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Chapter

Application of Organic Coagulants in Water and Wastewater Treatment

Emmanuel Kweinor Tetteh and Sudesh Rathilal

Abstract

Coagulation is an essential mechanism that occurs in most conventional water and wastewater treatment plants. This occurs in a physical purification unit involving transport processes and the addition of coagulants for chemical reactions, charge neutralization, and formation of smaller flocs to agglomerate into larger flocs. This enhances the effective removal of recalcitrant contaminants by downstream processes. However, poor treatment of wastewater might have a high negative impact on biodiversity and the environment in general. This chapter seeks to address the limitation of employing inorganic coagulants by evaluating the efficiency of organic coagulants and exploring the factors and mechanism governing coagulation in a physiochemical treatment process of water and wastewater resources. The effect of pH, coagulant type and dosage to ease the high sludge production and discharge of residual metals into the downstream waters is addressed. The emerging of organic coagulants and technology to mitigate the performance and recovery of mineral coagulants from wastewater treatment residual is been proposed.

Keywords: coagulation, organic polymers, water and wastewater, purification

1. Introduction

The deterioration of the natural source of fresh water supply correlates with the increase in global social economic growth and activities, which generates wastewater with a high content of pollutants [1, 2]. Due to the detrimental effects of pollution in wastewater, water-related technologies and materials development have become the utmost priority in most of the wastewater industrials [2, 3]. Among the numerous purification methods, integrating coagulation along with filtration [2–4], sedimentation or flotation [5, 6] have been well-known pre-treatment techniques in water and wastewater settings where water quality is cardinal [7]. However, a variation of inflow water quality and lack of optimized treatment facilities result in decreasing the treatability efficiency with the incurred cost of production [8, 9]. Chemical purification process, well known as coagulation, even though it’s essential in wastewater settings, sometimes is seen to be an expensive technology due to the cause of cost of chemical usage involved [10–12]. This method involves the precipitation of the soluble metal ions by using coagulants. Subsequently, the long-term application of metal-based coagulants (aluminum and iron) [11] has raised concerns associated with sludge generation and heavy metal residuals which are potentially toxic.
Organic Polymers

to the ecosystem [10–12]. This has resulted in most effluent not complying with the stringent Environmental Protection Agency’s standards for regulating the quality of effluent plants [8].

In a typical wastewater treatment plant (Figure 1), a mixture of inorganic and organic polymer additives are usually employed as a heterocoagulation technique [14, 15]. This is to accelerate the agglomeration and coalescing of weighted particles to be separated from the water either by sedimentation or flotation techniques [5, 6]. However, most of the industrial wastewaters from the oil refinery, food, and the agricultural processing industries contain organics, suspended and emulsified oil and grease that prefer to float than settle [10, 15, 16]. Also, to enhance dewatering and advanced treatment of sewage which includes the removal of phosphorus, the utilization of polymers has become a very common practice [14, 17, 18]. Although, coagulant chemicals and its derivatives are very resourceful in wastewater treatment settings, they may alter the characteristics of the effluents in terms of its physiochemical properties [11, 17]. Also, the problem related to disposal of huge sludge and metals in the effluents, for instance in the application of hydroxide precipitation [4, 13, 19], requires a technique to recover the valuable or toxic metals from the sludge [20, 21]. In response to this, Donnan membrane technology which requires a lower operating pressure than others has been one of the fields tested technique in the wastewater treatment settings. However, the cost of the membrane is one of the setbacks [20–22].

As some of the limitations associated with inorganic based coagulants are been mentioned, this study focuses on the option for the natural and composite inorganic-organic polymer to maximize the treatability performance in the wastewater settings. Therefore, the goal is to evaluate the efficiency of organic polymers as coagulant agents for the treatment of water and wastewater and also to provide an alternative option to metal salts for the chemical purification process. This is done by exploring the use of organic polymer coagulant techniques as compared to metal-based salt coagulants in existing conventional treatment methods on the basis of effectiveness. Furthermore, to identify some of the operating conditions that affect chemical purification process.

