Development of coagulation theory and new coagulants for water treatment: its past, current and future trend

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Abstract
This paper reviews the history of chemical coagulation and its effects on the water quality control and management, considers how the most favourable coagulant species and prepolymerised inorganic coagulants may be prepared by reference to the appropriate coagulant chemistry, and evaluates the overall performance of some pre-polymerised coagulants in comparison with that of conventional coagulants for water treatment.

Keywords Coagulation; coagulant chemistry, prepolymerised coagulants; water treatment

Introduction
Although coagulation history goes back to three thousand years ago, the modern use of coagulants for water treatment started approximately 100 years ago, when ferric chloride and aluminium sulphate were used as coagulants in full-scale water treatment plants. Scientific-based study on coagulation/flocculation also started then, when the well known Schultz–Hardy rule was proposed to explain the coagulation mechanism. In 1917, Smoluchowski developed the theory of particle collision function, which forms the basis of understanding the changes in particle number in the flocculation process. Mattson (1928) first derived that the hydrolysis products of aluminium and iron were more important than the trivalent ions themselves, although this approach was not widely accepted and accorded its proper position in coagulation chemistry until 30 years later. Black and coworkers (1934) conducted a series of studies on the effect of pH and various anions on the time of floc formation. For the next few years, the principal research emphasis on coagulation was the study of mechanical methods to produce better flocs and search for better coagulant aids including bentonite, silicates, and limestone. During this time, no new theories were proposed to further the understanding of coagulation itself.

From the late 1940s, a new coagulation theory was developed by Langelier and Ludwig (1949), who distinguished two mechanisms for the removal of colloidal impurities: (a) the double layer compression, a process to allow the particles to overcome the repulsive forces and thus agglomerate and precipitate; and (b) precipitate enmeshment, a process in which small particles are physically enmeshed by metal precipitates when they are forming and settling. These two mechanisms have been elaborated upon and substantiated on a theoretic basis by LaMar Healey (1963), who proposed the terms “coagulation” based on (a) and “flocculation” based on (b).

A significant step in the development of a comprehensive theory of coagulation during the 1960s was the introduction of micro-electrophoresis (Black and Willems, 1961) to the study of colloidal destabilisation which allowed the quantification of electrical charge on colloidal particles. Study of the stoichiometric relationship between the coagulant dose required to neutralise the colloids and the concentration of colloidal impurities in water also started in that decade. These studies pointed out the effect of chemical factors such as pH, ionic strength and the properties of impurities to be removed, on the charge of colloidal
particle. These studies also re-emphasised the importance of hydrolysis products, as originally proposed by Mattson, and established an adsorption model to detail the coagulation mechanism of hydrolysed metal coagulants.

Study of the coagulation mechanism and the approaches to improve the coagulation performance are always linked with the needs to match water quality standards. This was highlighted in the 1970s, when haloforms and other halogenerated organic compounds, e.g., trihalomethanes (THMs), were first found in the treated waters (Rook, 1974), which result from the disinfection process due to the reactions of natural organic matter (NOM) with disinfectant—chlorine. Reduction of NOM became the most important objective of coagulation/flocculation, although itself sometimes not enough reduce the NOM to an acceptable level. If activated carbon is used combined with coagulation/flocculation to minimise the organic matter, the coagulation/flocculation processes becomes extremely important. Activated carbon is an expensive unit process. Assuming the coagulation process can be optimised for NOM removal, the reduced load to the carbon column will extend the expected life of the carbon while improving the treated water quality and reducing treatment cost.

Since the 1980s, optimisation of coagulation performance for the removal of NOM has been systematically studied (AWWA Research Committee Report, 1989), using various real surface waters, by evaluation of a range of variables such as mechanical conditions for coagulation/flocculation, sequences of chemical addition, coagulant type and doses, coagulation pH, restabilisation zones and water quality characteristics including water temperature. Another tool added to the coagulation technology was the streaming current detector (SCD), e.g. Dental and Kinger (1989), which is used widely together with jar test in controlling the coagulant dose and hence, coagulation process.

In the 1990s, NOM and other precursors of the disinfection by-products are still the main impurities to cause concern. The outbreak of cryptosporidiosis in the USA (Mackenziel et al., 1994) led to the re-concern of microorganism impurities, including Cryptosporidium, Giardia, Legionella, and other viruses. Microbiological particulates can be controlled through a multiple barrier or integrated water treatment process design that uses coagulation, filtration and disinfection. To achieve the expected targets, coagulation is essential to ensure attachment of particulates to the filter media, therefore, the microbial particulates can be effectively removed.

