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# Environment Canada

Water Science and  
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Direction générale des sciences  
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## Environnement Canada

Coagulation and Flocculation

By:

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## **Coagulation and flocculation**

Kirsten Exall

### **Abstract**

Coagulants and flocculants are commonly used in the destabilization and aggregation of suspended solids during water and wastewater treatment. Both inorganic salts and organic polymers may be used as coagulants, and various synthetic and natural organic polymers are applied as flocculants. Organic matter is quite well removed during coagulation, although it often requires a higher coagulant dosage. Other factors that influence the effectiveness of coagulants and flocculants are pH, temperature, mixing conditions and other ions present in the water. This work summarizes the use of coagulation and flocculation as drinking water and wastewater treatment processes.

### **NWRI RESEARCH SUMMARY**

#### **Plain language title**

Coagulation and flocculation

#### **What is the problem and what do scientists already know about it?**

Coagulation and flocculation processes are used to improve solids removal in both drinking water and wastewater treatment, through destabilization and aggregation of suspended material. Various types of chemical coagulants and flocculants are used, and such factors as organic matter concentration, pH, temperature and water chemistry influence their abilities to aggregate and remove solids.

#### **Why did NWRI do this study?**

This work serves as a summary of the use of coagulation and flocculation in drinking water and wastewater treatment.

#### **What were the results?**

This work summarizes the use of coagulation and flocculation in drinking water and wastewater treatment, discusses the typical mechanisms of contaminant removal, and describes some of the factors that influence the effectiveness of these processes.

#### **How will these results be used?**

This work will form part of a reference text, the Encyclopedia of Water.

#### **Who were our main partners in the study?**

N/A

# **Coagulation et floculation**

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## **Résumé**

Les coagulants et les floculants sont couramment utilisés pour déstabiliser et agglomérer les matières en suspension durant le traitement de l'eau et des eaux usées. Les sels minéraux et les polymères organiques peuvent servir de coagulants alors que divers polymères organiques naturels et synthétiques peuvent être ajoutés comme floculants. L'élimination de la matière organique s'effectue relativement bien durant la coagulation quoiqu'il soit souvent nécessaire d'ajouter une dose plus forte de coagulant. Le pH, la température, les conditions du mélange et d'autres ions présents dans l'eau sont d'autres facteurs qui influent sur l'efficacité des coagulants et des floculants. Cet article présente sommairement la coagulation et la floculation utilisées comme méthodes de traitement de l'eau potable et des eaux usées.

## **Sommaire des recherches de l'INRE**

### **Titre en langage clair**

Coagulation et floculation

### **Quel est le problème et que savent les chercheurs à ce sujet?**

La coagulation et la floculation sont deux méthodes utilisées pour éliminer les matières solides par déstabilisation et agglomération des particules en suspension pendant le traitement de l'eau potable et des eaux usées. Pour ce faire, on emploie divers coagulants et floculants chimiques dont les performances dépendent de facteurs tels que la concentration de matière organique, le pH, la température et la composition chimique de l'eau.

### **Pourquoi l'INRE a-t-il effectué cette étude?**

Ce document expose dans les grandes lignes le procédé de coagulation-floculation dans le traitement de l'eau potable et des eaux usées.

### **Quels sont les résultats?**

Ce document expose dans les grandes lignes le procédé de coagulation-floculation dans le traitement de l'eau potable et des eaux usées, traite des méthodes classique d'élimination des contaminants et décrit un certain nombre de facteurs qui influent sur l'efficacité de ces procédés.

### **Comment ces résultats seront-ils utilisés?**

Cet article fera partie d'un ouvrage de référence portant le titre de Encyclopédie de l'eau.

### **Quels étaient nos principaux partenaires dans cette étude?**

S/O

## **Coagulation and flocculation**

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### **Introduction**

Removal of suspended or colloidal solids is an integral component of both drinking water and wastewater treatment. Natural water bodies from which drinking water is obtained contain a variety of particulates, including clays, silt, organic detritus and microorganisms. Municipal and industrial wastewaters contain high concentrations of solids, as well as nutrients, organics and pathogens. Many contaminants of concern to human and environmental health are commonly associated with particles (e.g., metals and many synthetic organic chemicals) or are of colloidal size themselves (e.g., some pathogenic organisms). Removal of suspended or colloidal particles is therefore necessary for reduction of many health-related risks.