Figure 1.
Schematic flow chart of a typical sewage treatment plant adapted from [13].
2. Chemical purification process

Chemical treatment using metal salts of iron and aluminum is widely applied in several wastewater treatment industries as primary treatments for the removal of particulate and organic matter effectively [23]. Figure 2 shows a typical chemical treatment process for both wastewater and drinking water settings, which usually consists of coagulation, flocculation, and sedimentation or flotation [24]. Coagulation is an indispensable mechanism that promotes the aggregation of the suspended solids, which are mostly responsible for turbidity, color, and taste and odor removal [24–26]. The flocculation facilitates the agglomeration of the coagulated particles to form larger flocs, thereby hastening the gravitational settling or flotation process for the removal of contaminants [24]. The spontaneous forming of flocs in suspension is termed as flocculation. This is usually applicable in water purification and sewage treatment. The cationic polyelectrolytes have been the most viable flocculants. Their low charge density makes it not to reverse the surface charge and hence they are less prone to induce destabilization.

Also, agglomeration of particles to form large and stable flocs involves mixing of the coagulants with the wastewaters usually monitored via Jar test. However, there are several types of coagulants which show the different potential application in treating drinking water or wastewater [11, 17, 27]. Due to the detrimental effects of discharging untreated wastewater, it is essential for purification systems to be well established and optimized [28, 29]. Ideally, the suitable operation conditions required depends on the characteristics of the wastewater and the coagulants, as well as the physical properties as shown in Table 1.

2.1 Types of chemical treatment processes

2.1.1 Coagulation and sedimentation

Coagulation, flocculation and sedimentation processes in water and wastewater treatment are crucial. The first stage in most chemical water treatment processes is coagulation, whose performance is dependent on coagulant concentration and the water chemistry [12, 14]. Essentially, there are four coagulation mechanisms for aggregation of particles to occur, namely (1) double layer compression;
Figure 3. Process of coagulation, flocculation, and sedimentation [24].

(2) sweep flocculation; (3) adsorption and charge neutralization; and (4) adsorption and interparticle bridging [13, 17–24]. This involves the reaction between the colloids and the added coagulant to destabilize and neutralize the electric charges in the particles, whereas the flocculation facilitates the agglomerated flocs in the colloidal suspension.

For instance (Figure 3), the addition of the coagulant is accountable for the creation of small scattered particles which come together into larger and more stable particle flocs. These then make the flocs heavier than the water, which settle as sediments and can be removed. This results in the removal of about 90% of the suspended matter [1, 2]. Furthermore, the coagulation step depends on conditions of time and agitation whereby the particles coalesced to form larger flocs could be eliminated by sedimentation.

2.1.2 Coagulation and flotation

Conventionally, flotation is a concentration process in which selective hydrophobic materials are separated from hydrophilic materials by a gravity separation process [30]. In a typical flotation process (Figure 4), the coagulated particles adhere to air bubbles lowering the apparent density below that of the water, which then allows the flocs to float to the surface. To cause a change in the separation phase

![Table 1. Factors that affect the chemical purification process [17].](image-url)
depends on four mechanisms such as (1) air bubble generation, (2) contact between air bubble and the particulates, (3) attachment of gas bubbles to particulates, and (4) rising up of the combined air bubble-particulate [31, 32].

The addition of the coagulant enhances the air bubbles and organic matter to form robust flocs that can resist breakage in the flotation zone [33]. However, this process is somehow complicated because it requires the hydrodynamics and surface chemistry interaction via the means of bubble attachment, where the bubbles are generated as a result of compressed air released into the flotation zone. Therefore, to obtain good performance, studies have shown that coagulation chemistry has a strong influence on flotation performance [34], such that the chemical reaction between the coagulants and the organic matter results in forming larger oil flocs, whereas, the flotation process facilitates separation [35, 36]. This allows the coagulated flocs to float on the surface as sludge, whereas clear water moves to the bottom of the floatation tank to the sewer as treated water.

2.2 Parameters affecting coagulation treatment efficiency

There are several operating factors that have an impact on the parallel and sequential reactions that occur when a coagulant is added to the wastewater. To promote the interparticle bridging and floc formation, there are a series of transportation mechanisms which occurs including Brownian diffusion and fluid motion. All these influence the efficiency and effectiveness of the coagulation process for wastewater treatment.

