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Sweep flocculation as a second form of charge neutralisation—a review

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ABSTRACT

The coagulation/flocculation (C/F) processes are mainly due to charge neutralisation (CN) and *sweep* flocculation (*SF*) mechanisms. However, the *SF* mechanism has also its CN property moreover than its well-known weighting characteristic. On this weighting characteristic, the literature has usually focused without taking in consideration the *SF*'s CN property. This review discusses the implicated mechanisms in destabilisation of colloids and aggregation of flocs. Colloids are very small particles that have extremely large surface area. The consequence of this smallness in size and mass and largeness in surface area is that in colloidal suspensions: gravitational effects are negligible and surface phenomena predominate. Hence, during C/F process, colloids are removed by CN and *SF* mechanisms which act on the anionic charge of the colloid by its neutralisation prior to its removal by sedimentation/filtration. The *sweep* flocs can be described as large aggregates of $Al(OH)_3$/$Fe(OH)_3$ that are formed when Al/Fe salt is added to water. Further, *sweep* flocs are positively charged and the colloids of clay minerals abundantly found in the water are negatively charged. As a result, the colloidal particles are electrostatically attached to the *sweep* flocs in the neutral pH water as to the hydrolysed metallic cations. Even if researches have greatly elucidated the growth, breaking and the re-growth of flocs, further research is required to understand CN and *SF* mechanisms and optimise the C/F process at the nano level.

Keywords: Coagulation/flocculation (C/F); Colloid; *Sweep flocculation* (*SF*); Charge neutralisation (CN); Mechanism; Aluminium; Iron

1. Introduction

Coagulation/flocculation (C/F) may be broadly described as chemical and physical processes that mix coagulating chemicals and flocculation aids with water [1–7]. The overall purpose is to form particles large enough to be removed by the subsequent settling or filtration processes [8–11]. Particles in source water that can be removed by C/F, sedimentation or flotation, and filtration include colloids, suspended material, bacteria, and other organisms [12–15]. The size of these particles may vary by several orders of magnitude. Some dissolved material can also be removed through the formation of particles in the C/F processes. The importance of dissolved material removal has become much more critical in recent years with increased regulatory emphasis on disinfection by-products (DBPs) and total organic carbon (TOC) removal [16].

On the other hand, the generic term of flocculation can be defined as a process of aggregation by any kinds

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of mechanisms involved [17–20]. Flocculation can be attained by the following mechanisms; approach to the point of zero charge (PZC), electrical double layer (EDL) compression, charge-patch neutralisation, polymer bridging, hydrophobic interaction, and enmeshment within *sweep* floc—*SF* [18–21].

SF is a non-selective aggregation of colloidal size particles within the flocs [22,23]. *Sweep* flocs can be described as large aggregates of aluminium hydroxide ($Al(OH)_3$) or ferric hydroxide ($Fe(OH)_3$) that are formed when alum or a ferric salt (coagulant) is added to water [18–20]. It has been found that *sweep* flocs formed in any conventional water treatment process are positively charged [24]. For example, the PZC of $Al(OH)_3$ and $Fe(OH)_3$ is ≈8.5 [25]. The colloids of clay minerals abundantly found in the water are negatively charged [18–20]. For example, the PZC of silica and kaolin is ≈2 and 4, respectively [26]. As a result, the colloidal particles are electrostatically attached to the *sweep* flocs in the neutral pH water. In addition, soluble contaminants (e.g., arsenate, chromate, mercury, cadmium, etc.) can adsorb on the *sweep* flocs and then they will be removed from the water [18–20].

Hence, *SF* may be considered as a second form of CN. The objectives of this review are to discuss the *SF* mechanism by illustrating its CN property moreover than its well-known weighting characteristic, to describe the evolution of floc size distributions under different conditions, and to evaluate flocculation mechanisms using the size distributions as direct performance criteria. This review starts with C/F definitions, properties of colloidal systems, destabilisation of colloids, and coagulation phenomena. Aggregate size distributions in *SF* and breakage and re-growth of flocs are discussed.

2. Coagulation/flocculation

Coagulation is a process for increasing the tendency of small particles in an aqueous suspension to attach to one another and to attach to surfaces such as the grains in a filter bed (Table 1) [16,27,28]. It is also used to effect the removal of certain soluble materials by adsorption or precipitation. The coagulation process typically includes promoting the interaction of particles to form larger aggregates [16]. It is an essential component of conventional water treatment systems in which the processes of coagulation, sedimentation, filtration, and disinfection are combined to clarify the water and remove and inactivate microbiological contaminants such as viruses, bacteria, and the cysts and oocysts of pathogenic protozoa [14,29,30]. Although the removal of microbiological contaminants continues to be an important reason for using coagulation, a newer objective, the removal of natural organic material (NOM) to reduce the formation of DBPs, is growing in importance [31–39].