The addition of chemical coagulants to aid solids removal is a key step of conventional drinking water treatment. In wastewater treatment, coagulants may be added to aid primary settling (known as chemically enhanced primary treatment or advanced primary treatment) or to aid separation of sludge in the secondary clarifier. Additionally, flocculants may be applied during sludge thickening and dewatering; this application has recently been discussed in Bache [1]. This work focuses on chemical coagulant addition and subsequent flocculation processes during drinking water and wastewater treatment; various factors that influence the effectiveness of these processes will be discussed.

### **Coagulation and flocculation**

Colloidal particles are those that are broadly defined to exist in the size range of nanometres to micrometres. Such particles do not readily settle out of suspension in natural water or wastewater due to very low settling velocities and do not aggregate quickly due to electrostatic or steric stabilizing influences. Many colloidal materials present in natural water and wastewater have negatively charged surfaces, which leads to the formation of an electrical double layer (the charged surface with adsorbed ions and a more diffuse, surrounding ion cloud). Repulsion between like-charged surfaces of neighbouring colloids imparts electrostatic stability to the particles. The degree of stability depends on the magnitude of the surface charge; the zeta potential of a particle is commonly used as an indirect measure of the surface charge, and therefore of electrostatic stability. Further discussion of the origins, impact and modeling of the electrical double layer and colloid stability (as they relate to water treatment) can be found in Letterman *et al.* [2].

The adsorption of polymer segments at a particle's surface leaves loops and tails extending into solution. Interactions with adsorbed polymers on nearby colloids lead to repulsion, as mixing or compression of the polymers increases the local concentration and reduces their freedom (a thermodynamically unfavourable condition). Such steric

stability in natural waters may arise from the adsorption of such materials as humic substances to colloid surfaces [2].

Coagulation in water treatment utilizes physicochemical processes to accelerate the kinetics of destabilization (coagulation) and aggregation (flocculation). Coagulation involves the addition of a chemical agent to destabilize colloids in the water and requires intensive mixing to rapidly disperse the coagulant. Flocculation, on the other hand, is the formation of aggregates, or flocs, of the destabilized colloids and requires gentle mixing to allow interparticle collisions to occur to form flocs, without shearing the aggregates apart [2]. Separation of the flocs and other particulate matter from the water may then occur by gravity settling (sedimentation), dissolved air flotation, or filtration [3].

Coagulation processes include double layer compression, charge neutralization, sweep coagulation and complex formation; these processes are described below:

- *Double layer compression* occurs on addition of simple salts (e.g.,  $\text{Na}^+$ ) to a colloidal suspension; this mechanism of colloid destabilization is impractical for water and wastewater treatment, as the salt concentrations required are high and particle aggregation is slow.
- *Charge neutralization* is a common mechanism of contaminant removal employed in water treatment, whereby cationic (positively charged) coagulant species adsorb to the negatively charged particle surface, neutralizing the surface charge and thereby reducing electrostatic stability. Addition of excess coagulant, or overdosing, can result in the reversal of surface charge and restabilization of the dispersion [2]. In the case of polymeric coagulants, neutralization is described by the electrostatic charge patch model, where polymer species adsorb to portions of the colloid surface, resulting in the formation of charge-neutral or positively charged "patches", which cause electrostatic attraction and aggregation of colloidal species [4, 5].
- In *sweep coagulation*, voluminous metal hydroxide flocs bring about removal of colloidal contaminants through enmeshment as they move through the suspension. The relationship between floc structure and operational problems during sweep coagulation has been reviewed by Bache *et al.* [6].
- Removal of dissolved contaminants, such as organic species or phosphate, may also be achieved by *formation of insoluble complexes* or by *adsorption* to flocs [2].