2.2.1 Effects of polymer molecular weight and charge density

Polymer molecular weight (MW) and charge density (CD) affects the interparticle bridging and electrostatic force mechanism which contributes to the coagulation efficiency [37, 38], such that an increase in molecular weight improves agglomeration and floc formation. Although anionic charge on the polymer can obstruct adsorption onto an undesirable surface, it promotes the polymer chain via mutual charge repulsion between polymer molecules [39]. Organic polymer concentration originates to be free of molecular weight but reliant on ionic strength. The CD is generally expressed as a percentage of ionic groups (both those that are charged, irrespective of pH and those that can become charged under certain pH conditions) relative to all the groups in the polymer. The CD is expressed in terms of length (qL), area (qA) and volume (qV) as shown in (1)–(3) as a function of the amount of ionic charge (qQ) per length (L), area (A) or volume (V) respectively.
2.2.2 Temperature

Temperature serves as the driving force for chemical reaction. This affects the coalescence and the physical properties of the polymer including viscosity, mobility, collision, and solubility, density, rising or settling velocity of the flocs. Thus, higher temperature hastens the rate of chemical reactions, whereas low temperatures stabilize the colloidal surfaces to reduce the hydrolysis reactions [38, 40]. This might affect the free movement of the particles and higher solubility as well as higher reaction kinetics of the polymer applied, which in turn decreases the coagulation efficiency.

2.2.3 Effects of mixing conditions

The degree of coagulation completion for effective treatment can be related to coagulant dosage and mixing conditions. Sequentially, destabilization and agglomeration of coagulated flocs occur through two mixing regimes, viz. rapid mixing and slow mixing as shown in Figure 5. The rapid or fast mixing occurs after the addition of the coagulants, which requires turbulent mixing to form a homogeneous solution [24, 25, 29]. Lack of rapid mixing might cause poor performance of the coagulants due to under dose or overdose. On the other hand, slow mixing comes soon after rapid mixing, and is intended to increase the particle entrapment and growth of the flocs.

Furthermore, consistent slow mixing accelerates the rate floc aggregation and entrapment of the particles in suspension to enhance separation. Slow mixing provides a velocity gradient for particles with similar size that can be larger than 1 \( \mu \text{m} \). Such that the relation between the aggregation of a given size and the polymer MW can enhance the bridging or breaking forces of the flocs to either settle or float [33, 36, 38]. In practice (Figure 5), this is achieved by a suspension being stirred at a high rate (250 rpm f) to cause floc breakage, and after the breakages, the slow mixing (30 rpm) is initiated to increase the floc size [24, 27]. In flotation principle, a lower dosage of the polymer can be used because the agitation creates a well-established suspension of smaller flocs to agglomerate to float [33, 41].

![Figure 5. Schematic steps of mixing in coagulation process.](image-url)
2.2.4 Effects of pH

The pH plays a dominant role in coagulant-particle interaction for effective neutralization and agglomeration of the flocs. In addition, the solubility of metal hydroxide species can be affected by pH (4–8) [36, 41]. Therefore pH adjustment prior to coagulant addition is very important to influence the chain reactions that will occur. The effective species of inorganic coagulants or polymers being a metal-based ion can affect the floc formation through a double-layer compression [24, 38]. With an increase in pH, these species become charged resulting in a change in mechanism. For instance, when the colloids are hydrophilic, e.g. acids, the pH will affect the protonation.

2.2.5 Coagulant type and dosage

There are various types of coagulants used in wastewater settings, such as inorganic and organic polymers. However, polymers are generally more costly than inorganic coagulants. This depends on the type and quantity of chemical the coagulant might contain. Selection of the suitable coagulant for wastewater treatment is very important, which also depends on the water chemistry, the hydrodynamics and operating conditions of the processing system [4, 41]. Coagulant dosage is an energetic factor in finding how the metal ions react with the organic matter in wastewater to enhance its clarity.