Coagulation/flocculation are affected by upstream treatment, e.g. pre-oxidation process, and affect the downstream processes, e.g. settling/floation, filtration, activated carbon adsorption, oxidation and disinfection. During this decade, the effect of pre-ozonation on the coagulation performance, the coagulation treatability of various raw waters and different fractions of NOM (i.e., NOM fractions with different molecular weight, surface charge and hydrophilic/hydrophobic affinity), and the impact of coagulation performance on the effectiveness of activated carbon adsorption have been, and still are being, studied. In addition enhanced coagulation, either by addition coagulant dose and lowering the coagulation pH (e.g. Cheng et al., 1995 and Crozes et al., 1995), or through developments in coagulant chemistry to prepare the more effective coagulants (Jiang and Graham, 1996), have been evaluated for improving the removal of NOM and general coagulation performance. Moreover, computer models of coagulation/flocculation have been developed and studied, including the models to predicate the coagulant dose required and the removal efficiency of NOM, and to describe the physical aspects of coagulation/flocculation, e.g. particle collisions.

Coagulant chemistry
Coagulation is a process for combining small particles into larger aggregates (flocs) and for adsorbing dissolved organic matter onto particulate aggregates so that these impurities can...
be removed in subsequent solid/liquid separation processes. Coagulants used for water and wastewater treatment are predominantly inorganic salts of iron and aluminium. When dosed into water the iron or aluminium ions hydrolyse rapidly and in an uncontrolled manner, to form a range of metal hydrolysis species. Various factors such as the nature of the water, the coagulation pH and the dose of coagulant together influence the species formed and subsequently, the treatment performance. Considerable interest and attention have been paid in recent years to preparing pre-hydrolysed metal-ion coagulants, based on either aluminium (e.g. poly-aluminium chloride), or ferric iron (e.g. polyferric sulphate), and/or, a mixed polymeric coagulant (e.g. poly-aluminium-iron-sulphate). These have been shown to perform better in some cases, in comparison with conventional coagulants such as aluminium sulphate (AS) or ferric sulphate (FS).

The aqueous equilibrium chemistry of Al in water has been explained, e.g. Baes and Mesmer (1976), by considering five monomers ($\text{Al}^{3+}$, $\text{Al}($OH$)_{2}^{+}$, $\text{Al}($OH$)_{3}^{+}$, $\text{Al}($OH$)_{3}$ (molecule) and $\text{Al}($OH$)_{3}^{4-}$), three polymeric species ($\text{Al}_{2}($OH$)_{2}^{4+}$, $\text{Al}_{3}($OH$)_{4}^{5+}$ and $\text{Al}_{13}O_{4}($OH$)_{24}^{7+}$) and a solid precipitate ($\text{Al}($OH$)_{3}^{(s)}$). Several other formulae for polymeric Al species can also be found in the literature, but it seems that $\text{Al}_{13}O_{4}($OH$)_{24}^{7+}$ (often denoted by $\text{Al}_{13}$) is the most effective and stable polymeric Al species in water treatment. Similarly, the Fe(III) hydrolysis products are considered, e.g. Flynn, 1984, to be five monomers ($\text{Fe}^{3+}$, $\text{Fe}($OH$)_{2}^{+}$, $\text{Fe}($OH$)_{3}^{+}$, $\text{Fe}($OH$)_{3}$ (molecule) and $\text{Fe}($OH$)_{3}^{3-}$), a dimer and trimer ($\text{Fe}_{2}($OH$)_{2}^{4+}$ and $\text{Fe}_{3}($OH$)_{4}^{5+}$) and a solid precipitate ($\text{Fe}($OH$)_{3}^{(am)}$). In addition, there exists a range of dissolved polymeric Fe(III) species with medium and high molecular mass during the hydrolysis process, prior to the formation of precipitates. These Fe(III) polymeric species may be represented by the following general formulations: $\text{Fe}_{x}($OH$)_{y}^{(3x-2y)^+}$ or $[\text{Fe}_{x}O_{y}($OH$)_{z}]^{(2x-2y-z)^+}$. These are kinetically stable and their thermodynamic equilibrium state depends on the conditions of preparation.

