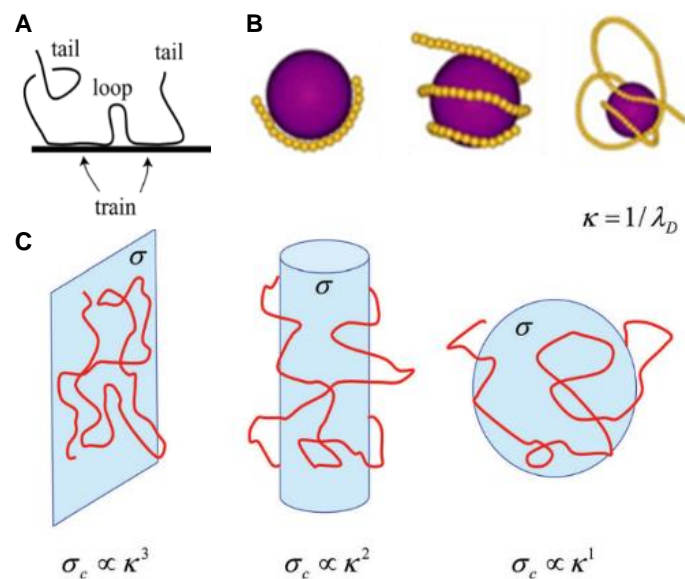


Figure 3.2 (a) A schematic representing the tail, loop, and train configuration of polymer adsorption on surfaces. Adapted with permission from Netz and Andelman, 2003⁹⁶. Copyright Elsevier, Physics Reports. (b) Illustration of U-shaped, solenoid, and rosette structures of PE-colloid complex from left to right. Adapted with permission from “The many facets of polyelectrolytes and oppositely charged macroions complex formation” Ulrich et al., 2006⁹⁸, Current Opinion in Colloid & Interface Science; Copyright (2006) Elsevier 2006. (c) Representation of how critical surface charge density of particle scales with curvature. Reproduced from Winkler et.al., ⁹⁹, 2011, Physical Chemistry Chemical Physics, with permission from Royal Society Chemistry.

Simulation studies have demonstrated that at low particle surface charge and constant PE concentration, the mechanism to aggregate shifted from direct contact between particles to bridging induced clusters by PEs¹⁰⁰. The adsorption of PE on colloid surfaces is significantly affected by ionic strength as well. An increase in the ionic strength reduces the electrostatic interactions between the PE and the colloid due to enhanced electrostatic screening (decreased Debye length κ^{-1}). The adsorption of polymer chains is weakened due to less exchange of entropy when surrounding counterions are released^{100,101}. Similar observations were made for flocculation of bovine albumin by PAH (polyallylamine hydrochloride), where complexation

accompanied by counterion release was thermodynamically favored as the entropy gained by counterion replacement balances out the loss of conformational entropy of the polymer chains¹⁰². The surface charge of polymer is also an important parameter, and simulations have shown⁹⁹ the existence of a critical polymer surface charge σ_c as a threshold below which adsorption is not favorable. σ_c depends on several parameters such as temperature, the curvature of the adsorbent and κ^{-1} ; the debye length⁹⁴. (In figure 3.2c) the modelling results, based on Wentzen-Kramers-Brillouin (WKB) method demonstrate that as the curvature of the adsorbent increases, the critical surface charge density σ_c goes from cubic ($\sigma_c \propto \kappa^3$) to square $\sigma_c \propto \kappa^2$ to linear $\sigma_c \propto \kappa^1$ relationship with κ as we move from planar to spherical surfaces⁸³. This means that for the same value of κ , minimum surface charge required for adsorption of PE chains will be highest for spherical surfaces. Hence, colloidal impurities are so stable and curvature is an important parameter, as seen in the case of silica nanoparticles, where the charge needed for flocculation is considerably higher than particles such as clay because they have a lower curvature. However, when the radius of curvature comes close to κ^{-1} , or when $\kappa a \sim 1$, σ_c becomes independent of the curvature scales as $\sigma_c \propto \kappa^3$. This typically happens at high ionic strength values where curvature becomes irrelevant. Besides the curvature of particles and ionic strength of the solution, the persistence length or flexibility of the PE is important as it affects the aggregate properties and interactions. Simulations have shown that surface coverage of colloids by PEs is significantly lower for rigid molecules as compared to flexible PE chains, which show extensive coverage owing to easier interaction with opposing charges and stronger adsorption (Figure 3.3a)^{45,97,103}. It was also further explored those flexible chains displayed self-folding at local scales rather than covering the colloid surface as compared to chains with intermediate stiffness, where maximum surface coverage was seen^{102,103}. It was also found in Ulrich and Stoll's work through simulation that long PE chains have both bigger loops and tails, and as a result, they cover less portion of the particle surface⁹⁸. Although most

systems are flocculated by multi-PE chain interactions, there have been cases where single chains have also flocculated colloidal systems via bridging and adsorption mechanism⁴⁵. For stiff polymer chains, complexes are much less compact, contact points decrease, and folded structures become rare as the bending energy of the chains exceeds the energy needed for forming multiple chain-ion contacts¹⁰².

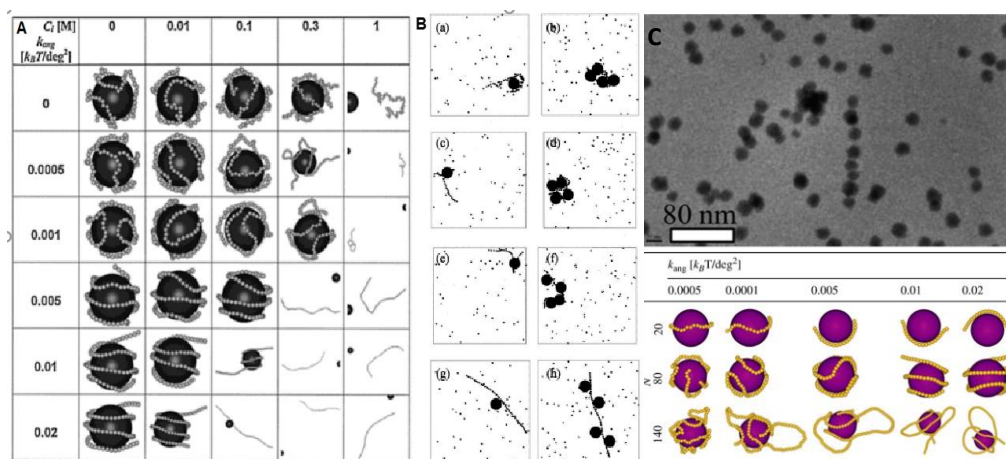


Figure 3.3 (a) Structures obtained from simulations where polymer persistence length increases from top to bottom and concentration increases horizontally. Adapted with permission from “Polyelectrolyte adsorption on an oppositely charged spherical particle. Chain rigidity effects” Stoll and Chodanowski, 2002¹⁰³, *Macromolecules*; Copyright American Chemical Society 2002 (b) Panels show a single PE chain with one particle (in the left column) and four particles (in the right column). The flexibility of polymer increases from top to bottom. Adapted with permission from Jonsson and Linse, 2001⁴⁵; Copyright 2001 *Journal of Chemical Physics*. (c) A cryo-TEM image showing rod-like structures formed in a solution with high silica and low biopolymer chitosan in it. Reproduced from Shi et al., 2013, *Soft Matter*, with permission from Royal Society of Chemistry. (d) PE-NP complex structures at different PE lengths (increasing from top to bottom) and persistence lengths (increasing from left to right). Adapted with permission from “The many facets of polyelectrolytes and oppositely charged macroions complex formation,” Ulrich et al., 2006⁹⁸; Copyright 2006 Elsevier.

Rigid PE chains do not diminish charge screening on the colloids as much, leading to interparticle repulsion in the complexes, culminating in more open structures. When at higher colloid concentrations, the binding of colloids to charge neutral complexes is stronger for rigid chains than flexible ones⁴⁵. This is because rigid chain complexes have more extended conformations, allowing un-complexed particles more access to monomers. For very rigid polymer chains, the PE remains rod-like with charged colloid particles attached to them, leading to more open structures described above^{45,103}. These nuances were deciphered using small-angle scattering (X-ray and neutron) and cryo-electron microscopy experiments “in systems with high PE and low colloid concentrations”⁸³. The ratio of persistence length L_p and the radius of the nanoparticle i.e., L_p/R has been noted as a critical parameter wherein for values close to 1 in flocculation of silica nanoparticles using chitosan, rod-like 1-D structures were seen, but for $L_p/R \sim 0.1$ in poly-l-lysine as PE, such rigid 1-D structures were not seen¹⁰⁴. The primary factor behind this anomaly was the persistence length; chitosan is a much stiffer PE than poly-l-lysine. Rod-like structures that looked similar to the chitosan ones were also seen when PE hyaluronan was used to flocculate a protein lysozyme¹⁰⁵.