Organic polymers by nature are very viscous solutions, which sometimes becomes problematic to be distributed homogeneously in a medium [15, 17]. However, they are very attractive towards particle surfaces, which is irreversible when attached. So uneven distribution of polymers in polluted wastewater might contribute to inefficiency and cost of the treatment process [17, 18, 24]. Thus, the dosage needs to be stepped up in other to compensate for the loss of the polymer.

2.2.6 Ionic strength

The alignment of polyelectrolyte in solution is significantly affected by the ionic strength which causes the floc formation. The metal ions hinders the hydrolysis activity when a metal-based coagulant is added to a solution [24, 38, 40]. In contrast, like-charges of a polymer chain tend to expand when there is a mutual repulsion. This is directed to an increase in viscosity of a polyelectrolyte solution as ionic strength decreases. Also, an increase in ionic strength shields the charged site of the polymer which then affects its hydrodynamic volume expansion by decreasing the viscosity of the solution [39, 40]. This causes a double layer compression to be formed around the floc surface area where there might be oppositely charged ions.

3. Coagulants

There are several types of coagulants which are applicable to water and wastewater treatment settings [42]. These can either be chemical, non-chemical, synthetic material or natural coagulants. However, each type of coagulant has its own unique properties with positive ions which will entrap the negative charge of the organic matter in the water that causes turbidity.

3.1 Inorganic coagulants

Aluminum and iron salts are the most commonly used inorganic coagulants in the wastewater treatment settings. These include based aluminum metals (aluminum
Organic coagulants are generally synthesized monomers of aluminum and iron-based coagulants, applicable in the wastewater settings as coagulant aids or floc builders [15, 17]. Table 3 shows some of the organic coagulants which are usually employed in potable and wastewater treatment after the addition of inorganic chloride, aluminum sulfate, sodium aluminate) and iron based metals (ferrous sulfate, ferric sulfate, ferric chloride) [13, 17, 18]. The addition of these coagulants to wastewater undergo a series of reactions with the hydroxyl ions (OH\(^{-}\)) producing monomeric and polynuclear species. These results in dissociation of their metal salts to release their trivalent ions, which hydrates to give complex water molecules of Al\((\text{H}_2\text{O})_6\text{Al}^{3+}\) and Fe\((\text{H}_2\text{O})_6\text{Fe}^{3+}\) for aluminum and iron respectively [26, 37, 39, 43]. This results in the replacement of the water molecules (H\(_2\)O) by OH\(^{-}\) ions to form soluble Al\((\text{OH})_3\) and Fe\((\text{OH})_3\) which increases the coagulation performance by the trivalent ions being strongly adsorbed onto the negative surface of the colloids [26, 29].

Consequently, metal-based coagulants are most widely used due to their low cost and availability; however, there are some drawbacks [17, 18]. These include high dosage dependence, a high requirement on pH, weakness to temperature disparity and high sludge generation. Some of these inorganic coagulants with their merits and demerits are presented in Table 2. Furthermore, an overdose of aluminum and iron in effluent poses a threat to both the ecosystem and human health such as intestinal constipation, abdomen colic and spasms. In addition, Ferric-based coagulants are very caustic and produce highly visible rust-colored stains associated with chemical spills and leaks [25, 33]. Therefore, there is great interest in improving inorganic coagulants by employing polymeric organic and natural coagulants for the treatment of wastewater.

### 3.2 Organic coagulants

Organic coagulants are generally synthesized monomers of aluminum and iron-based coagulants, applicable in the wastewater settings as coagulant aids or floc builders [15, 17]. Table 3 shows some of the organic coagulants which are usually employed in potable and wastewater treatment after the addition of inorganic