Aluminium and ferric iron salts have long been used to remove colour caused by NOM [40]. These organic substances are present in all surface waters and in many groundwaters [41]. They can be leached from soil, diffused from wetland sediments, and released by plankton and bacteria. NOM adsorbs on natural particles and acts as a particle-stabilising agent in surface water [38,39,42]. It may be associated with toxic metals and synthetic organic chemicals [43]. NOM includes precursor compounds that form health-related by-products when chlorine and other chemical disinfectants are used for disinfection and oxidation [44]. For these reasons, considerable attention is being directed at the removal of NOM by coagulation in water treatment, even when colour removal is not the principle objective [30]. A treatment technique requirement in the US Environmental Protection Agency's (USEPA's) Stage 1 DBPs Rule requires NOM removal in conventional treatment systems by the practice of *enhanced coagulation* [1–4,16,31–33,45–48].

Coagulation has been an important component of high-rate filtration plants in the United States since the 1880s. Alum and iron (III) salts have been employed as coagulant chemicals since the beginning, with alum having the most widespread use [5–7]. In the 1930s, Baylis perfected activated silica as a "coagulant aid". This material, formed on site, is an anionic polymer or a small, negatively charged colloid [49]. Synthetic organic polymers were introduced in the 1960s, with cationic polymers having the greatest use [50–52]. Natural starches were employed before the synthetic compounds. Polymers have helped change pretreatment and filtration practice, including the use of multimedia filters and filters with deep, uniform grain-size media, high-rate filtration, direct filtration (rapid mixing, flocculation, and filtration, but no sedimentation), and in-line filtration (rapid mixing and filtration only) [31–33,53].

Coagulants are also being used to enhance the performance of membrane microfiltration systems and in pretreatment that prolongs the bed life of GAC contactors [54,55]. The development of new chemicals, advances in floc removal process and filter design, and particle removal performance standards and goals have stimulated substantial diversity in the design and operation of the coagulation process, and change can be expected to continue into the future [56–58].

2.1. Properties of colloidal systems

Colloids are very small particles that have extremely large surface area [59–61]. Colloidal particles are larger than atoms and ions but are small enough that they are usually not visible to the naked eye [62]. They range in size from 0.001 to 10 μm resulting in a very small ratio of mass to surface area. The consequence of this smallness

Table 1
Terms used in coagulation literature [16]

Term	Definition
Coagulation	The process in which chemicals are added to water, causing a reduction of the forces tending to keep particles apart. Particles in source water are in a stable condition. The purpose of coagulation is to destabilise particles and enable them to become attached to other particles so that they may be removed in subsequent processes. Particulates in source waters that contribute to colour and turbidity are mainly clays, silts, viruses, bacteria, fulvic and humic acids, minerals (including asbestos, silicates, silica, and radioactive particles), and organic particulates. At pH > 4.0, particles or molecules are generally negatively charged. The coagulation process physically occurs in a rapid mixing process.
Mixing	Commonly referred to as *flash mixing, rapid mixing,* or *initial mixing.* The purpose of rapid mixing is to provide a uniform dispersion of coagulant chemical throughout the influent water.
Enhanced coagulation	A phrase used by the US Environmental Protection Agency (USEPA) in the Disinfectants and Disinfection By-products Rule. The rule requires that the coagulation process of some water supplies be operated to remove a specified percentage of organic material (OM) from the source water, as measured by TOC. Enhanced coagulation (removal of TOC) can be achieved in most cases by either increasing coagulant chemical dosage or adjusting the pH during the coagulation reaction.
Coagulant chemicals	Inorganic or organic chemicals that, when added to water at an optimum dosage, cause particle destabilisation. Most coagulants are cationic when dissolved in water and include chemicals such as alum, ferric salts, lime, and cationic organic polymers.
Flocculation	The agglomeration of small particles and colloids to form settleable or filterable particles (flocs). Flocculation begins immediately after destabilisation in the zone of decaying mixing energy following rapid mixing, or as a result of the turbulence of transporting flow. In some instances, this incidental flocculation may be an adequate flocculation process. A separate flocculation process is most often included in the treatment train to enhance contact of destabilised particles and to build floc particles of optimum size, density, and strength.
Flocculation aids	Chemicals used to assist in forming larger, denser particles that can be more easily removed by sedimentation or filtration. Cationic, anionic, or non-ionic polymers are most often used in dosages of less than 1.0 mg l^{-1}.
Direct filtration	A treatment train that includes C/F, and filtration, but excludes a separate sedimentation process. With direct filtration, all suspended solids are removed by filtration. In the process sometimes called in-line filtration, flocculation occurs in the conduit between the rapid mixing stage and the filter, in the volume above the filter media, and within the filter media.
Solids contact clarifiers	Proprietary devices that combine rapid mixing, flocculation, and sedimentation in one unit. These units provide separate C/F zones and are designed to cause contact between newly formed floc and settled solids.

in size and mass and largeness in surface area is that in colloidal suspensions: (1) gravitational effects are negligible, and (2) surface phenomena predominate [63].