3.3 Phase Behavior of Polyelectrolyte-Colloidal Complexes

Aggregates formed by adsorption of PEs on colloidal surfaces eventually phase separate predominantly due to interparticle bridging of colloids by PEs in most water treatment regimes. Understanding such phase behavior is therefore critical for the better design of water treatment methods. It is frequently seen through experiments¹⁰⁶ that the cloudiness of the treated solution generally increases initially. This tangible property is known as turbidity and has been at the core of water-quality assessments. As the colloidal flocs grow to the range of a few microns, there is a visual increase in turbidity. This property can be quantified by turbidimetry tests which include a spectrum of experimental techniques. Jar Test is a cheap and scalable technique

still followed by industry and absorption/extinction tests that involve shining UV light through a sample volume and detecting the intensity of transmitted light to estimate the concentration of impurities in the solution through calibration curves^{52,97,105–108}. Nowadays, several advanced techniques such as Small Angle X-ray scattering (SAXS), Small-Angle Neutron Scattering (SANS), and cryo-Transmission Electron Microscopy (TEM) are being used to better understand these complexes¹⁰⁴. Once again, looking at the phase diagrams in work by Shi et.al 2013 on the removal of silica nanoparticles via chitosan, we can gather some insights into phase behavior through SAXS, SANS and cryo-TEM results, reflected in the phase diagrams. By varying the number of silica nanoparticles and semi-flexible chitosan chains, it was found that there are biphasic and monophasic regions with well-defined structures in each of these regions depicted in Figure 3.4a. When the chitosan added was low, the region was monophasic irrespective of the amount of chitosan added. It was only above a specific chitosan concentration that phase separation owing to “complex coacervation”^{104,109,110} was observed.

When the composition for each component was similar, a biphasic region was seen. In the region of excess PEs, the complexes indicated the presence of branched chains with distended ends; in the biphasic region, globular complexes were common, and the case of excess nanoparticles, single polymer chains with a multitude of silica nanoparticles attached to them in a rod-like fashion was observed. These phase diagrams were explored more through mean-field self-consistent field theory (SCFT) (Figure 3.4b)⁹⁵. In this model, the aggregates were classified according to the “radial distribution function $g(r)$ ”⁹⁵, wherein for aggregates where the peak in $g(r)$ was seen at distances comparable to interparticle distances, those aggregates were classified as “particle aggregates,” and when distances were larger than interparticle distances, they were classified as “polymer-bridged aggregates (PB).” Further classification based on the fraction of particles in the clusters was done: “monomer dominated small aggregates (M), large aggregates (A), and highly networked extended aggregates known as

percolated aggregates (P). Particle charge proved to be directly proportional to the tendency to flocculate due to more electrostatic repulsions, except for polymer bridging, which is seen at a much higher particle charge¹⁰⁰. Cluster formation is directly proportional to polymer concentration except at a very high particle charge when repulsion dominates and particles are interrupted from coming closer. Polymer bridging is encountered concomitantly with a high polymer charge. A large body of work on similar PE-protein complex studies can be accredited to motivation for applications in applications including protein purification and preservation, drug delivery, and gene therapy^{65,101,111–113}. These studies can be helpful because protein-PE interactions are comparable to colloidal nanoparticle (NP) interactions. The size range of proteins is comparable, the surface of these molecules has both positive and negatively charged centers, and at varying pH values of the solution, their surface charges can be categorized as constant, i.e., only positive or negative. Hence conclusions from these studies would be helpful for all colloidal systems.

Along similar lines, the study of lysozyme flocculation is a globular protein with cationic surface charge and anionic polystyrene sulfonate (PSS)¹¹⁴, has revealed several salient properties via SANS measurements. At a low concentration of PSS (charge ratio of anionic PE (-) and cationic proteins (+), $[-]/[+] < 1$), charge-neutral globular structures dominate, and when PSS concentration is high ($[-]/[+] > 1$), the center of aggregates is still neutral, but now the signal is noisy which might indicate the dangling end of chains or protruding parts of polymer chains. At a pH = 3 it was seen that the lysozyme maintained a cationic charge which can be comparable to constant charge colloidal systems. At a specific concentration of chains C^* , these chains interconnect to form a gel-like structure and below that solution is clear liquid-like even though some complexation might have occurred. At lower PSS concentrations liquid-like system was seen with globular protein molecules distended in solution Figure 3.4¹⁰⁴. It was seen that for PSS in Lysozyme, the PE (L_p) persistence chain length decreased. This helped

quantify the transition from gel to cluster formation of this system, which occurs at a critical concentration value of C^* of PSS, which was inversely proportional to the persistence chain length. Approximately spherical clusters begin to form when the system is phase separating, and such clusters can bear a cumulative positive or negative charge even though the charge at the core remains neutral. It was also shown that chain length does not matter in the formation of these clusters. The transition from gel to cluster formation was found to occur at a critical concentration value of C^* of PSS, which was inversely proportional to the persistence chain length¹¹⁴.

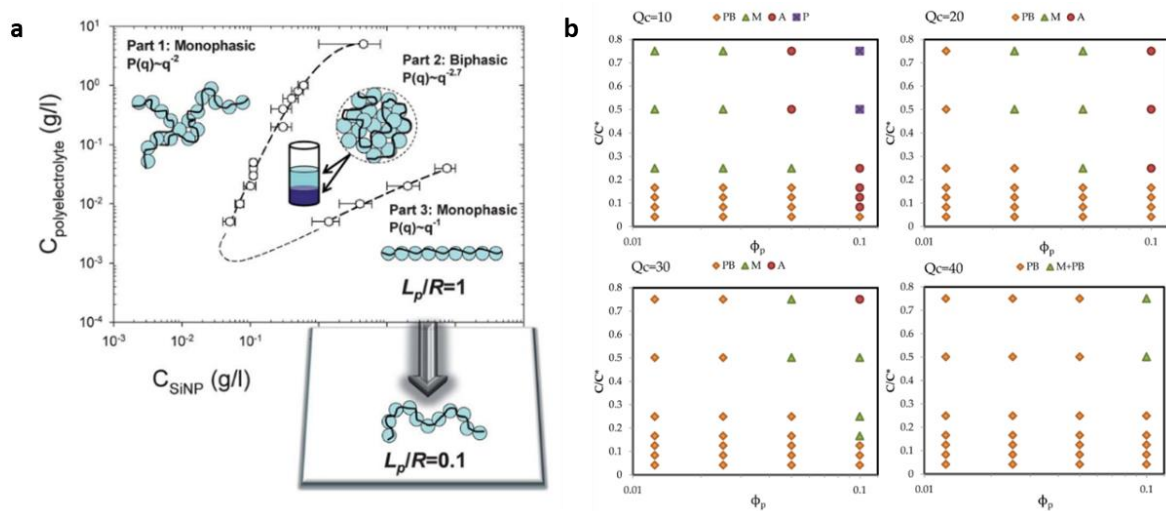


Figure 3.4 (a) A general phase diagram for turbidity in PE-NP complexes with respect to the concentration of PE and NPs. Reproduced from “Control over the electrostatic self-assembly of nanoparticle semi-flexible bio polyelectrolyte complexes” Shi et al., 2013¹⁰⁴, Soft Matter; with permission from Royal Society of Chemistry. **(b)** Polymer bridged (PB), monomer dominated aggregates (M), aggregates (A) and percolated aggregates (P) identified in simulations of PE-NP complexes for different PE and NP concentrations and NP charge (Q_c). Adapted with permission from Pandav et. al 2015⁹⁵; Copyright (2015) American Chemical Society.

When the charge ratio of cationic PE (+) and anionic nanoparticles (-) was close to unity, the persistence length of the PE is low and compact aggregates are formed, which phase separate¹¹⁵. In another study, the size of spherical complexes formed by the interaction between small PE chains and proteins was seen to increase with the introduced charge ratio of [-]/[+], which corresponds to decreasing Debye length and reduced electrostatic screening. The inner charge ratio of these complexes was seen to be hovering around ~ 1 , irrespective of the charge ratio introduced into the solution. The outer charge ratio of such a system depended on the introduced charge ratio, which could be attributed to excess charges clinging onto the surface of globular complexes. This indicates that the overall colloidal aggregation mechanism is reaction controlled¹¹⁶. In an equilibrium between gel state and a complex globular state, excess polymer favored the formation of a gelled state, and greater ionic strength favored globular complexes (Figure 3.5)¹¹⁷.

A similar study also provided insights on the reorganization of complexes on the addition of excess salt, dilution, and excess PSS¹¹⁸. Dilution caused complexes to lose stability, salt causes agglomeration into more extensive complexes due to enhanced screening, and the addition of PSS causes no reorganization. Such fundamental understanding of PE-colloid interaction is critical for a rational design of PEs for developing more efficient and targeted water treatment methods in the industry where similar systems can be found due to protein-based or colloidal impurities. This would also shine a light on other applications of such systems, such as in drug delivery and protein segregation. The ionic strength of water is a crucial parameter that dictates PE-colloid interaction. This impacts the screening of charges which is also an important phenomenon that needs consideration. The persistence length of the coagulant PE is another critical characteristic of the PE, which affects the size and density of flocs.