In the conventional coagulation process the appropriate dose of a Al/Fe(III) salt is added directly to the raw water. In the pH range of natural waters, approximately 6 to 8, this causes extremely rapid and uncontrolled hydrolysis, and frequently, very rapid precipitation. A major drawback in the use of Al/Fe(III) salts is the inability to control the nature of the coagulant species formed, and the performance of Al/Fe(III) coagulants may worsen with changes in water temperature and in the nature of the raw water. It is possible that Al/Fe(III) hydrolysis products may adsorb to colloidal surfaces to neutralize the charge or may chemically interact with dissolved components in the raw water. For these phenomena the rate of coagulant–impurity interaction must be faster than the rate of the hydroxide precipitation. Typically this condition is only met for waters with a pH $< 6$, with a relatively low dose of Al or Fe(III) and with a colloidal concentration above a critical value (moderate to high concentrations). However, it may be difficult to operate a treatment process in an optimal dose range if it is too narrow or if the raw water quality frequently changes. In addition, if the coagulation is operated at low pH (pH $< 6$) and the coagulant dose exceeds the optimum, the treated water quality will worsen due to colloidal restabilisation caused by charge reversal at the colloidal surface. To guarantee the treated water quality and to cope with changes in temperature and the nature of raw water, water treatment plants normally operate coagulation at high doses and elevated pH (pH $> 6$). As a result, greater operational costs are incurred due to the high coagulant dose used and a larger amount of sludge to be disposed of.

One successful and important method of improving the effectiveness of inorganic Al/Fe(III) coagulants is to partially hydrolyse the Al/Fe(III) salts prior to their addition to the raw water and thus preform optimal polymeric Al/Fe(III) species, the actual coagulants. In this way, the coagulant chemistry can be controlled and the preferred solution conditions for the formation of the desired coagulant species can be maintained. The resulting advantages of the preformed polymeric Al/Fe(III) coagulants are that they can work efficiently
over a wide pH range and cope with changes in the water temperature and the nature of the raw water. Thus, by use of pre-polymerised inorganic coagulants, water treatment plants can be operated over a wider range of chemical and physical characteristics of the raw water with less change in the operational conditions.

Pre-polymerised Al/Fe(III) coagulants

Pre-polymerised Al/Fe(III) coagulants could be prepared at laboratory scale through a series of experiments involving investigation of the effects of the basic ratio \( r \), defined as the molar ratio of the metal ions to hydroxide ions, base concentration, base addition rate, initial metal concentrations, aging time, and aging temperature, to allow the prepared Al/Fe(III) solutions to contain the maximum proportion of polymeric species.

Alternative procedures for preparing polyferric coagulants have been developed, e.g. Jiang (1995), and in some cases this involves the oxidation of ferrous state iron solution under the conditions of high temperature and/or high pressure, and subsequently aging with heating and/or base addition. By controlling various preparation conditions, polymeric iron species can not only be produced but are stable for a reasonable period.

A variety of techniques can be used to characterise the resulting polymeric solutions. Commonly used techniques are a timed ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid) colorimetric method (Murphy et al., 1975), and a membrane ultrafiltration method, e.g. Jiang (1995). The ferron-timed colorimetric technique is based on the differences in the rates of reactions of various Al/Fe species with ferron to assess the properties of monomeric, polymeric and precipitated Al/Fe species. The size distribution of Al/Fe species in the polymeric solutions were evaluated using a membrane ultrafiltration technique, with decreasing molecular weight (MW) cutoff, apparent MW distributions can be obtained by measurement of the metal concentration in the solutes. Such distributions can only be taken as an indication of the actual species present in the polymeric Al/Fe solution.

In addition to the above two common characterisation techniques, a nuclear magnetic resonance (NMR) spectroscopy method and a radiation scattering technique are used to specifically investigate the nature and the structure of the pre-formed polymeric Al/Fe species.

Figure 1 shows a MW distribution of the polyferric sulphate (PFS), which is a pre-polymeric form of iron coagulant. It can be seen that with increasing \( r \) values, the 0.5 to 10 K MW fractions increased and reached a maximum at \( r = 0.3 \). The fraction decreased

![Figure 1](https://iwaponline.com/ws/article-pdf/1/4/57/109067/57.pdf)
from the maximum as the $r$ value increased between 0.3 and 0.6. Moreover, the fraction of smaller MW species (<0.5 K) decreased with increasing $r$ values. Figure 2 presents the variation of the electrophoretic mobility (EM) of PFS solutions versus $r$-values. It can be seen that when $r = 0.3$, the PFS carried the greatest cationic charge. By comparing the results of MW distributions (Figure 1) with those of EM (Figure 2), it can be concluded that the polymeric species with MW of 0.5 to 10 K carried the largest proportion of cationic charge. Thus, the greater the percentage of 0.5 to 10 K species, the greater the cationic charge in PFS products.