Because of their tremendous surface, colloidal particles have the tendency to adsorb various ions from the surrounding medium that impart to the colloids an electrostatic charge relative to the bulk of surrounding water [49,64]. The developed electrostatic repulsive forces prevent the colloids from coming together and, consequently, contribute to their dispersion and stability.

2.1.1. Electrokinetic properties

The electrokinetic properties of colloids can be attributed to the following three processes [31–33,63]:

1. Ionisation of groups within the surface of particles.
2. Adsorption of ions from water surrounding the particles.
3. Ionic deficit or replacement within the structure of particles.

Organic substances and bacteria acquire their surface charges as a result of the ionisation of the amino and carboxyl groups as shown below [49]:

$$R - NH_3^+ \rightarrow R - NH_2 + H^+ \tag{1}$$

$$R - COOH \rightarrow R - COO^- + H^+ \tag{2}$$

The resulting charge on the surface of such particles is a function of the pH [49]. At high pH values or low hydrogen ion concentrations, the above reactions shift to the right and the colloid is negatively charged. At a low pH, the reactions shift to the left, the carboxyl group is not ionised, and the particle is positively charged due to the ionised amino group. When the pH is at the isoelectric point (IEP), the particle is neutral, that is, neither negatively nor positively charged. Proteinaceous material, containing various combinations of both amino and carboxyl groups, are usually negatively charged at pH values above 4 [59–61].

Oil droplets adsorb negative ions, preferably hydroxides (OH^-), from solution and, consequently, they develop a negative charge [49,64]. Some other neutral particles adsorb selected ions from their surrounding medium such as calcium (Ca^{2+}) or phosphate (PO_4^{3-}) ions rendering them either positively or negatively charged, respectively.

Clays and other colloidal minerals may acquire a charge as a result of a deficit or imperfection in their internal structure [49]. This is known as isomorphic replacement [59–61]. Clays consist of a lattice formed of cross-linked layers of silica and alumina. In some clays there are fewer metallic atoms than nonmetallic ones within the mineral lattice producing a negative charge [49]. In others, higher valency cations may be replaced by lower valency cations during the formation of the mineral lattice that renders the clay particles negatively charged [49]. Examples of such imperfection include (a) the substitution of an aluminium ion (Al^{3+}) by either Mg^{2+} or Fe^{2+} and (b) the replacement of Si^{4+} cation by Al^{3+}. According to Letterman et al. [31–33], the type and strength of the charge resulting from this imperfection in the clay structure are independent of the surrounding water properties and pH. This is in contrast to the first two processes discussed above, in which both pH and ionic makeup of the surrounding solution play a big role in determining the sign and magnitude of the acquired charge on colloidal particles [59–61].

2.1.2. Hydration

Water molecules may also be sorbed on the surface of colloids, in addition to or in place of, other molecules or ions. The extent of this hydration depends on the affinity of particles for water. Colloidal particles that have water-soluble groups on their surface such as hydroxyl, carboxyl, amino, and sulfonic exhibit high affinity for hydration and cause a water film to surround the particles. Such colloids are classified as *hydrophilic* particles. On the other hand, colloids that do not show affinity for water and do not have bound water films are classified as *hydrophobic* [59–61].

2.1.3. Brownian movement

Colloids exhibit a continuous random movement caused by bombardment by the water molecules in the dispersion medium [65]. This action, called *Brownian movement*, imparts kinetic energy to the particles that tends to cause an increase in the frequency of collisions, thus promoting coagulation. Elevated temperature increases molecular velocity resulting in more kinetic energy and more intense Brownian movement [58–61].

2.1.4. Tyndall effect

Because colloidal particles have an index of refraction different from water, light passing through the dispersion medium and hitting the particles will be reflected. The turbid appearance due to this interference with the passage of light is termed the *Tyndall effect*. However, it should be noted that this might not always be the case. Water-loving, hydrophilic, colloids may produce just a diffuse Tyndall cone or none at all. The reason for this behaviour can be attributed to the bound water layer surrounding colloids. These particles will have an index of refraction not very different from that of the surrounding water. Hence, the dispersed phase and the dispersion medium behave in a similar fashion toward the passage of light [59–61].