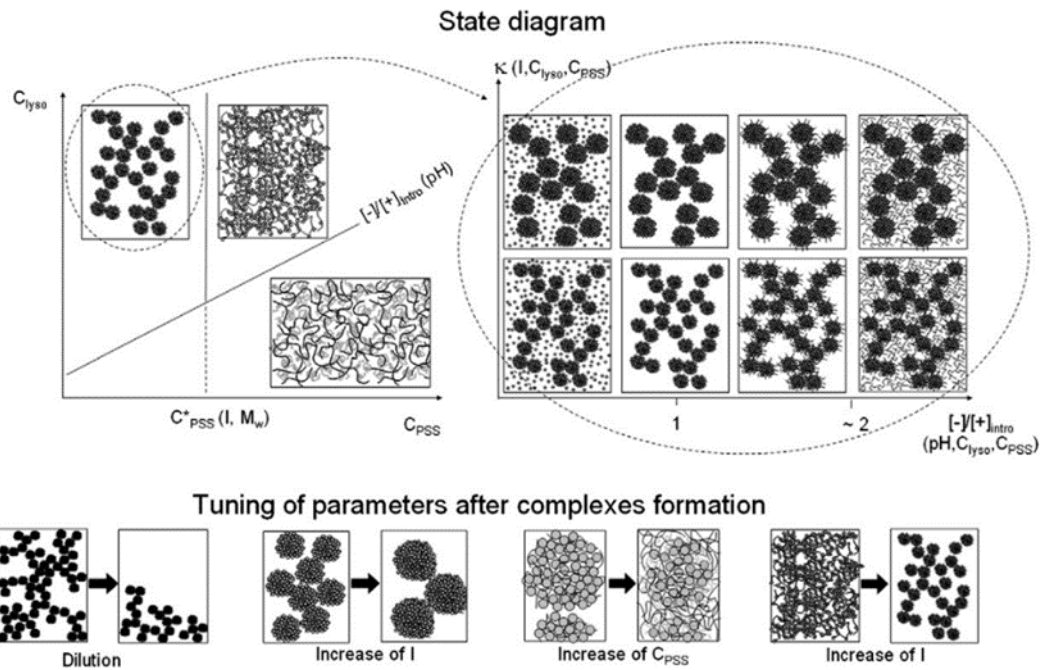


Figure 3.5 Different structures protein-PE made of PSS and lysozyme, depicting their dependence on PE and protein concentrations, ionic strength, and PE persistence length. Adapted with permission from “ Multiple scale reorganization of electrostatic complexes of poly(styrene-sulfonate) and lysozyme” Gummel et al., 2008¹¹⁷. Advances in Colloid and Interface Science.; Copyright (2011) Elsevier.

3.4 BIOPOLYMER FLOCCULANTS

Biopolymers have garnered much interest due to their low toxicity and their promise of being ecologically sustainable. Since historical times as early as 2000 BC, they have been reported, such as “crushed nuts of Nirmali tree *Strychnos Potatorum Linn*”^{140, 62}, which is an anionic PE. Other popular biopolymer flocculants are Moringa Oleifera tree seeds, Guar Gum, Tannin, Starches, Chitosan, Sodium Alginate, among which Chitosan and Starch based flocculants are discussed in detail in the sections below. Several biopolymers were found to perform exceptionally well in the removal of organics such as humic acid⁷³. Inorganic coagulants produce a large amount of sludge and especially in the case of alum. Floccs formed require

diligent pH and temperature control for optimum mechanical strength to be phase-separated³⁰. With synthetic polymer-based flocculants and coagulants, the problem lies in the lack of biodegradability and contamination due to unreacted monomers in the effluents, some of which have even been classified as carcinogenic⁵². Acrylamide-based polymer flocculants are carcinogenic to animals, affecting their organs and glands, their lethal dose “LD₅₀ being 100-250 mg/kg”^{62,119,120}. Remnants of monomers and reaction-by-products of these prove to be very harmful to marine and aquatic life⁵². In particular, products such as N-nitrosodimethylamine (NDMA) have been categorized as a carcinogen by USEPA and are generally generated as a by-product of chlorination of water treated with synthetic PEs⁶². Dimethylamine (DMA) is a known precursor to NDMA and was found to be present in common synthetic PE flocculants in their active form, with NDMA formation tendency being “Mannich Polymer >> Polyamine >> PDADMAC >> Cationic PAM”¹²¹. Hence, we should realize the importance of developing and investing in the research of such biopolymer flocculants.

3.4.1 Chitosan Based Flocculants

Chitosan is the “second most abundant polymer in nature”¹⁰⁴ and has been one of the most commonly used biopolymer flocculants because of its eco-friendliness, availability, and ease of production³⁰. It is composed of D-glucosamine and N-acetyl-D-glucosamine and is “synthesized by deacetylation of chitin by a strong base like NaOH”^{30,122} and is suitable for coagulation of inorganic¹²³ as well as organic impurities¹²⁴. Molecular weight along with the extent of esterification of chitosan, dosage, and pH are critical parameters for optimal performance^{30,124}. It is very effective in producing thick sludge and works in low temperatures, unlike inorganic coagulants³⁰. Chitosan has a massive range of applications reported in research. Its action on effluents of all kinds of food, dye, and mineral effluents in wastewater

has been studied³⁰. Chitosan flocculates through bridging and patch flocculation. In some instances, chitosan has been modified with added functional groups through overall strategies of graft polymerization and esterification reactions to help improve their performance. This has been only possible because of the presence of “free amines and hydroxyl groups present on the chitosan backbone”¹²⁵. These modifications significantly improve their spectrum of applicability. For example, grafting acrylamide to chitosan improved its performance on kaolinite suspensions, wherein now, the hybrid polymer performed more efficiently over a broader range of pH. This can be ascribed to better adherence to impurities due to the new flexibility brought by the flexible polyacrylamide component¹²⁶. Similarly, amination of chitosan with compounds like 3-chloro-2-hydroxypropyl trimethylammonium chloride (CTA) (cationic)¹²⁷ or organic acids such as Monochloroacetic acid¹²⁸ are considered for improving the performance of these flocculants. These modifications were thereby influencing the efficiency of bridging and charge neutralization due to the functional groups now present on the backbone of chitosan¹²⁵. Cost-effectiveness is a significant limiting factor for chitosan-based flocculants. A multitude of studies done has proven that the cost to yield ratio of using chitosan is not viable as compared to synthetic polymer flocculants^{113,129,130}. The key lies in finding a cost-effective way to segregate and mass-produce chemically pure and stable versions of chitosan-based flocculants.

3.4.2 Starch-Based Flocculants

Starch is basically “highly polymerized carbohydrates”⁶² naturally found in rice, potatoes, yams, etc. Naturally, starch is a neutral polymer. They benefit from the same advantages of excellent availability, low cost, and biodegradability as chitosan^{108,125,131,132}. Similar to chitosan, starch has a wide range of applicability to various impurities such as biomass¹³³, humic acid¹⁰⁸, kaolin clay¹³⁴, and heavy metals¹³⁵. Hybrid starch flocculants have been reported by blending, esterification, etherification, oxidation, crosslinking, and graft

polymerization to improve the performance of such coagulants^{136,137}. Starch molecules grafted with charged ammonium group have demonstrated better removal of silica nanoparticles¹³⁸ while also showing antimicrobial properties, specifically *E. coli*, significantly reducing disinfection cost in downstream treatment¹³¹. Removal and recovery of heavy metals (zinc and copper) were made easy by creating a dual functionality hybrid starch material responsive to temperature and pH, formed by etherifying starch with 2-chloro-4,6- diglycino-1,3,5-triazine (CDT) (Figure 3.6a)¹³⁵. These materials utilized “reversible phase transitions in aqueous media” for this functionality. pH responsiveness of this flocculant depended on the degree of substitution of starch, polymer concentration, and changing ionic strength by introducing salts. On changing the pH (de)protonation of carboxyl and amine groups was seen (Figure 3.6b). This flocculant displayed excellent cyclability and effectiveness. Starch-based polymer (2,4-bis(dimethylamino)-[1,3,5]- triazine-6-yl)-starch proved effective in removing anionic dyes from wastewater¹³⁹.

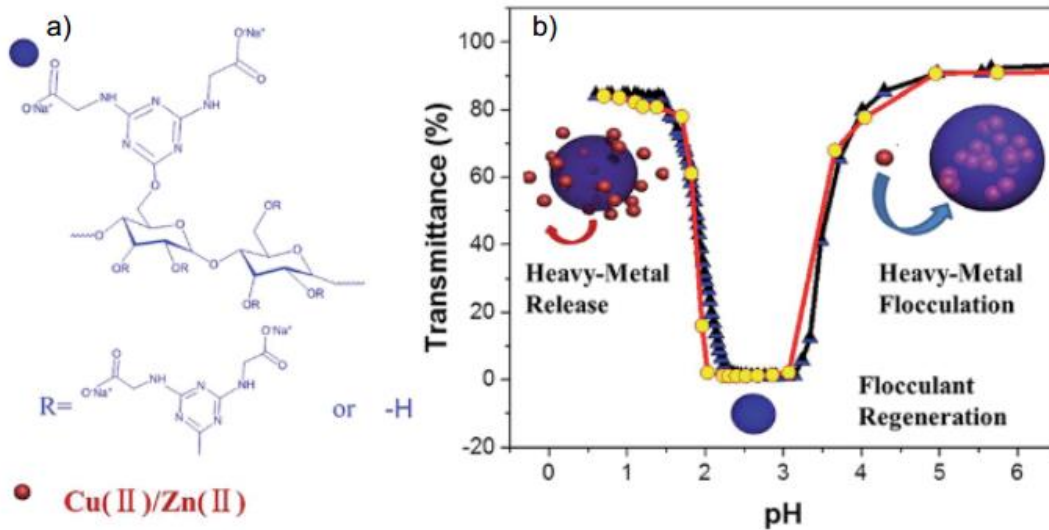


Figure 3.6 (a) Depicts the variation in the molecular structure of a starch-based flocculant that can respond to pH (PRAS). (b) Schematic representation of the cyclic flocculation/regeneration process along with the observed turbidity in the solution as a function of solution pH. Adapted with permission from “Amphoteric starch derivatives as reusable flocculant for heavy-metal removal” Wu et al. 2018,¹³⁵; Copyright © Creative Commons License Attributed 3.0 Unported License.

4. POLYELECTROLYTE USAGE AND PERFORMANCE IN WATER

TREATMENT

Adapted with Permission from

Polyelectrolyte Coagulants and Flocculants in Water Treatment: A Fundamental Perspective. D. J. Iyer, A. Holkar, and S. Srivastava, In *Advances in Water Desalination Technologies*, Y. Cohen (ed.), *in press* (2021).