Flocs are aggregates of primary particles, bound together by intermolecular forces. Flocculation, or floc growth, occurs through interparticle collisions. Both particle collision frequency and collision efficiency (sticking) influence the formation of flocs, while floc strength and mixing intensity, or shear, influence the final floc size [7]. Polymer flocculants (described below) can aid flocculation through adsorption and interparticle bridging. In this mechanism of flocculation, segments of a polyelectrolyte are bound to one colloid particle, but loops and dangling chains of the polymer extend into solution and can attach to nearby particles, leading to an increase in the size of the agglomerate [4, 5]. It may be difficult to distinguish between charge neutralization and bridging when applying polymers, as both processes may take place simultaneously [8].

### Coagulants and flocculants

Coagulation has been utilized as an aid to sedimentation for the production of household water since ancient times. Common coagulants include both metal salts and charged polymers (also termed polyelectrolytes), while flocculants are typically composed of high molecular mass polymers.

### Inorganic coagulants

When simple inorganic coagulants, such as aluminum sulfate (alum) or ferric chloride, are added to water, the salts dissociate and the metal ions undergo hydrolysis reactions to form a variety of hydroxo-aluminum or hydroxo-iron species. In these reactions, the acidity of the metal cation causes deprotonation of waters of hydration. The formed species may be cationic, anionic or neutral, and can include an insoluble metal hydroxide form; the distribution of species depends on the concentration of the metal ion, pH, and other materials present in the water.

Successive reactions in a solution of an aluminum salt lead to the formation of the species  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_4^-$ . Note that for the sake of simplicity, the waters of hydration (e.g.,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ) are conventionally not shown. At higher concentrations or pH values, both  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  are converted to insoluble hydroxides, which form as voluminous, amorphous flocs. These flocs are responsible for sweep coagulation, and can enmesh colloidal material as they pass through the suspension. Depending on the conditions of hydrolysis, polynuclear aluminum species (those containing more than one aluminum ion) may also be formed. These have been suggested to include dimeric (e.g.,  $\text{Al}_2(\text{OH})_2^{4+}$ ), trimeric ( $\text{Al}_3(\text{OH})_4^{5+}$ ) and tridecameric ( $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ) forms [9]. Similar reactions occur when using iron salts, and equivalent mononuclear and polynuclear iron species exist [2].

### Prehydrolyzed coagulants

Various prehydrolyzed coagulants have been prepared and investigated, including polyaluminum chloride (PACl) [e.g., 10, 11], polyaluminum silicate sulfate (PASS) [12], polyaluminum sulfate (PAS, also known as polyaluminum hydroxysulfate, PAHS) [e.g., 13, 14], and various iron-based and mixed Fe-Al coagulants [15, 16]; PACl is the most common of these [9]. Prehydrolyzed coagulants are formed by partial neutralization of a simple salt solution, such as aluminum chloride, with a base. The degree of prehydrolysis is expressed as a hydroxide-to-metal ion ratio, and can be expressed as a percent basicity [10], where

$$\text{Basicity (\%)} = 100 * [\text{OH}^-] / (3 * [\text{M}_T]) \quad (1)$$

At a basicity of 100%, sufficient hydroxide (or equivalent base) has been added such that all metal ion present could be converted to the amorphous solid form,  $\text{Al}(\text{OH})_{3(\text{am})}$  or  $\text{Fe}(\text{OH})_{3(\text{am})}$ .

Prehydrolysis has been shown to favour the formation of soluble polynuclear species, such as the dimer and tridecamer. The rate of particle destabilization has been found to be faster with PACl than with alum, and the prehydrolyzed product, PACl, has also been shown to be less dependent on pH for efficient coagulation. The performance of prehydrolyzed Al coagulants, such as polyaluminum chloride (PACl) and polyaluminum hydroxysulfate (PAHS), has also been shown to be less affected by low temperatures than is that of alum [9, and references therein]. While effective in organic matter removal, prehydrolyzed coagulants do not appear to be superior to alum in this regard [9], and may even display higher sensitivity to organic matter concentration [19]. Other reported benefits of prehydrolyzed coagulants have included lower Al residuals, reduced sludge volume, less alkalinity consumption, and improved settling efficiency [9, 18].