2.2. Destabilisation of colloids

Destabilisation of colloidal particles is accomplished by coagulation through the addition of hydrolysing electrolytes such as metal salts and/or synthetic organic polymers [58,66]. Upon being added to the water, the action of the metal salt is complex [31–33,59–61]. It undergoes dissolution, the formation of complex highly charged hydrolysed metal coagulants (hydroxyoxides of metals), interparticle bridging, and the enmeshment of particles into flocs [1–4,58]. Polymers work either on the basis of particle destabilisation or bridging between the particles [67].

The destabilisation process is achieved by the following four mechanisms of coagulation [1–4,67,68]:

1. EDL compression,
2. Adsorption and CN,
3. Entrapment of particles in precipitate (*SF*),
4. Adsorption and bridging between particles.

2.2.1. Electrical double layer compression

When high concentrations of simple electrolytes are introduced into a stabilised colloidal dispersion, the added counter-ions penetrate into the diffuse double layer surrounding the particles rendering it denser and hence thinner and smaller in volume [65]. The addition of counter-ions with higher charges [49], such as divalent and trivalent ions, will result in even steeper electrostatic potential gradients and more rapid decrease in charge with distance from the surface of the particles.

The net repulsive energy would become smaller or even would be completely eliminated, allowing the particles to approach each other and agglomerate [59–61].

A mathematical model that describes this coagulation mechanism is explained in detail in [69,70]. The prediction of this model is in agreement with what is known as the *Schulze–Hardly rule*. This rule states that the coagulation of colloidal particles is achieved by ions of added electrolytes, which carry opposite charge to that of the colloids, and that the destabilisation capability of the ions rises sharply with ion charge [58]. Table 2 illustrates the relative effectiveness of various electrolytes in the coagulation of negatively and positively charged colloids. For example, the relative power of Al^{3+}, Mg^{2+}, and Na^+ for the coagulation of negative colloids is shown to vary in the ratio of 1000:30:1. A similar ratio is observed for the relative capability of PO_4^{3-}, SO_4^{2-}, and Cl^- for the coagulation of positively charged colloids [63].

2.2.2. Adsorption and CN

For all practical purposes, the ability of a chemical substance to destabilise and coagulate colloidal particles is the result of a combination of several mechanisms. Long-chained organic amines are often mentioned as being typical coagulants that function by adsorption and electrostatic neutralisation [31–33,59–61,63]. The positively charged organic amine molecules ($R–NH_3^+$) are easily and quickly attached to negatively charged colloidal particles. The charge on the particles gets neutralised and the electrostatic repulsion is decreased or eliminated resulting in the destabilisation of the colloids and hence their agglomeration [49]. The organic amines are hydrophobic because there is a lack of interaction between the CH_2 groups in their R–chain and the surrounding water. As a result, these positively charged ions are driven out of the water and get adsorbed on the particulate interface. An overdose of $R–NH_3^+$ counter-ions, however, can lead to charge reversal from negative to positive and the restabilisation of the dispersion system.

When coagulants such as metal salts are added to water, they dissociate yielding metallic ions, which undergo hydrolysis and form positively charged metallic hydroxyoxide complexes [59–61]. The commonly used coagulants, trivalent salts of aluminium and iron, produce numerous species because the hydrolysis products themselves tend to polymerise to give polynuclear metallic hydroxides [59–61]. Examples of aluminium salt polymers are $Al_6(OH)_{15}^{3+}$ and $Al_7(OH)_{17}^{4+}$ and of iron salt polymers are $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$. When such polyvalent complexes possessing high positive charges get adsorbed on to the surface of the negatively charged colloids, the result is again a neutralisation of the charges, decrease in the repulsion energy, and destabilisation of the colloids. In a similar fashion to what occurs with the organic amines, an overdose of metallic salts could reverse the colloidal charge and restabilise the particles.

Table 2
Relative coagulation power of electrolytes [59–61]

Electrolyte	Relative power of coagulation	
	Positive colloid	Negative colloid
NaCl	1	1
Na_2SO_4	30	1
Na_3PO_4	1000	1
$BaCl_2$	1	30
$MgSO_4$	30	30
$AlCl_3$	1	1000
$Al_2(SO_4)_3$	30	>1000
$FeCl_3$	1	1000
$Fe_2(SO_4)$	30	>1000

2.2.3. Entrapment of particles in precipitate

When the coagulants alum [$Al_2(SO_4)_3$] or ferric chloride ($FeCl_3$) are added in high enough concentration, they will react with hydroxides (OH^-) to form metal hydroxide precipitates, $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$ respectively. The colloidal particles get entrapped in the precipitates either during the precipitate formation or just after. This type of coagulation by enmeshment of colloids in precipitates is commonly called *SF* [31–33,59–61].