<table>
<thead>
<tr>
<th>Name</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum sulfate (Alum)(\text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O})</td>
<td>Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 75</td>
<td>Adds dissolved solids (salts) to water; effective over a limited pH range</td>
</tr>
<tr>
<td>Sodium aluminate(\text{Na}_2\text{Al}_2\text{O}_4)</td>
<td>Effective in hard waters; small dosage usually needed</td>
<td>Often used with alum; high cost; ineffective in soft waters</td>
</tr>
<tr>
<td>Polyaluminium chloride (PAC)(\text{Al}<em>n(\text{OH})</em>{20}\text{SO}_4\cdot\text{Cl}_3)</td>
<td>In some applications, Floc formed is denser and faster settling than alum</td>
<td>Not commonly used; little full-scale data compared to other aluminum derivatives</td>
</tr>
<tr>
<td>Ferric sulfate (\text{Fe}_2(\text{SO}_4)_3)</td>
<td>Effective between pH 4–6 and 8.8–9.2</td>
<td>Adds dissolved solids (salts) to water; usually, need to add alkalinity</td>
</tr>
<tr>
<td>Ferric chloride (\text{FeCl}_3\cdot6\text{H}_2\text{O})</td>
<td>Effective between pH 4 and 11</td>
<td>Adds dissolved solids (salts) to water; consumes twice as much alkalinity as alum</td>
</tr>
<tr>
<td>Ferrous sulfate (\text{FeSO}_4\cdot7\text{H}_2\text{O})</td>
<td>Not as pH sensitive as lime</td>
<td>Adds dissolved solids (salts) to water; usually need to add alkalinity</td>
</tr>
<tr>
<td>Lime (\text{Ca(OH)}_2)</td>
<td>Commonly used; very effective; may not add salts to effluent</td>
<td>pH-dependent; produces large quantities of sludge; overdose can result in poor effluent quality</td>
</tr>
</tbody>
</table>

*Table 2. Advantage and disadvantage of inorganic coagulants [18, 33, 41].*
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There are various types of organic coagulants, which have different covalent charges and bonds of their polymeric molecules. These include the charge or ionic polymers (polyelectrolytes) and no charge or non-ionic polymers [15, 25]. In respect to the charge polymers, those with a positive charge are termed as cationic polymers, whereas those with negative charges are called anionic polymers.

4. General characteristics of coagulants

There are two characteristics of polymers that defines them to be used as coagulant or floculent aids [15, 17]. These include (1) they have a very high charge density to neutralize the negative charges present on the surface of the colloidal material, and (2) they have a relatively low molecular weight (MW) which allows good diffusion of the cationic charges around the particles. This enhances good distribution of the coagulant in the effluent, when not concentrated at low viscosity of less than $2 \times 10^3$ centipoises, and when concentrated at a high viscosity of $20 \times 10^3$ centipoises [14, 15, 24]. Organic polymers have long chain molecular weights, which consists of repeating chemical units called monomers. This makes them be classified as low with MW less than $10^5$, and medium and high when they are between $10^5$ and $10^6$ and more than $10^6$ respectively [14, 15, 17].

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Typical properties</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaluminium chlorohydrate (ACH) Al$_2$(OH)$_3$Cl</td>
<td>PAC 23</td>
<td>* 23–24% Al$_2$O$_3$ or 40–41% w/w ACH</td>
<td>Used in lieu of alum where raw water has low pH &amp; alkalinity. Has little impact on pH</td>
</tr>
<tr>
<td></td>
<td>MEGAPAC 23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ALCHEM</td>
<td>* SG 1.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>* 83–84% basicity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PROFLOC A23</td>
<td>* 8.9% w/w Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 535 g/l</td>
<td></td>
</tr>
<tr>
<td>Polyaluminium chloride (PACl) Al$_2$(OH)$_3$Cl</td>
<td>PAC-10 LB</td>
<td>* 10–12% Al$_2$O$_3$ or 20–23% w/w PACl</td>
<td>Used in lieu of alum where raw water has low pH &amp; alkalinity. Has greater impact on pH than ACH</td>
</tr>
<tr>
<td></td>
<td>MEGAPAC 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* SG 1.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 50% basicity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 10.5% w/w Cl</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 245 g/l</td>
<td></td>
</tr>
<tr>
<td>Polyaluminium silicon sulphate</td>
<td>PASS®</td>
<td>* 10% Al$_2$O$_3$ or 5.3% w/w Al</td>
<td>Forms flocs easily</td>
</tr>
<tr>
<td>Al$<em>2$(OH)$</em>{2.2}$Si$<em>{3.1}$O$</em>{18}$</td>
<td></td>
<td>* SG 1.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 54% basicity</td>
<td></td>
</tr>
<tr>
<td>Polyferric sulfate Fe$<em>2$(OH)$</em>{6.4}$(SO$<em>4$)$</em>{2.7}$</td>
<td>PFS®</td>
<td>* 12.2% w/w Fe(III) or 43.7% w/w Fe$_2$(SO$_4$)$_3$</td>
<td>Mostly used for oil emulsified wastewater</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* SG 1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 10% basicity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>* 673 g/l</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Examples of organic polymer coagulants for water and wastewater treatment [16, 24].