Applications of PEs as coagulants and flocculants, as already discussed in previous sections, are ubiquitous, ranging from treatment of dyes, oil well cementation, and protein purification^{39,140,141}. The primary use of these polyelectrolytes is encountered in the primary treatment stages. One of the first industrial usages of PEs for water treatment was seen in Umgeni, South Africa, where epichlorohydrin-dimethylamine (epi-DMA) was utilized to reduce operational costs with excellent results. Operational costs were reduced by 30%, and the polymer dosage required was significantly lower than inorganic coagulants, which were used before, accompanied by low sludge production^{142,143}. However, close monitoring of dosage in such systems is essential as excess polymer showed restabilization of the system primarily due to charge reversal of flocs¹⁴³. The advantages of PEs on the end of sludge volume reduction have been proven by other research works¹⁴⁴. For instance, Figure 4.1b shows improvement of SS removal on the addition of chitosan at lower Al dosage while maintaining a constant sludge production. Another factor that showed noticeable improvement by the addition of PEs was an improvement in flocs' settling speed as polymer dosage was increased¹⁴⁴. Hybrid coagulant systems by mixing polymer flocculants with metal oxides (such as Fe₂O₃, Al₂O₃, and MnO₂) further increase the propensity of flocculation of organic impurities in wastewater. These metal oxides serve as “adsorption sites for ligand exchange and hydrogen bonding”⁸³, resulting in a cleaner water treatment method⁵⁶. This strategy has been termed “Chemical Enhanced Primary Treatment (CEPT),”⁶² which involves a combination of metallic salts and polyelectrolytes for wastewater treatment. There have been

reported cases of more than 70% removal of suspended solid particulates and more than 40% removal of Chemical Oxygen Demand (COD)¹⁴⁵. Such CEPT methods have been implemented in big municipalities, such as Los Angeles, Orange County, and San Diego, and cities such as Hong Kong, Mexico City, and Sao Paulo. Here water treatment plants were revamped with CEPT systems, and added costs were recovered quickly with significant improvement in water quality standard¹⁴⁶. Although polyelectrolyte systems have such benefits and widespread applicability, detailed studies on their toxicity and eco-friendliness need to be investigated further to reduce the risk to the environment and human health^{143,145}. The first step is to optimize the dosage for minimum residual unreacted toxic polymer by-products and active reagents present in effluents. The key to this would come from developing specific and targeted systems that will help offset downstream costs in quality control¹⁴⁵. For instance, flocculation of negatively charged clay suspensions with polypropylene oxide (PPO) grafted PAM showed increased dewaterability and higher solid content than linear PAM chains¹⁴⁰. Making a choice of the correct polymer and additives for a particular system is rooted in the fundamental understanding of the properties of colloids, polymers, and operating conditions, and the nature of flocculated aggregates, as we have discussed in this work.

5. CONCLUSION AND FUTURE PERSPECTIVES

Polymer-based coagulants have gained massive impetus in the last few decades owing to their improved performance and widespread applicability as primary coagulants, flocculant aids, and sludge conditioners. However, remnants left behind after treatment by PEs are known to be toxic and include chemicals such as acrylamide, ethyleneimine, and trimethylolmelamine, all of which are classified as toxic by government agencies worldwide^{56,62}. Hence the development of biodegradable or bio-based hybrid PE flocculants for water treatment seems to be the way forward for water treatment systems. Challenges of developing systems also include design aspects and better material characterization methods which can be incorporated into industrial treatment plants. The hurdle there is to have a feasible and scalable experimental procedure that will incentivize the industry. As the reader might have gauged by reading the thesis, a fundamental understanding of polyelectrolyte-protein complexes has shed light on microstructural phenomena and weave together critical polymer characteristics such as persistence length, flexibility, charge density, and colloidal properties with coagulation or flocculation efficiency. This is great for engineering novel materials. Also with better characterization techniques reported in the literature such as SANS, SAXS, cryo-TEM, and spectroscopy, although expensive to implement on an industrial scale, through proper experimental design and pilot testing, can save huge processing costs downstream. Better molecular design and understanding of PE-nanoparticle interactions and complex behavior can help find that optimum dosage with minimum residue. This does not in any way disregard the need for developing better control systems for live monitoring of feed and effluents in water treatment plants, but not the focus of this study. The goal here was to illuminate and discuss various polyelectrolyte systems in recent and early studies to give the reader a well-rounded

perspective on the theory, fundamentals, and possibilities in coagulants and flocculants, particularly polyelectrolytes in water treatment systems.

REFERENCES

- (1) Boretti, A.; Rosa, L. Reassessing the Projections of the World Water Development Report. *Nat. Partn. Journals Clean Water* **2019**, 2–15. <https://doi.org/10.1038/s41545-019-0039-9>.
- (2) Hinrichsen, D.; Tacio, H. *Finding the Source: The Coming Freshwater Crisis Is Already Here*; 2002.
- (3) UN World Water Development Report 2020 | UN-Water <https://www.unwater.org/publications/world-water-development-report-2020/> (accessed Jun 7, 2021).
- (4) The United Nations world water development report 2018: nature-based solutions for water - UNESCO Digital Library <https://unesdoc.unesco.org/ark:/48223/pf0000261424> (accessed May 27, 2021).
- (5) Com, I. *UN-WATER GLOBAL ANALYSIS AND ASSESSMENT OF SANITATION AND DRINKING-WATER GLAAS 2019 REPORT*; 2019.
- (6) Bratby, J. *Introduction, Coagulation and Flocculation in Water and Wastewater Treatment*, Third.; 2016.
- (7) Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent Developments in Photocatalytic Water Treatment Technology: A Review. *Water Res.* **2010**, 44 (10), 2997–3027. <https://doi.org/10.1016/j.watres.2010.02.039>.
- (8) Graziano, G. No-Filter Filtration. *Nat. Rev. Chem.* **2017**, 6 (May), 1. <https://doi.org/10.1038/s41570-017-0049>.
- (9) Moussas, P. A.; Tzoupanos, N. D.; Zouboulis, A. I. Advances in

- Coagulation/Flocculation Field: Al- and Fe-Based Composite Coagulation Reagents. *Desalin. Water Treat.* **2011**, *33* (1–3), 140–146. <https://doi.org/10.5004/dwt.2011.2622>.
- (10) Ngombolo, A.; Mpupa, A.; Moutloali, R. M.; Nomngongo, P. N. Wastewater Treatment Using Membrane Technology. *IntechOpen* **2016**, *i*, 13. <https://doi.org/http://dx.doi.org/10.5772/57353>.
- (11) Szyguła, A.; Guibal, E.; Palacín, M. A.; Ruiz, M.; Sastre, A. M. Removal of an Anionic Dye (Acid Blue 92) by Coagulation-Flocculation Using Chitosan. *J. Environ. Manage.* **2009**, *90* (10), 2979–2986. <https://doi.org/10.1016/j.jenvman.2009.04.002>.
- (12) Teh, C. Y.; Budiman, P. M.; Shak, K. P. Y.; Wu, T. Y. Recent Advancement of Coagulation-Flocculation and Its Application in Wastewater Treatment. *Ind. Eng. Chem. Res.* **2016**, *55* (16), 4363–4389. <https://doi.org/10.1021/acs.iecr.5b04703>.
- (13) Israelachvili, J. N. *Intermolecular & Surface Forces*; 2011; Vol. 3. <https://doi.org/https://doi.org/10.1016/C2009-0-21560-1>.
- (14) Matilainen, A.; Vepsäläinen, M.; Sillanpää, M. Natural Organic Matter Removal by Coagulation during Drinking Water Treatment: A Review. *Adv. Colloid Interface Sci.* **2010**, *159* (2), 189–197. <https://doi.org/10.1016/j.cis.2010.06.007>.
- (15) Zhan, X.; Gao, B.; Yue, Q.; Wang, Y.; Cao, B. Coagulation Behavior of Polyferric Chloride for Removing NOM from Surface Water with Low Concentration of Organic Matter and Its Effect on Chlorine Decay Model. *Sep. Purif. Technol.* **2010**, *75* (1), 61–68. <https://doi.org/10.1016/j.seppur.2010.07.012>.
- (16) Sillanpää, M.; Ncibi, M. C.; Matilainen, A.; Vepsäläinen, M. Removal of Natural Organic Matter in Drinking Water Treatment by Coagulation: A Comprehensive Review. *Chemosphere* **2018**, *190*, 54–71.

<https://doi.org/10.1016/j.chemosphere.2017.09.113>.

- (17) Murcott, S.; Harleman, D. R. F. MIT Jar Tests of the Natural Polymer Chitosan with Fresh Pond Water from the Cambridge Water Department, November-December, 1992. 1993.
- (18) Tzoupanos, N. D.; Zouboulis, a I. Coagulation-Flocculation Processes in Water / Wastewater Treatment : The Application of New Generation of Chemical Reagents. *6th IASME/WSEAS Int. Conf. HEAT Transf. Therm. Eng. Environ.* **2008**, No. January, 309–317.
- (19) Amokrane, A.; Comel, C.; Veron, J. Landfill Leachates Pretreatment by Coagulation-Flocculation. *Water Res.* **1997**, *31* (11), 2775–2782. [https://doi.org/10.1016/S0043-1354\(97\)00147-4](https://doi.org/10.1016/S0043-1354(97)00147-4).
- (20) American Water Works Association. Operational Control of Coagulation and Filtration Processes. **2011**, 226.
- (21) Xavier, L. D.; Yokoyama, L.; de Oliveira, V. R.; Ribeiro, G. T.; Araújo, O. The Role of Coagulation-Flocculation in the Pre-treatment of Reverse Osmosis in Power Plant. *J. Sustain. Dev. Energy, Water Environ. Syst.* **2020**, *8* (1), 118–131. <https://doi.org/10.13044/j.sdewes.d7.0266>.
- (22) Renou, S.; Givaudan, J. G.; Poulain, S.; Dirassouyan, F.; Moulin, P. Landfill Leachate Treatment: Review and Opportunity. *J. Hazard. Mater.* **2008**, *150* (3), 468–493. <https://doi.org/10.1016/j.jhazmat.2007.09.077>.
- (23) Guigui, C.; Roucha, J. C.; Durand-Bourlierb, L.; Bonnelyeb, V.; Aptel, P. DESALINATION ELSEVIER Desalination 147 (2002) 95-100 Impact of Coagulation Conditions on the in-Line CoagulationKJF Process for Drinking Water Production.