There are three elements that influence this coagulation mechanism [59–61]:

1. Oversaturation: The rate of precipitation is a function of oversaturation with the metal hydroxide. To obtain fast precipitation and efficient *SF*, high concentrations of $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$ are required.
2. Presence of anions: The rate of precipitation is improved by the presence of various anions in water. The most effective anions in this respect are the sulphate ions.
3. Concentration of colloids: The rate of precipitation is also improved with higher concentration of colloidal particles. The reason for this is that the colloids themselves could act as nuclei for the formation of precipitates. In this case, it can be concluded that lower rather than higher coagulant dosage will be required to coagulate water having higher colloidal particle concentration.

2.2.4. Adsorption and bridging between particles

Polymers destabilise colloidal particles through the formation of bridges that extend between them [59–61].

The polymers have reactive groups that bind to specific sites on the surface of the colloidal particles. When a group on a polymer molecule attaches to a colloid, the remainder of the long-chain molecule extends away into the water. Once the extended portion of the polymer gets attached to another colloidal particle, the two particles become tied together or bridged by the polymer. If no other particle is available or if there is an overdose of polymer, the free extended portions of the polymer molecule would wrap around the same original particle, which could effectively bring about the restabilisation of the colloid. Restabilisation can also occur due to aggressive mixing or extended agitation, which may break the interparticle bridging and allow the folding back of the freed polymer portions around the same original particle.

2.3. Phenomena of coagulation

Coagulation results from two basic phenomena: (1) perikinetic (or electrokinetic) coagulation, in which collisions among particles is caused by Brownian diffusion and the zeta potential (ZP) is reduced by ions or colloids of opposite charge to a level below the van der Waals attractive forces and (2) orthokinetic coagulation (fluid motion), in which the micelles aggregate and form clumps that agglomerate the colloidal particles [27,71–74].

The addition of high-valence cations depresses the particle charge and the effective distance of the double layer, thereby reducing the ZP [71]. As the coagulant dissolves, the cations serve to neutralise the negative charge on the colloids [75]. This occurs before visible floc formation, and rapid mixing which "coats" the colloid is effective in this phase [58]. Microflocs are then formed which retain a positive charge in the acid range because of the adsorption of H^+. These microflocs also serve to neutralise and coat the colloidal particle. Flocculation agglomerates the colloids with a hydrous oxide floc. In this phase, surface adsorption is also active. Colloids not initially adsorbed are removed by enmeshment in the floc [27,53].

A desired sequence of operation for effective coagulation was outlined [27]. If necessary, alkalinity should first be added (bicarbonate has the advantage of providing alkalinity without raising the pH). Alum or ferric salts are added next; they coat the colloid with Al^{3+} or Fe^{3+} and positively charged microflocs. Coagulant aids such as activated silica and/or polyelectrolyte for floc build-up and ZP control, are added last. After addition of alkali and coagulant, a rapid mixing of 1–3 min is recommended, followed by flocculation, with addition of coagulant aid, for 20–30 min [50–53,56,57,76]. Destabilisation can also be accomplished by the addition of cationic polymers, which can bring the system to the IEP without a change in pH. Although polymers are 10–15 times as effective as alum as a coagulant they are considerably more expensive (Tables 3 and 4) [77,78].

However, EDL compression and CN may be classified as electrokinetic coagulation and *SF* and bridging between particles may be attributed to orthokinetic coagulation [74,79].

3. Aggregate size distributions in *SF*

Since conventional raw water treatment is oriented toward the removal of turbidity caused by colloidal particles suspended in water, many flocculation processes have been designed to minimise the value of turbidity in the finished water. Most investigators in the water treatment field use residual turbidity as a parameter to measure the effectiveness of the flocculation process [18–20]. O'Melia [80] noted that turbidity may not be the best parameter for evaluation of process effectiveness, and measurement of particle number and particle size distribution should be used to understand and control the removal of the suspended particles. Kavanaugh et al. [81] have reviewed the importance of using particle

Table 3
Coagulants and flocculants, adjustment of conditions or addition of specific chemicals achieves required increase in particle size [77]

- Metal salts, especially of aluminium or ferric iron
- $(Al_2(SO_4)_3\bullet 18H_2O; Fe_2(SO_4)_3\bullet 9H_2O)$
- Natural flocculants
  - Starch
  - Gums
  - Tannin
  - Alginic acid
  - Sugar/sugar acid polymers
  - Polyglucosamine (chitosan)
- Synthetic flocculants
  - Polyacrylamides
  - Polyamines/imines
  - Cellulose derivatives (e.g., carboxymethyl cellulose)
  - Polydiallydimethyl ammonium chloride
- Chilling temperatures below 20°C, particularly yeast cells pH adjustment in range 3–6
- Concentration—increases particle concentration, increasing collision frequency