The evidence of the existence of pre-polymerised species has been confirmed by a study on the chemical nature of precipitates formed with PFS and FS (Jiang and Graham, 1998a). The test is based on the assumption that if identical precipitates were formed by each coagulant, PFS and FS, then upon dissolution they should show the same reactivity with ferron. If the nature of the precipitates of the two coagulants were different, then their reactivity with ferron would be different. The results indicated that the species in the re-dissolution solutions from FS precipitates were predominantly Fe(OH)$_3$, whilst those from PFS precipitates were predominantly higher MW polymers. This was also evident from the investigation of their zeta potential pH behaviour. Re-suspended precipitates of PFS carry a

![Figure 2](image1.png)

Figure 2 The effect of the $r$ values on electrophoretic mobility of polyferric species (after Jiang, 1995)

![Figure 3](image2.png)

Figure 3 Iso-electric point of re-suspended PFS and FS precipitates (after Jiang, 1995)
significantly higher cationic charge compared to those of FS (Figure 3). The preliminary characterisation of precipitates using the ferron technique, and particle size and electrophoretic mobility measurements, has confirmed that there are distinct differences in the nature of the precipitates formed by PFS and FS. However, a detailed examination of the chemical structure of the two types of precipitates to explain the different behaviour is the subject of further work.

Comparative coagulation performance of pre-polymerized and traditional coagulants
Pre-polymerised inorganic coagulants have been shown to have superior performance in water and waste water treatment, and these can be concluded by their wider working pH range, a lower sensitivity to low water temperature, lower doses required to achieve the equivalent treatment efficiency, and lower residual metal-ion concentrations, e.g. Jiang (1995). For removing particulate materials and NOM from surface water, PFS has shown a superior performance than conventional coagulants. The reduction of turbidity and NOM was found to be greater with PFS than ferric sulphate (FS) for the same coagulant dose used in comparison to AS and FS, the use of PFS in water treatment is expected to reduce treatment costs through a lower coagulant dose and subsequently lower sludge handling requirements. PFS has also demonstrated high removal efficiency for algae and algal-derived organic matter (Jiang et al., 1993). However, in some cases, polyferric chloride (PFCl), e.g. Leprince et al. (1984) has not shown a superior performance in comparison to ferric chloride (FCI) for removing colour and NOM from natural surface waters. Nevertheless, one advantage of the use of PFCl is its lower sensitivity to water temperature variation, which is of particular benefit to the water industry.

Poly-alumino-iron sulphate (PAFS) is relatively a new kind of pre-polymerised coagulant (Jiang and Graham, 1998b). An example of the comparative performance of PAFS in comparison with the FS and AS at two water temperatures (18°C and 4°C) for treating a model coloured water can be seen in Table 1. Generally, PAFS behaved better than the
other two coagulants, and the performance of PAFS was unaffected by the water temperature, but FS and AS were significantly affected, with evidence of a reduction in the removal percentages of colour, UV-abs and DOC, and an increase in residual concentrations of the metal in the treated waters at 4°C.

The appeared advantage in using pre-polymerised coagulants in water treatment is of lower residual metal concentrations in the treated waters. Table 2 shows the comparative residual concentrations in the treated water when treating a model coloured water. It is evident that the residual concentrations with PAFS and PFS are consistently lower than those treated with AS and FS, respectively. A significant advantage using PAFS for water treatment is that it can achieve the lower residual concentrations of Al and Fe.

Conclusions

Fundamental studies of coagulation chemistry indicate that a range of hydrolysed Al/Fe species, but not Al or Fe salt itself, are responsible for the removal of suspended particles and dissolved impurities in the water. By development and uses of polymeric inorganic coagulants, the coagulation performance with Al and Fe coagulants could be improved for removing both particles and dissolved organic matter.

Coagulation/flocculation has played, and will still play an important role, directly or indirectly, in the control of particulates, microorganisms, NOM, synthetic organic carbon, precursors of disinfection by-products (DBPs), and some inorganic ions and metals, and ultimately, in the control of drinking water quality. The water and environmental industry worldwide continues to regard the performance of coagulation/flocculation processes as a major factor in improving overall water treatment efficiency, and is paying particular attention to aspects such as: the development and use of more effective coagulants/flocculants; the optimisation of treatment configuration, dosing control, sludge handling and process design; and to more fundamental studies of the properties and behaviour of coagulating chemicals.

References