- 2002**, *147*, 95–100.
- (24) Jang, N. Y.; Watanabe, Y.; Minegishi, S. Performance of Ultrafiltration Membrane Process Combined with Coagulation/Sedimentation. *Water Sci. Technol.* **2005**, *51* (6–7), 209–219. <https://doi.org/10.2166/wst.2005.0640>.
- (25) Kimura, K.; Hane, Y.; Watanabe, Y.; Amy, G.; Ohkuma, N. Irreversible Membrane Fouling during Ultrafiltration of Surface Water. *Water Res.* **2004**, *38* (14–15), 3431–3441. <https://doi.org/10.1016/j.watres.2004.05.007>.
- (26) Marañón, E.; Castrillón, L.; Fernández-Nava, Y.; Fernández-Méndez, A.; Fernández-Sánchez, A. Coagulation-Flocculation as a Pretreatment Process at a Landfill Leachate Nitrification-Denitrification Plant. *J. Hazard. Mater.* **2008**, *156* (1–3), 538–544. <https://doi.org/10.1016/j.jhazmat.2007.12.084>.
- (27) Wiesner, M. R.; Clark, M. M.; Mallevalle, J. Membrane Filtration of Coagulated Suspensions. *J. Environ. Eng. (United States)* **1989**, *115* (1), 20–40. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1989\)115:1\(20\)](https://doi.org/10.1061/(ASCE)0733-9372(1989)115:1(20)).
- (28) Zhu, Z. Theory on Orthokinetic Flocculation of Cohesive Sediment: A Review. *J. Geosci. Environ. Prot.* **2014**, *02* (05), 13–23. <https://doi.org/10.4236/gep.2014.25003>.
- (29) States, U. Wastewater Treatment Works... The Basics. **1998**, No. May, 1–6.
- (30) Renault, F.; Sancey, B.; Badot, P. M.; Crini, G. Chitosan for Coagulation/Flocculation Processes - An Eco-Friendly Approach. *Eur. Polym. J.* **2009**, *45* (5), 1337–1348. <https://doi.org/10.1016/j.eurpolymj.2008.12.027>.
- (31) Spellman, F. *Handbook of Water and Wastewater Treatment Plant Operations*; 2003. <https://doi.org/10.1201/9780203489833>.

- (32) Healy, T. W.; La Mer, V. K. The Adsorption-Flocculation Reactions of a Polymer with an Aqueous Colloidal Dispersion. *J. Phys. Chem.* **1962**, *66* (10), 1835–1838. <https://doi.org/10.1021/j100816a014>.
- (33) Chemistry of Water Treatment - Samuel D. Faust, Osman M. Aly - Google Books https://books.google.com/books?hl=en&lr=&id=bkwPEAAAQBAJ&oi=fnd&pg=PP1&ots=O4wxhZAYuQ&sig=gpHHkct3_3rDHF2dCSM7a2QKH24#v=onepage&q&f=false (accessed Jun 7, 2021).
- (34) Jiang, J. Q.; Zeng, Z.; Pearce, P. Evaluation of Modified Clay Coagulant for Sewage Treatment. *Chemosphere* **2004**, *56* (2), 181–185. <https://doi.org/10.1016/j.chemosphere.2004.03.007>.
- (35) Jahn, S. A. A. From Clarifying Pearls and Gems to Water Coagulation with Alum History, Surviving Practices, and Technical Assessment. *Anthropos* **1999**, *94* (4–6), 419–430.
- (36) Austen, P.T., and F.A. Wilbur. “Report of the State Geologist of New Jersey, 1884 - Google Search <https://www.google.com/search?q=Austen%2C+P.T.%2C+and+F.A.+Wilbur.+%20Report+of+the+State+Geologist+of+New+Jersey%2C+1884&oq=Austen%2C+P.T.%2C+and+F.A.+Wilbur.+%20Report+of+the+State+Geologist+of+New+Jersey%2C+1884&aqs=chrome..69i57j69i59j69i60.669j0j9&sourceid=chrome&ie=UTF-8> (accessed Jun 7, 2021).
- (37) Chaudhari, P. K.; Majumdar, B.; Choudhary, R.; Yadav, D. K.; Chand, S. Treatment of Paper and Pulp Mill Effluent by Coagulation. *Environ. Technol.* **2010**, *31* (4), 357–363. <https://doi.org/10.1080/09593330903486665>.

- (38) Yin, C. Y. Emerging Usage of Plant-Based Coagulants for Water and Wastewater Treatment. *Process Biochem.* **2010**, *45* (9), 1437–1444. <https://doi.org/10.1016/j.procbio.2010.05.030>.
- (39) Riera-Torres, M.; Gutiérrez-Bouzán, C.; Crespi, M. Combination of Coagulation-Flocculation and Nanofiltration Techniques for Dye Removal and Water Reuse in Textile Effluents. *Desalination* **2010**, *252* (1–3), 53–59. <https://doi.org/10.1016/j.desal.2009.11.002>.
- (40) Rodrigues, A. C.; Boroski, M.; Shimada, N. S.; Garcia, J. C.; Nozaki, J.; Hioka, N. Treatment of Paper Pulp and Paper Mill Wastewater by Coagulation-Flocculation Followed by Heterogeneous Photocatalysis. *J. Photochem. Photobiol. A Chem.* **2008**, *194* (1), 1–10. <https://doi.org/10.1016/j.jphotochem.2007.07.007>.
- (41) Zhao, Y. X.; Gao, B. Y.; Shon, H. K.; Cao, B. C.; Kim, J. H. Coagulation Characteristics of Titanium (Ti) Salt Coagulant Compared with Aluminum (Al) and Iron (Fe) Salts. *J. Hazard. Mater.* **2011**, *185* (2–3), 1536–1542. <https://doi.org/10.1016/j.jhazmat.2010.10.084>.
- (42) Cao; Gao; Xu; Fu; Liu. Effects of PH on Coagulation Behavior and Floc Properties in Yellow River Water Treatment Using Ferric Based Coagulants. *Chinese Sci. Bull.* **2010**, *55* (14), 1382–1387. <https://doi.org/10.1007/s11434-010-0087-5>.
- (43) Particle Deposition and Aggregation: Measurement, Modelling and Simulation - M. Elimelech, J. Gregory, X. Jia - Google Books <https://books.google.com/books?hl=en&lr=&id=R6g3BQAAQBAJ&oi=fnd&pg=PP1&dq=Electrical+properties+of+interfaces.+In+Particle+Deposition+%26+Aggregation:+Measurement,+Modelling+and+Simulation,+%28World+Scientific%29,&ots=NFZyIaWl74>

- &sig=tJoyCh97n0sNTgtzjY7BzREpNs0#v=onepage&q=Electrical properties of interfaces. In Particle Deposition %26 Aggregation%3A Measurement%2C Modelling and Simulation%2C (World Scientific)%2C&f=false (accessed Jun 7, 2021).
- (44) Physical Chemistry of Polyelectrolytes. Surfactant Science Series. Volume 99 Edited by Tsetska Radeva (Bulgarian Academy of Sciences). Marcel Dekker: New York, Basel. 2001. xvi + 882 pp. \$250.00. ISBN: 0-8247-0463-0 | Request PDF https://www.researchgate.net/publication/238626041_Physical_Chemistry_of_Polyelectrolytes_Surfactant_Science_Series_Volume_99_Edited_by_Tsetska_Radeva_Bulgarian_Academy_of_Sciences_Marcel_Dekker_New_York_Basel_2001_xvi_882_pp_25000_ISBN_0-8247-0463-0 (accessed Jun 7, 2021).
- (45) Jonsson, M.; Linse, P. Polyelectrolyte-Macroion Complexation. II. Effect of Chain Flexibility. *J. Chem. Phys.* **2001**, *115* (23), 10975–10985. <https://doi.org/10.1063/1.1417508>.
- (46) Metin, C. O.; Bonnacaze, R. T.; Lake, L. W.; Miranda, C. R.; Nguyen, Q. P. Aggregation Kinetics and Shear Rheology of Aqueous Silica Suspensions. *Appl. Nanosci.* **2014**, *4* (2), 169–178. <https://doi.org/10.1007/s13204-012-0185-6>.
- (47) Physik, N. F.-Z. für; 1934, undefined. Über Die Stabilität Und Aufladung Der Aerosole. *Springer*.
- (48) Reerink, H.; Overbeek, J. T. G. The Rate of Coagulation as a Measure of the Stability of Silver Iodide Sols. *Discuss. Faraday Soc.* **1954**, *18*, 74–84. <https://doi.org/10.1039/DF9541800074>.
- (49) Nagasawa, M. *Physical Chemistry of Polyelectrolyte Solutions*; 2015; Vol. 158. <https://doi.org/10.1002/9781119057338>.