Table 4
Properties of variety of coagulants [78]

Type of water	Alum	Ferric salts	Polymer
Type 1: high turbidity, high alkalinity (easiest to coagulate)	Effective over pH range 5–7. No need to add alkalinity or use coagulant aid	Effective over pH range 6–7. No need to add alkalinity or use coagulant aid.	Cationic polymers usually very effective. Anionic and non-ionic may also work
Type 2: high turbidity, low alkalinity	Effective over pH range 5–7. May need to add alkalinity to control pH. Coagulant aid not needed	Effective over pH range 6–7. May need to add alkalinity to control pH. Coagulant aid not needed	Cationic polymers usually very effective. Anionic and non-ionic may also work
Type 3: low turbidity, high alkalinity	Relatively high dose needed to form sufficient floc, pH ≈7. Coagulant aid may help	Relatively high dose needed to form sufficient floc. Coagulant aid may help	Will not work well alone due to low turbidity. Adding a clay to increase turbidity may be effective
Type 4: low turbidity, low alkalinity (most difficult to coagulate)	Relatively high dose needed to form sufficient floc, pH ≈7. Alkalinity or clay needs to be dosed produce type 2 or 3 water	Relatively high dose needed to form sufficient floc, pH ≈7. Alkalinity or clay needs to be dosed to produce type 2 or 3 water	Will not work well alone due to low turbidity. Adding a clay to increase turbidity may be effective

number and particle size distribution as the direct performance criteria. They found that these criteria were useful in the selection of a water treatment process, for design criteria, and for process control strategies. Lawler and Wilkes [82] have also shown that particle number and particle size distribution are important criteria to measure and predict flocculation performance. These criteria can be used to measure the performance of the actual process used in a water softening plant [18–20]. However, the measurement of these criteria using electrical sensing technique of a modified Coulter Counter is difficult, time-consuming and prone to sampling errors [18–20]. Researchers [83,84] used the light scattering technique of Microtrac X-100 Tri Laser Particle Size Analyzer to successfully evaluate aggregate (floc) size distributions resulting from hydrophobic and polymeric flocculation respectively [18–20].

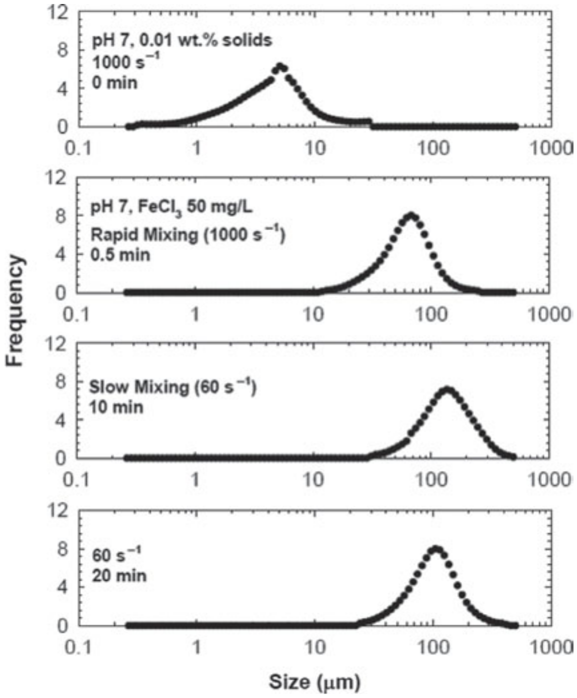

Fig. 1. The evolution of floc size distributions as a function of rapid/slow mixing intensity and time for 0.01 wt.% kaolin suspension, flocculated at pH 7 with 50 mg l^{-1} ferric chloride, and rapid-mixed at 1000 s^{-1} for 0.5 min followed by slow mixing at 60 s^{-1} for varying times in the 800 ml standard mixing tank [18–20].

Floc size distribution obtained from the light scattering technique was used by Rattanakawin [18–20] to evaluate the mechanisms of *SF*. The evolution of floc size distribution as a result of a combination of rapid/slow mixing times is shown in Fig. 1 [18–20]. It can be seen that all the floc size distributions show a unimodal characteristic. The distribution progresses rapidly to the larger floc size in the rapid mixing step with mixing intensity of 1000 s^{-1} for 0.5 min. In the slow mixing step, at a mixing intensity of 60 s^{-1}, the distributions become coarser and reach the largest floc size at 10 min. After this time, continued slow mixing reverses the process and the distribution shifts back to the smaller size [18–20]. This result indicated that *sweep* flocs are produced at high formation rate in the rapid mixing step as also noted by Amirtharajah and Mill [85]. The growth of the *sweep* floc is continuously increased in the slow mixing step up until the floc breakage dominates. It is intuitive that the *sweep* flocs are weak and prone to breakage. For this reason the rapid/slow mixing scheme is always employed in any *SF* [18–20].