coagulants to enhance its treatment efficiency [15]. There are various types of organic coagulants, which have different covalent charges and bonds of their polymeric molecules. These include the charge or ionic polymers (polyelectrolytes) and no charge or non-ionic polymers [15, 25]. In respect to the charge polymers, those with a positive charge are termed as cationic polymers, whereas those with negative charges are called anionic polymers.
4.1 Methods of polymerization

Organic polymer coagulants can exist in different forms which is due to the method of polymerization such as liquid, beads, powder, emulsion, and dispersion [15, 24].

(a) Powders: The polymerized monomers are obtained in a gel form, which is then grounded and dried.

(b) Beads: The monomers are polymerized by adding a solvent to be made to be a suspension. The solvent is later evaporated to obtain microspheres. This prevents dust and enhances rapid dissolution.

(c) Emulsions: The monomers are emulsified in a solvent before being polymerized. Afterwards, a surfactant is added to make it dissolvable in water.

(d) Liquids: The monomers are polymerized at low concentration in aqueous solutions, making it effortless to use.

(e) Dispersions: In this case, the monomers are usually dispersed in brine before being polymerized. This is done as direct feed inline without any solvent or surfactant and aging time. These are applicable in the flotation process, making it a cost-effective process for the treatment of oil refinery wastewater. Figure 6 shows the dissociation of the ionic charge of the polymer when introduced into a receiving medium (emulsion of oil-water).

4.2 Types of polymeric coagulants

Hydrophobic organic coagulants adapted from inorganic coagulants have gained attention in application due to their unique characteristics. Organic polymers, in general, are classified as natural and synthetic polymers [14, 15, 17]. Natural polymers are hydrophilic compounds which carry natural characteristics as being nontoxic to humans, readily available and environmentally friendly. However, the use of natural polymers only might not be effective in all cases in wastewater.
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treatment settings. This might be due to their properties which cannot be modified (e.g. Chitosan, tannin, starch, *Moringa oleifera*). Natural polymers are usually mixed with inorganic coagulants to enhance their treatability efficiency, although synthetic polymers can at times be toxic to humans [11, 14, 44].

Organic polymers can easily be modified and optimized during the manufacturing process for wider application. Several polymers are produced with polymer chains of the linear, branched or cross-linked form of structures [11, 18]. For instance, Figure 7 shows the chemical structure of poly diallyl dimethyl ammonium chloride (pDADMAC), epichlorohydrin/dimethylamine polymers (ECH/DMA) and cationic polyacrylamides (CPAMs) are examples of cationic synthetic polymers while chitosan is an example of the cationic natural polymer [15, 17, 24].

### 4.2.1 Anionic polymers

Anionic polymers are amphoteric polymers, which gets a negative charge when their ionic groups dissociate in a medium [15, 17]. Their polymerization is very sensitive, involving a change in molecular weight, charge groups and density as well their structure being linear or branched as shown in Figure 8. This is usually instigated by using either active anionic species like sodium, nitrile, hydroxide or cationic species such as hydrochloric acid, sulfuric acid, and phosphoric acid. Subsequent hydrolysis of the polyacrylamide under basic pH conditions produces a polymer with anionic charges. Table 4 shows the molecular formulas of anionic APAMs or PAMs, containing changing proportions of acrylamide co-monomers in terms of charge density (mol%) and a theoretical basis in meq/g of polymer.