- (50) Corbett, J. C.; McNeil-Watson, F. Electrophoretic Light Scattering. In *Encyclopedia of Biophysics*; Springer Berlin Heidelberg, 2018; pp 1–10. https://doi.org/10.1007/978-3-642-35943-9_288-1.
- (51) Israelachvili, J. N. Chapter 14 - Electrostatic Forces between Surfaces in Liquids. In *Intermolecular and Surface Forces*; Elsevier, 2011; pp 291–340. <https://doi.org/10.1016/b978-0-12-375182-9.10014-4>.
- (52) Bolto, B.; Gregory, J. Organic Polyelectrolytes in Water Treatment. *Water Res.* **2007**, *41* (11), 2301–2324. <https://doi.org/10.1016/j.watres.2007.03.012>.
- (53) Krishna, R.; Sahu, O. Reduction of COD and Color by Polymeric Coagulant (Chitosan). *J. Polym. Biopolym. Phys. Chem.* **2013**, *1* (1), 22–25. <https://doi.org/10.12691/JPBPC-1-1-4>.
- (54) Duan, J.; Gregory, J. Coagulation by Hydrolysing Metal Salts. *Adv. Colloid Interface Sci.* **2003**, *100–102* (SUPPL.), 475–502. [https://doi.org/10.1016/S0001-8686\(02\)00067-2](https://doi.org/10.1016/S0001-8686(02)00067-2).
- (55) Ghernaout, D.; Ghernaout, B. Sweep Flocculation as a Second Form of Charge Neutralisation-A Review. *Desalin. Water Treat.* **2012**, *44* (1–3), 15–28. <https://doi.org/10.1080/19443994.2012.691699>.
- (56) Bolto, B.; Dixon, D.; Eldridge, R.; King, S. Cationic Polymer and Clay or Metal Oxide Combinations for Natural Organic Matter Removal. *Water Res.* **2001**, *35* (11), 2669–2676. [https://doi.org/10.1016/S0043-1354\(00\)00552-2](https://doi.org/10.1016/S0043-1354(00)00552-2).
- (57) Bratby, J. Treatment with Polymer, Coagulation and Flocculation in Water and Wastewater Treatment. *Water Intell. Online* **2016**, *15* (AUG.), 9781780407500–

9781780407500. <https://doi.org/10.2166/9781780407500>.
- (58) Pelssers, E. G. M.; Stuart, M. A. C.; Fler, G. J. *Kinetics of Bridging Flocculation Role of Relaxations in the Polymer Layer*; 1990; Vol. 86.
- (59) Yang, R.; Li, H.; Huang, M.; Yang, H.; Li, A. A Review on Chitosan-Based Flocculants and Their Applications in Water Treatment. *Water Res.* **2016**, *95* (2015), 59–89. <https://doi.org/10.1016/j.watres.2016.02.068>.
- (60) Malik, Q. H. Performance of Alum and Assorted Coagulants in Turbidity Removal of Muddy Water. *Appl. Water Sci.* **2018**, *8* (1), 1–4. <https://doi.org/10.1007/s13201-018-0662-5>.
- (61) Bratby, J. Colloids and Interfaces, Coagulation and Flocculation in Water and Wastewater Treatment. *Water Intell. Online* **2016**, *15*, 9781780407500–9781780407500. <https://doi.org/10.2166/9781780407500>.
- (62) Bratby, J. *Treatment with Metal Coagulants, Coagulation and Flocculation in Water and Wastewater Treatment*; 2016.
- (63) Stumm, W.; O’Melia, C. R. Stoichiometry of Coagulation. *J. Am. Water Works Assoc.* **1968**, *60* (5), 514–539. <https://doi.org/10.1002/j.1551-8833.1968.tb03579.x>.
- (64) Blankert, B.; Betlem, B. H. L.; Roffel, B. Development of a Control System for In-Line Coagulation in an Ultrafiltration Process. *J. Memb. Sci.* **2007**, *301* (1–2), 39–45. <https://doi.org/10.1016/j.memsci.2007.05.033>.
- (65) Gao; Holkar; Srivastava. Protein–Polyelectrolyte Complexes and Micellar Assemblies. *Polymers (Basel)*. **2019**, *11* (7), 1097. <https://doi.org/10.3390/polym11071097>.
- (66) Gao, L. X.; Gu, H.; Rahardianto, A.; Christofides, P. D.; Cohen, Y. Self-Adaptive Cycle-

- to-Cycle Control of in-Line Coagulant Dosing in Ultrafiltration for Pre-Treatment of Reverse Osmosis Feed Water. *Desalination* **2017**, *401*, 22–31. <https://doi.org/10.1016/j.desal.2016.09.024>.
- (67) Ahmad, A. L.; Sumathi, S.; Hameed, B. H. Coagulation of Residue Oil and Suspended Solid in Palm Oil Mill Effluent by Chitosan, Alum and PAC. *Chem. Eng. J.* **2006**, *118* (1–2), 99–105. <https://doi.org/10.1016/j.cej.2006.02.001>.
- (68) Banu, R. J.; Do, K. U.; Yeom, I. T. Phosphorus Removal in Low Alkalinity Secondary Effluent Using Alum. *Int. J. Environ. Sci. Technol.* **2008**, *5* (1), 93–98. <https://doi.org/10.1007/BF03326001>.
- (69) Beltrán-Heredia, J.; Sánchez Martín, J. Azo Dye Removal by Moringa Oleifera Seed Extract Coagulation. *Color. Technol.* **2008**, *124* (5), 310–317. <https://doi.org/10.1111/j.1478-4408.2008.00158.x>.
- (70) Cao, B.; Gao, B.; Liu, X.; Wang, M.; Yang, Z.; Yue, Q. The Impact of PH on Floc Structure Characteristic of Polyferric Chloride in a Low DOC and High Alkalinity Surface Water Treatment. *Water Res.* **2011**, *45* (18), 6181–6188. <https://doi.org/10.1016/j.watres.2011.09.019>.
- (71) Saritha, V.; Srinivas, N.; Srikanth Vuppala, N. V. Analysis and Optimization of Coagulation and Flocculation Process. *Appl. Water Sci.* **2017**, *7* (1), 451–460. <https://doi.org/10.1007/s13201-014-0262-y>.
- (72) Verma, S.; Prasad, B.; Mishra, I. M. Pretreatment of Petrochemical Wastewater by Coagulation and Flocculation and the Sludge Characteristics. *J. Hazard. Mater.* **2010**, *178* (1–3), 1055–1064. <https://doi.org/10.1016/j.jhazmat.2010.02.047>.
- (73) Narkis, N.; Rebhun, M. Stoichiometric Relationship between Humic and Fulvic Acids

- and Flocculants. *J. / Am. Water Work. Assoc.* **1977**, 69 (6), 325–328.
<https://doi.org/10.1002/j.1551-8833.1977.tb06752.x>.
- (74) Yang; Gao; Yue; Wang. Effect of PH on the Coagulation Performance of Al-Based Coagulants and Residual Aluminum Speciation during the Treatment of Humic Acid-Kaolin Synthetic Water. *J. Hazard. Mater.* **2010**, 178 (1–3), 596–603.
<https://doi.org/10.1016/j.jhazmat.2010.01.127>.
- (75) Black, A. P.; Chen, C. Electrokinetic Behavior of Aluminum Species in Dilute Dispersed Kaolinite Systems. *J. Am. Water Works Assoc.* **1967**, 59 (9), 1173–1183.
<https://doi.org/10.1002/j.1551-8833.1967.tb03504.x>.
- (76) Xu; Xiao; Wang; Ye. Survey of Treatment Process in Water Treatment Plant and the Characteristics of Floccs Formed by Two New Coagulants. *Colloids Surfaces A Physicochem. Eng. Asp.* **2014**, 456 (1), 211–221.
<https://doi.org/10.1016/j.colsurfa.2014.05.036>.
- (77) Morris, J. K.; Knocke, W. R. Temperature Effects on the Use of Metal-Ion Coagulants for Water Treatment. *J. / Am. Water Work. Assoc.* **1984**, 76 (3), 74–79.
<https://doi.org/10.1002/j.1551-8833.1984.tb05302.x>.
- (78) Hanson, A. T.; Cleasby, J. L. Effects of Temperature on Turbulent Flocculation. Fluid Dynamics and Chemistry. *J. / Am. Water Work. Assoc.* **1990**, 82 (11), 56–73.
<https://doi.org/10.1002/j.1551-8833.1990.tb07053.x>.
- (79) Fitzpatrick, C. S. B.; Fradin, E.; Gregory, J. Temperature Effects on Flocculation, Using Different Coagulants. *Water Sci. Technol.* **2004**, 50 (12), 171–175.
<https://doi.org/10.2166/wst.2004.0710>.
- (80) Phalakornkule, C.; Mangmeemak, J.; Intrachod, K.; Nuntakumjorn, B. Pretreatment of

- Palm Oil Mill Effluent by Electrocoagulation and Coagulation. *ScienceAsia* **2010**, *36* (2), 142–149. <https://doi.org/10.2306/scienceasia1513-1874.2010.36.142>.
- (81) Marriott, N. G.; Robertson, G. *Essentials of Food Sanitation*; Robertson, G., Ed.; Food Science Texts Series; Springer US: Boston, MA, 1997. <https://doi.org/10.1007/978-1-4615-6045-6>.
- (82) Shak, K. P. Y.; Wu, T. Y. Coagulation-Flocculation Treatment of High-Strength Agro-Industrial Wastewater Using Natural Cassia Obtusifolia Seed Gum: Treatment Efficiencies and Flocc Characterization. *Chem. Eng. J.* **2014**, *256*, 293–305. <https://doi.org/10.1016/j.cej.2014.06.093>.
- (83) Iyer Divya Jayaram , Holkar Advait, and S. S. Polyelectrolyte Coagulants and Flocculants in Water Treatment:: A Fundamental Perspective. In *In Advances in Water Desalination Technologies*.
- (84) Miller, S. M.; Fugate, E. J.; Craver, V. O.; Smith, J. A.; Zimmerman, J. B. Toward Understanding the Efficacy and Mechanism of Opuntia Spp. as a Natural Coagulant for Potential Application in Water Treatment. *Environ. Sci. Technol.* **2008**, *42* (12), 4274–4279. <https://doi.org/10.1021/es7025054>.
- (85) Okuda; Baes; Nishijima; Okada. Isolation and Characterization of Coagulant Extracted from Moringa Oleifera Seed by Salt Solution. *Water Res.* **2001**, *35* (2), 405–410. [https://doi.org/10.1016/S0043-1354\(00\)00290-6](https://doi.org/10.1016/S0043-1354(00)00290-6).
- (86) Ghebremichael, K. A.; Gunaratna, K. R.; Henriksson, H.; Brumer, H.; Dalhammar, G. A Simple Purification and Activity Assay of the Coagulant Protein from Moringa Oleifera Seed. *Water Res.* **2005**, *39* (11), 2338–2344. <https://doi.org/10.1016/j.watres.2005.04.012>.