The variation of floc size distributions as a function of a combination of rapid/slow mixing time is shown in the cumulative percent finer versus floc size curves in Fig. 2 [18–20]. Interestingly, the *S*-shape curves are shifted in a parallel manner with the mixing times. The parallel shift of these curves implies the development of the so-called self-preserving size distributions. To confirm the self-preserving size form, the normalised curve of cumulative percent finer as a function of dimensionless floc size (d/d_{50}) is plotted and shown in Fig. 3 [18–20]. It can be seen that all the curves are lumped into one single curve. The dimensionless d/d_{50} is not a function of mixing times. This confirmation leads to the conclusion that the *SF* in this study indeed produces self-preserving size distributions [18–20]. The self-preserving size distribution obtained during flocculation has been observed by many researchers [86–91].

In the absence of uniform size distribution of particles, the number size distribution of aquatic suspensions is often found to follow some form of a mathematical function, for example, power function [92]. If the volumetric distributions of floc size progress with the same function during *SF* as shown in Fig. 2, it is possible to use some parameters of this function to construct a model and predict the flocculating performance [18–20]. The construction of the model from the number distributions of floc size to evaluate the effects of various raw water characteristics and design parameters on the performance of water treatment plant has been developed at length by Lawler et al. [92].

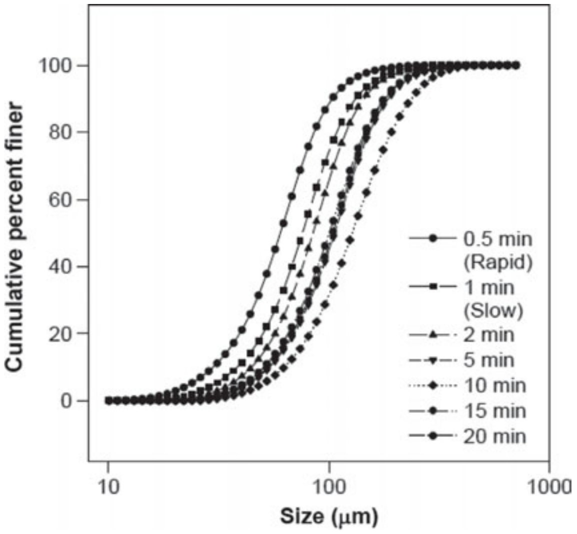

Fig. 2. The variation of floc size distributions (cumulative percent finer against size) as a function of rapid/slow mixing intensity and time for 0.01 wt.% kaolin suspension, flocculated at pH 7 with 50 mg l^{-1} ferric chloride, and rapid-mixed at 1000 s^{-1} for 0.5 min followed by slow mixing at 60 s^{-1} for varying times in the 800 ml standard mixing tank [18–20].

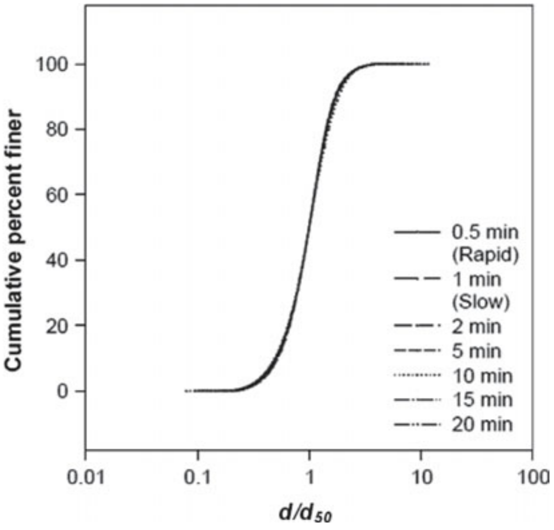

Fig. 3. Normalised curves of cumulative percent finer as a function of dimensionless floc size (d/d_{50}) with various mixing intensities and times for 0.01 wt.% kaolin suspension, flocculated at pH 7 with 50 mg l^{-1} ferric chloride, and rapid-mixed at 1000 s^{-1} for 0.5 min followed by slow mixing at 60 s^{-1} for varying times in the 800 ml standard mixing tank [18–20].