### 4.2.2 Cationic polymers

Cationic polymers are positively charged natural or synthetic based organic coagulants. Some of these polymers have charge ammonium groups making them strong electrolytes irrespective of their pH variation [15, 17]. For instance, pDADMAC, ECH/DMA and CPAMs are synthetic cationic polymers while Chitosan is a...
natural cationic polymer as mentioned previously. The hydrolysis of the ester groups and consequent loss of cationic charge is CD and pH dependent. Table 5 outlines the CD of various cationic polymers in mol% and meq/g of polymer. The higher charge density shows that the polymer has a greater loop which enhances interparticle bridging and effective destabilization of the medium. Figure 9 shows the cationic polymer structure, denoting polymerization of acrylamide followed by partial hydrolysis.

4.2.3 Natural or non-ionic polymers

There are several naturally-occurring polymers that have inherent cationic properties, which can be modified to yield a cationic polyelectrolyte to be used for solid-liquid separations as flocculants [11]. Non-ionic polymers vary in structure, molecular weight and degradability. Some examples include polyacrylamides (PAMs), Chitosan, starch without substitutions, cellulose derivative, and glues [17, 38, 44]. Chitosan, like most natural polymers, is toxic free which makes them generally acceptable on health grounds. The use of chitosan in water purification applications has been referenced to decolorizing dye house effluents, the treatment of food-processing wastes, metal ion removal and sludge conditioning.

Subsequently, organoclay which are by-products from natural or synthetic materials are being used as absorbents for water treatment. They are generally known as low-cost adsorbents which are readily available. These include ball clay, bentonite and kaolin. Organoclay is also a result of merging sodium montmorillonite clay with a cationic quaternary amine salt which interchanges the adsorbed sodium through ion exchange [17, 25].

Furthermore, plants and minerals are a cardinal source of natural polymers. Some examples includes: Nirmali seeds, Moringa oleifera, Tannin, eggplant seed and radish seed which are locally available from vegetables for treatment [14, 15, 44]. These coagulants are nontoxic, renewable, produce lower sludge, biodegradable and relatively cost-effective. Moreover, natural coagulants have a wide range of effective

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>CD (mol %)</th>
<th>CD (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((C_3H_3O_2Na)_{0.25})</td>
<td>100</td>
<td>10.2</td>
</tr>
<tr>
<td>((C_3H_3O_2Na)<em>{0.25}(C_3H_5ON)</em>{0.75})</td>
<td>75</td>
<td>8.5</td>
</tr>
<tr>
<td>((C_3H_3O_2Na)<em>{0.50}(C_3H_5ON)</em>{0.50})</td>
<td>50</td>
<td>6.1</td>
</tr>
<tr>
<td>((C_3H_3O_2Na)<em>{0.25}(C_3H_5ON)</em>{0.75})</td>
<td>25</td>
<td>3.3</td>
</tr>
<tr>
<td>((C_3H_3O_2Na)<em>{0.25}(C_3H_5ON)</em>{0.75})</td>
<td>10</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 4. Charge densities of anionic polyacrylamides [17].
dosage and do not change the value of pH for the treated water. Another example of a plant-based coagulant using unexploded waste is cassava peel. Fresh cassava peels have three main efficiencies: spread very rapidly, contain phytates, and huge amounts of cyanogenic glycosides [3, 44].

4.2.4 Application of organic polymers

Organic polymers and inorganic coagulants over the years have been used in chemical treatment and purification of water and wastewater [41]. These are used in chemical treatment to assist sedimentation of sewage solids to enhance the removal of suspended matter. Coagulation used ahead of gravity settling may be expected to yield suspended solid removals of about 90% as compared to without coagulation [1, 11]. This concept is also applicable to primary coagulation of industrial wastewaters where the separation may be based on flotation, as in examples from the leather, steel, wool scouring, cosmetic, detergent, plastics, dyehouse, paper, food processing, and brewing industries. The cationic polymer which is hydrophobically modified is significant in the case of soap, oil and grease removal. Table 6 shows some examples for the application of organic polymers for the treatment of wastewater.