#### Organic polymers

Synthetic polymers are commonly employed as coagulants or flocculants in water and wastewater treatment [4, 20, 21]. Typical polymers employed include polyacrylamide (PAM), polydiallyldimethyl ammonium chloride (PolyDADMAC), epichlorohydrin-dimethylamine (Epi-DMA). Derivatized versions of these, such as polyacrylamides altered by the addition of charged functional groups to improve coagulation characteristics, are also common. The behaviour of the polymer is governed by the nature of the charge it possesses, whether cationic (positively charged), anionic (negatively charged), zwitterionic (containing both positively and negatively charged groups) or nonionic. Although anionic and nonionic polymers are effective at removal of colloidal contaminants under some conditions and may be used as flocculants in conjunction with inorganic coagulants, the polymers used as primary coagulants in water and wastewater treatment are most often cationic [2, 4, 20].

Synthetic polymers may be used as either coagulants or flocculants, depending on the molecular character and mode of action on suspended solids. Polymer coagulants typically have a low molecular weight and high charge density, and commonly act on colloids to bring about coagulation through charge neutralization. In this case, removal is considered to progress by the electrostatic charge patch model (discussed above). As with inorganic coagulants, charge reversal and restabilization is possible with polymer coagulants. Polymer flocculants, on the other hand, generally have very high molecular weight and low charge density, and typically act through a bridging mechanism. Flocculants are also commonly known as coagulant aids, as they are often used in conjunction with inorganic or polymeric coagulants [4, 5].

The effectiveness of polymers (particularly the large molecular weight flocculants) can strongly depend on their conformation, which in turn depends on the preparation of polymer solution. Many flocculants are supplied in concentrated, highly entangled forms, often as dispersions or emulsions in mineral oils. The polymer must be dissolved in water and at least partially disentangled, or 'activated', for optimal flocculation behaviour. The intensity of mixing employed during dispersion can impact the dissolution process, and a balance must be achieved between rapid dispersion of the polymer and rupture of polymer chains under high shear conditions [8]. Other factors

that may influence the effectiveness of a polymer solution include other ions present in the water [8] and the age of a polymer solution [22].

Concerns over the use of synthetic polymers in water and wastewater treatment have been raised with regard to toxicity of residual trace levels in the effluent and formation of toxic by-products on reaction of residues with disinfectants (e.g., 23, 24). Polymers are expected to be largely partitioned into the solid phase, but the amount of residual polymer remaining in the liquid stream depends on the dosage applied. Careful dosage selection and control is therefore needed. Other concerns exist with respect to contaminant monomer concentrations (e.g., acrylamide in polyacrylamide formulations); many countries regulate the composition and allowed dosages of polymers to be applied in drinking water treatment [2, 25, 26].

#### Natural coagulants

Natural products, including chitosan (a derivative of chitin, found in the shells of crustaceans), starch derivatives, seed extracts of such plants as *Moringa oleifera*, tannin- and lignin- based materials, and alginate have also been studied for use in municipal water or wastewater treatment [4, 27]. These products have primarily been examined for use in developing countries, but often provide many of the advantages of synthetic polymeric coagulants and flocculants, while providing the additional benefits of biodegradability and reduced toxicity [27].

#### Ballasted flocculation

Under such conditions that would lead to formation of poorly settling flocs, such as low solids and high organics concentrations, ballasted flocculation may be employed. In this technique, additional solids are added with (or shortly after) the coagulant, in order to aid floc formation and settling. Polymers may be added to improve adhesion of the forming flocs to the solids, and the solids may be recovered and recycled through the process [4, 28]. Various solids have been employed as ballast, including bentonite, fly ash, powdered magnetite and microsand [3, 29].

#### Organic matter removal

Organic species exist in many forms in natural waters and wastewaters and, even when not directly harmful to human health, can serve as carriers of harmful contaminants and interfere with treatment processes. Reaction of organic matter (OM) with disinfectants may also lead to the formation of harmful disinfection by-products [2]. In drinking water treatment, the term 'enhanced coagulation' refers to the practice of optimizing coagulation conditions for removal of natural organic matter (NOM), which is typically accomplished through increased coagulant dosage and adjustment of pH [30].