- (87) Okuda; Baes; Nishijima; Okada. Improvement of Extraction Method of Coagulation Active Components from Moringa Oleifera Seed. *Water Res.* **1999**, *33* (15), 3373–3378. [https://doi.org/10.1016/S0043-1354\(99\)00046-9](https://doi.org/10.1016/S0043-1354(99)00046-9).
- (88) Okuda; Baes; Nishijima; Okada. Coagulation Mechanism of Salt Solution-Extracted Active Component in Moringa Oleifera Seeds. *Water Res.* **2001**, *35* (3), 830–834. [https://doi.org/10.1016/S0043-1354\(00\)00296-7](https://doi.org/10.1016/S0043-1354(00)00296-7).
- (89) Sci, P. P.; Bolt, B. A. Pergamon SOLUBLE POLYMERS IN WATER PURIFICATION This Review Focuses on the Use of Soluble Polymers for the Preparation of Drinking Water from Low Quality Sources and in Cleaning up Wastewaters of Domestic or Industrial Origin . Potable Water Production . **1995**, *20*, 987–1041.
- (90) La Mer, V. K. Filtration of Colloidal Dispersions Flocculated by Anionic and Cationic Polyelectrolytes. *Discuss. Faraday Soc.* **1966**, *42*, 248–254. <https://doi.org/10.1039/DF9664200248>.
- (91) Hall, T.; Hyde, R. . *Water Treatment Processes and Practices*; Swinton, Wilts, 1992.
- (92) Park, S. J.; Seo, M. K. *Intermolecular Force*; Elsevier, 2011; Vol. 18. <https://doi.org/10.1016/B978-0-12-375049-5.00001-3>.
- (93) La Mer, V. K.; Mer, V. K. La. Filtration of Colloidal Dispersions Flocculated by Anionic and Cationic Polyelectrolytes. *Discuss. Faraday Soc.* **1966**, *42*, 248–254. <https://doi.org/10.1039/DF9664200248>.
- (94) Cherstvy, A. G.; Winkler, R. G. Polyelectrolyte Adsorption onto Oppositely Charged Interfaces: Unified Approach for Plane, Cylinder, and Sphere. *Phys. Chem. Chem. Phys.* **2011**, *13* (24), 11686. <https://doi.org/10.1039/c1cp20749k>.
- (95) Pandav, G.; Pryamitsyn, V.; Errington, J.; Ganesan, V. Multibody Interactions, Phase

- Behavior, and Clustering in Nanoparticle-Polyelectrolyte Mixtures. *J. Phys. Chem. B* **2015**, *119* (45), 14536–14550. <https://doi.org/10.1021/acs.jpcc.5b07905>.
- (96) Netz, R. R.; Andelman, D. Neutral and Charged Polymers at Interfaces. *Phys. Rep.* **2003**, *380* (1–2), 1–95. [https://doi.org/10.1016/S0370-1573\(03\)00118-2](https://doi.org/10.1016/S0370-1573(03)00118-2).
- (97) Cooper; Goulding; Kayitmazer; Ulrich; Stoll; Turksen; Yusa; Kumar; Dubin. Effects of Polyelectrolyte Chain Stiffness, Charge Mobility, and Charge Sequences on Binding to Proteins and Micelles. *Biomacromolecules* **2006**, *7* (4), 1025–1035. <https://doi.org/10.1021/bm050592j>.
- (98) Ulrich, S.; Seijo, M.; Stoll, S. The Many Facets of Polyelectrolytes and Oppositely Charged Macroions Complex Formation. *Curr. Opin. Colloid Interface Sci.* **2006**, *11* (5), 268–272. <https://doi.org/10.1016/j.cocis.2006.08.002>.
- (99) Winkler, R. G.; Cherstvy, A. G. Adsorption of Weakly Charged Polyelectrolytes onto Oppositely Charged Spherical Colloids. In *Journal of Physical Chemistry B*; American Chemical Society, 2007; Vol. 111, pp 8486–8493. <https://doi.org/10.1021/jp068489r>.
- (100) Pandav, G.; Pryamitsyn, V.; Ganesan, V. Interactions and Aggregation of Charged Nanoparticles in Uncharged Polymer Solutions. *Langmuir* **2015**, *31* (45), 12328–12338. <https://doi.org/10.1021/acs.langmuir.5b02885>.
- (101) Xu, X.; Angioletti-Uberti, S.; Lu, Y.; Dzubiella, J.; Ballauff, M. Interaction of Proteins with Polyelectrolytes: Comparison of Theory to Experiment. *Langmuir* **2019**, *35* (16), 5373–5391. <https://doi.org/10.1021/acs.langmuir.8b01802>.
- (102) Akinchina, A.; Linse, P. Monte Carlo Simulations of Polyion-Macroion Complexes: 1. Equal Absolute Polyion and Macroion Charges. *Macromolecules* **2002**, *35* (13), 5183–5193. <https://doi.org/10.1021/ma012052u>.

- (103) Stoll, S.; Chodanowski, P. Polyelectrolyte Adsorption on an Oppositely Charged Spherical Particle. Chain Rigidity Effects. *Macromolecules* **2002**, *35* (25), 9556–9562. <https://doi.org/10.1021/ma020272h>.
- (104) Shi; Carn; Bou; Mosser; Buhler. Control over the Electrostatic Self-Assembly of Nanoparticle Semiflexible Biopolyelectrolyte Complexes. *Soft Matter* **2013**, *9* (20), 5004–5015. <https://doi.org/10.1039/c3sm27138b>.
- (105) Morfin, I.; Buhler, E.; Cousin, F.; Grillo, I.; Boué, F. Rodlike Complexes of a Polyelectrolyte (Hyaluronan) and a Protein (Lysozyme) Observed by SANS. *Biomacromolecules* **2011**, *12* (4), 859–870. <https://doi.org/10.1021/bm100861g>.
- (106) Sakhawoth, Y.; Michot, L. J.; Levitz, P.; Malikova, N. Flocculation of Clay Colloids Induced by Model Polyelectrolytes: Effects of Relative Charge Density and Size. *ChemPhysChem* **2017**, *18* (19), 2756–2765. <https://doi.org/10.1002/cphc.201700430>.
- (107) Kizilay, E.; Kayitmazer, A. B.; Dubin, P. L. Complexation and Coacervation of Polyelectrolytes with Oppositely Charged Colloids. *Adv. Colloid Interface Sci.* **2011**, *167* (1–2), 24–37. <https://doi.org/10.1016/j.cis.2011.06.006>.
- (108) Wang, Y.; Shi, Y.; Xu, M.; Wu, L.; Jia, X.; Wei, T.; Zhang, S.; Guo, X. Smart Flocculant with Temperature and PH Response Derived from Starch. *RSC Adv.* **2016**, *6* (50), 44383–44391. <https://doi.org/10.1039/c6ra04060h>.
- (109) De Kruif, C. G.; Weinbreck, F.; De Vries, R. Complex Coacervation of Proteins and Anionic Polysaccharides. *Current Opinion in Colloid and Interface Science*. Elsevier December 1, 2004, pp 340–349. <https://doi.org/10.1016/j.cocis.2004.09.006>.
- (110) G Bungenberg De Jong, B. H.; Kruyt, H. R. *Chemistry.-Coacervation (Partial Miscibility in Colloid Systems). (Preliminary Communication)*; 1929.

- (111) Comert, F.; Dubin, P. L. Liquid-Liquid and Liquid-Solid Phase Separation in Protein-Polyelectrolyte Systems. *Adv. Colloid Interface Sci.* **2017**, *239*, 213–217. <https://doi.org/10.1016/j.cis.2016.08.005>.
- (112) Cooper, C. L.; Dubin, P. L.; Kayitmazer, A. B.; Turksen, S. Polyelectrolyte-Protein Complexes. *Curr. Opin. Colloid Interface Sci.* **2005**, *10* (1–2), 52–78. <https://doi.org/10.1016/j.cocis.2005.05.007>.
- (113) Kayitmazer, A. B.; Seeman, D.; Minsky, B. B.; Dubin, P. L.; Xu, Y. Protein-Polyelectrolyte Interactions. *Soft Matter* **2013**, *9* (9), 2553–2583. <https://doi.org/10.1039/c2sm27002a>.
- (114) Cousin; Gummel; Combet; Boué. The Model Lysozyme-PSSNa System for Electrostatic Complexation: Similarities and Differences with Complex Coacervation. *Adv. Colloid Interface Sci.* **2011**, *167* (1–2), 71–84. <https://doi.org/10.1016/j.cis.2011.05.007>.
- (115) Gummel, J.; Boue, F.; Deme, B.; Cousin, F. Charge Stoichiometry Inside Polyelectrolyte-Protein Complexes: A Direct SANS Measurement for the PSSNa-Lysozyme System. 2006.
- (116) Gummel, J.; Boué, F.; Clemens, D.; Cousin, F. Finite Size and Inner Structure Controlled by Electrostatic Screening in Globular Complexes of Proteins and Polyelectrolytes. *Soft Matter* **2008**, *4* (8), 1653–1664. <https://doi.org/10.1039/b803773f>.
- (117) Gummel, J.; Cousin, F.; Boue, F. Structure Transition in PSS/Lysozyme Complexes: A Chain-Conformation-Driven Process, as Directly Seen by Small Angle Neutron Scattering. *Macromolecules* **2008**, *41* (8), 2898–2907. <https://doi.org/10.1021/ma702242d>.