Their many advantages associated with organic polymers been used as primary coagulants, however, it is sometimes quite challenging selecting the suitable one for specific water treatment. The selection of the right polymer to use under the

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular formula</th>
<th>CD (mol %)</th>
<th>CD (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDADMAC</td>
<td>C₆H₈NCl</td>
<td>100</td>
<td>6.2</td>
</tr>
<tr>
<td>ECH/DMA</td>
<td>C₆H₁₂ONCl</td>
<td>100</td>
<td>7.3</td>
</tr>
<tr>
<td>CPAM</td>
<td>C₆H₁₀O₂NCl</td>
<td>100</td>
<td>5.2</td>
</tr>
<tr>
<td>CPAM</td>
<td>(C₆H₁₀O₂NCl)₁₀(C₃H₅ON)₅₀</td>
<td>50</td>
<td>3.8</td>
</tr>
<tr>
<td>CPAM</td>
<td>(C₆H₁₀O₂NCl)₂₁(C₅H₇ON)₁₅</td>
<td>25</td>
<td>2.5</td>
</tr>
<tr>
<td>CPAM</td>
<td>(C₆H₁₀O₂NCl)₃₂(C₅H₇ON)₇₅</td>
<td>10</td>
<td>1.2</td>
</tr>
<tr>
<td>Chitosan</td>
<td>C₆H₁₁O₂N.HCl</td>
<td>100</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Table 5. Charge densities of cationic polyelectrolytes [17].
circumstances in question depends on their molecular weight, charge density, and structure, dose, mixing condition, amount and type of impurities found in the water and pH dependency. However, to achieve optimum stabilization and agglomerating of flocs requires optimum dosage, which is inversely dependent on the size of the particles in suspension [39, 40].

5. Conclusion

Coagulation is one of the simplest methods for the treatment of water and wastewater, especially for non-settleable solids, turbidity, and color from effluents. Application of coagulation is expected to enhance the gravity system for the removal of suspended solids of about 90% as compared to a system without coagulation. Thus, the issue of sludge sedimentation which must be floated is relatively low to flotation systems utilizing organic polymers rather than inorganic coagulants. This chapter addresses the limitation associated with coagulation using inorganic coagulants, by highlighting some of the eco-friendly organic coagulants and operating parameters of coagulation for water and wastewater treatment. Also, composite polymerization and impregnation of organic polymers with inorganic coagulants as a research area should be focused for commercialization and industrialization.

Acknowledgements

The authors wish to thank the Durban University of Technology and National Research Foundation South Africa for their support.

<table>
<thead>
<tr>
<th>Industries</th>
<th>Coagulant</th>
<th>Dosing</th>
<th>Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp and paper</td>
<td>Poly-aluminum-silicate-chloride</td>
<td>40 mg/l</td>
<td>93.13% COD</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>91.12% turbidity</td>
<td></td>
</tr>
<tr>
<td>Textile industry</td>
<td>PAC</td>
<td>25 mg/l</td>
<td>90.17% COD, 74.09% TDS and 93.47% turbidity</td>
<td>[37]</td>
</tr>
<tr>
<td>Dye wastewater</td>
<td>Polyferric chlorides (PFCs)</td>
<td>30 mg/l</td>
<td>55% reduction</td>
<td>[46]</td>
</tr>
<tr>
<td>Vegetable tannery</td>
<td>PACI (poly aluminum chloride)</td>
<td>60 mg/l</td>
<td>45%TSS, 20% COD and 80% turbidity</td>
<td>[47]</td>
</tr>
<tr>
<td>wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palm oil effluent</td>
<td>PAC</td>
<td>0.5 g/l, 8.0 and 60 g/l</td>
<td>99% SOG</td>
<td>[48]</td>
</tr>
</tbody>
</table>

Table 6. Application of organic polymers in wastewater settings.
Author details

Emmanuel Kweinor Tetteh* and Sudesh Rathilal
Faculty of Engineering and the Built Environment, Department of Chemical Engineering, Durban University of Technology, Durban, South Africa

*Address all correspondence to: ektetteh34@gmail.com
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