In general, the presence of organic matter increases the dosage of a metal salt coagulant required; once the coagulant demand is met, turbidity and NOM removal occur simultaneously [31, 32, 33]. There often exists a linear relationship between OM concentration and the coagulant dose required to bring about coagulation. The presence of such a 'stoichiometric' relationship between concentration of humic substances and



alum dosage was first described by Hall and Packham [31] and has since been observed with various coagulants and organic species [e.g., 33, 34].

The nature of the organic matter present affects its removal by coagulation. Many researchers [e.g., 32, 33] have observed preferential removals of hydrophobic dissolved organic carbon compounds over hydrophilic organic fractions and of higher molar mass organic matter over lower molar mass compounds.

Metal ion concentration and pH are important factors governing the mechanism of OM removal by coagulation. Two distinct regions of organic matter or colour removal have been observed [32, 34, 35]; one near pH 5.5 and one centred near pH 7. The two domains have been explained in terms of removal mechanisms. The lower pH and Al concentration region is thought to represent removal by charge neutralization / precipitation, where cationic Al species interact directly with OM to bring about removal [2, 32]. The higher pH / higher coagulant dosage domain is thought to indicate sweep coagulation, where organic species adsorb directly to the surface of formed  $\text{Al}(\text{OH})_3$  flocs [32, 35]. Removal of OM may not occur by a single, simple mechanism, however. It has been suggested that even the OM that is ultimately removed by adsorption to  $\text{Al}(\text{OH})_3$  surfaces may first be complexed by cationic coagulant species [17, 33].

The presence of organic matter removal also increases the dosage required of polymer coagulants and flocculants, often increasing the cost of treatment excessively [4, 44]. As with metal salts, the more hydrophobic OM fractions are more easily removed by polymer, and increasing polymer charge density has been shown to improve OM removal [43]. Polymer molecular weight also appears to influence organic matter removal, although the effect varies [42, 43].

#### Factors affecting efficiency of coagulation and flocculation

Many variables may influence the progression of coagulation and flocculation processes, but the primary factors include pH, temperature, mixing conditions and the presence of other ions.

#### pH dependence

The speciation of Al and Fe in aqueous solution are highly dependent on pH. Under acidic conditions, cationic coagulant species (e.g.,  $\text{Al}(\text{OH})^{2+}$ ) are dominant, while in highly basic solution, the anionic hydroxo-aluminum ( $\text{Al}(\text{OH})_4^-$ ) or iron form predominates. At intermediate pH values, both the pH and metal ion concentration affect the speciation of Al or Fe, in turn influencing the interactions between the coagulant species and colloidal solids or organic matter [2]. The optimum pH for solids and organic matter removal may differ slightly, and depends on the mechanism of coagulation (discussed above) [32, 34, 35].

In order to minimize residual Al or Fe in treated water, it is preferable to conduct coagulation under conditions of minimum metal hydroxide solubility. Aluminum hydroxide exhibits a minimum in solubility at 25°C at approximately pH 6.3, while the

minimum solubility of iron at the same temperature is encountered at approximately pH 8 [2]. In general, synthetic polymers are much less sensitive to pH than are metal salt coagulants [4, 20].

#### Temperature

It has long been known that cold temperatures increase the coagulant dose required and change the nature of the flocs produced during coagulation with simple salts [36]. Many reasons for the temperature effects have been suggested, including changes to water viscosity (which could affect mixing efficiency), change in the rate and extent of hydrolysis reactions, and changes in the size and strength of flocs formed at lower temperatures [37, 38].

The effect of pH has been seen to vary in cold waters; the optimum pH value for coagulation and flocculation changes with both coagulant concentration and temperature [36]. Kang and Cleasby [37] noted that the value of  $pK_w$  is temperature-dependent, and adjusting the pH of the solution such that a constant pOH value was held in cold and warm waters was found to be partially effective in reducing the impact of low temperature on flocculation kinetics.