- (118) Cousin, F.; Gummel, J.; Clemens, D.; Grillo, I.; Boué, F. Multiple Scale Reorganization of Electrostatic Complexes of Poly(Styrenesulfonate) and Lysozyme. *Langmuir* **2010**, *26* (10), 7078–7085. <https://doi.org/10.1021/la904398z>.
- (119) Letterman, R. D.; Pero, R. W. Contaminants in Polyelectrolytes Used in Water Treatment. *J. / Am. Water Work. Assoc.* **1990**, *82* (11), 87–97. <https://doi.org/10.1002/j.1551-8833.1990.tb07056.x>.
- (120) Packham R. (1967). Polyelectrolytes in water clarification... - Google Scholar https://scholar.google.com/scholar?hl=en&as_sdt=0%2C5&q=ackham+R.+%281967%29.+Polyelectrolytes+in+water+clarification+%28including+discussions%29.+Proc.+Soc.+Wat.+Treat.+Exam.%2C+16%2C+88-111&btnG= (accessed Jun 7, 2021).
- (121) Park, S. H.; Wei, S.; Huang, C.-H.; Mizaikoff, B.; Aral, M. M. *A STUDY OF THE EFFECT OF POLYMERS ON POTENTIAL N-NITROSODIMETHYLAMINE (NDMA) FORMATION AT WATER AND WASTEWATER TREATMENT PLANTS*; 2007.
- (122) Kurita, K. Chitin and Chitosan: Functional Biopolymers from Marine Crustaceans. *Mar. Biotechnol.* **2006**, *8* (3), 203–226. <https://doi.org/10.1007/s10126-005-0097-5>.
- (123) Roussy, J.; Van Vooren, M.; Guibal, E. Chitosan for the Coagulation and Flocculation of Mineral Colloids. *J. Dispers. Sci. Technol.* **2004**, *25* (5), 663–677. <https://doi.org/10.1081/DIS-200027325>.
- (124) Guibal, E.; Roussy, J. Coagulation and Flocculation of Dye-Containing Solutions Using a Biopolymer (Chitosan). *React. Funct. Polym.* **2007**, *67* (1), 33–42. <https://doi.org/10.1016/j.reactfunctpolym.2006.08.008>.
- (125) Yang, R.; Li, H.; Huang, M.; Yang, H.; Li, A. A Review on Chitosan-Based Flocculants and Their Applications in Water Treatment. *Water Res.* **2016**, *95* (2015), 59–89.

<https://doi.org/10.1016/j.watres.2016.02.068>.

- (126) Wang, J. P.; Chen, Y. Z.; Zhang, S. J.; Yu, H. Q. A Chitosan-Based Flocculant Prepared with Gamma-Irradiation-Induced Grafting. *Bioresour. Technol.* **2008**, *99* (9), 3397–3402. <https://doi.org/10.1016/j.biortech.2007.08.014>.
- (127) Ali, S. A.; Pal, S.; Singh, R. P. Flocculation Performance of Modified Chitosan in an Aqueous Suspension. *J. Appl. Polym. Sci.* **2010**, *118* (5), 2592–2600. <https://doi.org/10.1002/app.32580>.
- (128) Cai, Z.-S.; Yang, C.-S.; Zhu, X.-M. Preparation of Quaternized Carboxymethyl Chitosan and Its Capacity to Flocculate COD from Printing Wastewater. *J. Appl. Polym. Sci.* **2010**, *118* (1), 299–305. <https://doi.org/10.1002/app.32323>.
- (129) Hwang, D. C.; Damodaran, S. Selective Precipitation and Removal of Lipids from Cheese Whey Using Chitosan. *J. Agric. Food Chem.* **1995**, *43* (1), 33–37. <https://doi.org/10.1021/jf00049a008>.
- (130) Gupta, S. K.; Kumar, M.; Guldhe, A.; Ansari, F. A.; Rawat, I.; Kanney, K.; Bux, F. Design and Development of Polyamine Polymer for Harvesting Microalgae for Biofuels Production. *Energy Convers. Manag.* **2014**, *85*, 537–544. <https://doi.org/10.1016/j.enconman.2014.05.059>.
- (131) Huang, M.; Liu, Z.; Li, A.; Yang, H. Dual Functionality of a Graft Starch Flocculant: Flocculation and Antibacterial Performance. *J. Environ. Manage.* **2017**, *196*, 63–71. <https://doi.org/10.1016/j.jenvman.2017.02.078>.
- (132) Sen, G.; Kumar, R.; Ghosh, S.; Pal, S. A Novel Polymeric Flocculant Based on Polyacrylamide Grafted Carboxymethylstarch. *Carbohydr. Polym.* **2009**, *77* (4), 822–831. <https://doi.org/10.1016/j.carbpol.2009.03.007>.

- (133) Anthony, R.; Sims, R. Cationic Starch for Microalgae and Total Phosphorus Removal from Wastewater. *J. Appl. Polym. Sci.* **2013**, *130* (4), 2572–2578. <https://doi.org/10.1002/app.39470>.
- (134) Wang, J. P.; Chen, Y. Z.; Ge, X. W.; Yu, H. Q. Optimization of Coagulation-Flocculation Process for a Paper-Recycling Wastewater Treatment Using Response Surface Methodology. *Colloids Surfaces A Physicochem. Eng. Asp.* **2007**, *302* (1–3), 204–210. <https://doi.org/10.1016/j.colsurfa.2007.02.023>.
- (135) Wu, L.; Zhang, X.; Chen, L.; Zhang, H.; Li, C.; Lv, Y.; Xu, Y.; Jia, X.; Shi, Y.; Guo, X. Amphoteric Starch Derivatives as Reusable Flocculant for Heavy-Metal Removal. *RSC Adv.* **2018**, *8* (3), 1274–1280. <https://doi.org/10.1039/c7ra12798g>.
- (136) Haroon, M.; Wang, L.; Yu, H.; Abbasi, N. M.; Zain-Ul-Abdin; Saleem, M.; Khan, R. U.; Ullah, R. S.; Chen, Q.; Wu, J. Chemical Modification of Starch and Its Application as an Adsorbent Material. *RSC Adv.* **2016**, *6* (82), 78264–78285. <https://doi.org/10.1039/c6ra16795k>.
- (137) Zia-ud-Din; Xiong, H.; Fei, P. Physical and Chemical Modification of Starches: A Review. *Crit. Rev. Food Sci. Nutr.* **2017**, *57* (12), 2691–2705. <https://doi.org/10.1080/10408398.2015.1087379>.
- (138) Pal, S.; Mal, D.; Singh, R. P. Cationic Starch: An Effective Flocculating Agent. *Carbohydr. Polym.* **2005**, *59* (4), 417–423. <https://doi.org/10.1016/j.carbpol.2004.06.047>.
- (139) Shi, Y.; Ju, B.; Zhang, S. Flocculation Behavior of a New Recyclable Flocculant Based on PH Responsive Tertiary Amine Starch Ether. *Carbohydr. Polym.* **2012**, *88* (1), 132–138. <https://doi.org/10.1016/j.carbpol.2011.11.076>.

- (140) Gumfekar, S. P.; Vajihinejad, V.; Soares, J. B. P. Advanced Polymer Flocculants for Solid-Liquid Separation in Oil Sands Tailings. *Macromol. Rapid Commun.* **2019**, *40* (1), 1800644. <https://doi.org/10.1002/marc.201800644>.
- (141) Du, X.; Dubin, P. L.; Hoagland, D. A.; Sun, L. Protein-Selective Coacervation with Hyaluronic Acid. *Biomacromolecules* **2014**, *15* (3), 726–734. <https://doi.org/10.1021/bm500041a>.
- (142) Nozaic, D. J.; Freese, S. D.; Thompson, P. Longterm Experience in the Use of Polymeric Coagulants at Umgeni Water. **2018**, No. August, 43–50.
- (143) Nozaic, D. J.; Freese, S. D.; Thompson, P. *Longterm Experience in the Use of Polymeric Coagulants at Umgeni Water*; 2001.
- (144) Odegaard, H. Optimized Particle Separation in Primary Step Of Wastewater Treatment. **1998**, *37* (10), 43–53. [https://doi.org/10.1016/S0273-1223\(98\)00297-2](https://doi.org/10.1016/S0273-1223(98)00297-2).
- (145) Shewa, W. A.; Dagne, M. Revisiting Chemically Enhanced Primary Treatment of Wastewater: A Review. *Sustain.* **2020**, *12* (15). <https://doi.org/10.3390/SU12155928>.
- (146) Morrissey, S. P.; Harleman, D. R. F. Retrofitting Conventional Primary Treatment Plants for Chemically Enhanced Primary Treatment in the USA. In *Chemical Water and Wastewater Treatment II*; Springer Berlin Heidelberg, 1992; pp 401–416. https://doi.org/10.1007/978-3-642-77827-8_26.