Prehydrolyzed coagulants are generally less susceptible to temperature changes than are simple aluminum or iron salts [11, 18]. Synthetic polymers are also not as sensitive to water temperature as metal salt coagulants, although storage of polymer solutions at elevated temperatures may increase the rate of degradation, lowering the effective polymer concentration [22].

#### Mixing effects

Coagulation and flocculation processes require both a rapid mix phase in order to achieve complete and uniform distribution of the coagulant in the water to be treated, and a slow mix phase, which promotes interparticle collisions so that flocs may form and grow. Both mixing phases influence the efficiency of contaminant removal.

Although the intensity of rapid mixing is not particularly important for sweep coagulation processes (where contaminant removal occurs by physical interaction between amorphous metal hydroxide flocs and colloids), charge neutralization with metal salt coagulants requires contact between the rapidly-changing cationic Al or Fe species and the colloids in the water before hydrolysis is complete and the metal hydroxide solid forms. For effective charge neutralization to occur, the coagulant species must therefore be distributed throughout the water sample as quickly as possible. Optimization of the rapid mix parameters has been shown to improve turbidity removal considerably for a given water sample and to lower the required coagulant dosage [39]. In order to optimize the rapid mixing phase of treatment, the intensity of mixing (often expressed as the velocity gradient,  $G$ ), duration of mixing and container geometry should all be considered. The optimal combination of these rapid mixing parameters has been shown to depend on initial conditions of the water to be treated, as well as the coagulant used [41].

Increased agitation accelerates floc formation and aggregation through interparticle collisions; if mixing is too vigorous, however, turbulent shear forces cause the break-up of flocs. Interparticle collisions occur through transport by fluid shear, which is controlled by characteristics of the slow mixing phase of treatment, such as vessel geometry, flow patterns, and the turbulence and intensity of mixing [2]. Floc break-up may occur through surface erosion of primary particles or fracture of the relatively fragile floc aggregate, and is dependent on the intensity of the slow mix phase. The competing processes of aggregation and floc break-up result in a stable floc size for a given set of formation conditions [7].

Mixing is important in both the activation and application of polymer flocculants [8, 40]. In general, higher intensity mixing (higher energy input) is required for the dispersion of polymers than with metal salts [20, 40].

#### Other ions

A number of aspects of water quality impact coagulation processes, including the alkalinity of the water. At very low alkalinity, small additions of an acidic metal coagulant can depress the pH of the water below that of efficient coagulation, while with very high alkalinity, coagulant demand may be extremely high [32].

Some anions, such as fluoride, phosphate and certain organic acids, can complex cationic metal species, inhibiting coagulation by reducing the free cation in solution [2]. The presence of divalent cations, such as  $\text{Ca}^{2+}$ , typically broadens the pH range for effective removal and lowers coagulant dosage required. This is likely due to the complexation of such cations with anionic organic functional groups, lowering the stability of the organic species and thereby decreasing demand on the coagulant [32, 45]. Sulfate may enhance coagulation by suppressing charge reversal, or by catalyzing the kinetics of precipitation by forming outer-sphere complexes with Al ions [45].

The selection and effectiveness of polymers may also be affected by the ionic strength of the system. The addition of simple salts (such as NaCl) causes a contraction in polymer conformation, reducing the effectiveness of polymer flocculants [5].

#### Summary

Coagulants and flocculants are commonly used in the destabilization and aggregation of suspended solids during water and wastewater treatment. Both inorganic salts and organic polymers may be used as coagulants, and various synthetic and natural organic polymers are applied as flocculants. Organic matter is quite well removed during coagulation, although it often requires a higher coagulant dosage. Other factors that influence the effectiveness of coagulants and flocculants are pH, temperature, mixing conditions and other ions present in the water. This work summarizes the use of coagulation and flocculation as drinking water and wastewater treatment processes.

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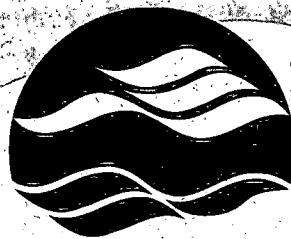
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