Due to the lack of the coagulation theory of particles with continuous size distribution, the early flocculation models can be obtained empirically from laboratory or pilot plant studies [18–20]. By verifying of the existence of the self-preserving size distribution, it is possible to simplify the classic Smoluchowski [93] population balance model of the particles with broad size distribution. Hogg et al. [94], for example, derived the simplified population balance model for simultaneous floc growth and breakage by assuming that the self-preserving size distribution occurs in a flocculation process. This simplified model was appropriate for measuring the flocculating performance of fine-particle suspensions by continuous addition of polymer to an agitated suspension. Together with an expression, relating the effects of process variables on the model parameters: agglomeration and breakage rate constants, the model can be used to establish criteria for equipment selection and process design [18–20].

Rattanakawin [18–20] concluded that volumetric floc size distribution obtained from light scattering technique is very useful to study the *SF* of kaolin suspensions [18–20]. By monitoring the distributions of floc size, it is possible to distinguish clearly among floc formation, growth and breakage. The floc size distribution maintains the same *S*-shape characteristic over the range of rapid/slow mixing times. Parameters from the function may be used to construct a mathematical model and predict the flocculating performance. Therefore further construction of the model from the distribution is suggested. The parallel shift of the *S*-shape curves indicates that self-preserving size distribution occurred in this *SF*. The finding of the self-similar distribution may be used to simplify the derivation of standard population balance model [18–20].

4. Breakage and re-growth of flocs

According to Yu et al. [95], the efficiency of C/F can be significantly improved through flocs breakage and re-growth under appropriate conditions. These authors examined the formation, breakage and re-growth of flocs formed by kaolin or the mixture of kaolin and humic acid (HA) with alum or polyaluminum chloride (PACl). The reversibility and mechanism in the process of flocs breakage and re-growth were explored through conventional jar test procedure and continuous optical monitoring (PDA). There was full re-growth of flocs in kaolin water coagulated in CN (alum or PACl), which indicated a significant reversibility of flocs break-up process (Fig. 4); the process displayed a distinct irreversibility in *SF*. The addition of HA weakened the reversibility, and alum showed better shear resistance than PACl. The residual turbidity after breakage and re-growth was lower than before breakage when CN dominates the coagulate mechanism, but the result was reverse in *SF* [95]. Table 5 summarises the mechanism of the formation, breakage, and re-growth of flocs [95].

In the same perspective, Wang et al. [96,97] investigated the formation, breakage and re-formation of flocs.

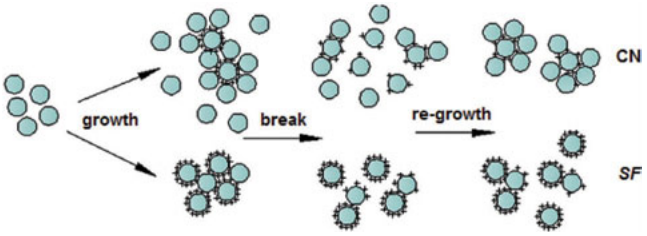

Fig. 4. Mechanism of flocs formation, breakage and re-growth in CN and *SF* [95].

These researchers tested different Al coagulants—conventional Al salt ($AlCl_3$), polyaluminum chloride (PAC-1) and the purified polyaluminum chloride (PAC-2) – for the coagulation of HA. The results showed the properties of HA flocs depend on which species of aluminum used. The monomeric and dimeric aluminum species formed the largest and strongest HA flocs with longest growth time. The HA flocs formed by $Al_{13}O_4(OH)_{24}^{7+}$ (Al_{13}) is the smallest and weakest. The properties of HA flocs made it possible to investigate the relationship between the flocs growth process and aluminum species [96,97].

Similar work was done by Yu et al. [98] on the effect of additional coagulant on the re-growth of alum–kaolin flocs. More recently, Yu et al. [99] examined the role of mixing conditions on floc growth, breakage and re-growth. Finally, a good review of floc strength and breakage has been presented by Jarvis et al. [100] who concluded that smaller flocs tend to have greater strength

Table 5
The mechanism of formation, breakage, and re-growth of flocs [95]

Formation, breakage, and re-growth of flocs	
1.	During the break-up process, the newly exposed surfaces of aggregates may have a net negative, positive or neutral charge and this may depend on the nature of the original coagulation process.
2.	As shown in Fig. 4, when CN dominates the coagulant mechanism, some of the particles in water, adsorb Al^{3+} or its variation unevenly, contain positive charge and flocculate with negative particles. There also exist many particles that cannot congregate with other particles, and they can be therefore considered as residual turbidity. Normally, the flocs formed by CN could be more compact in structure and surface-erosion breakage model would happen. Also the broken flocs will coagulate with the residual particles.
3.	When *SF* dominates the coagulate mechanism, almost all the particles will trap positive charge, while only a small portion of particles trap few positive charges and remain negative charged. These two species of particles can coagulate sufficiently with each other. The flocs, with loose and branchy structure which were formed by sweeping mechanism, showed large fragment breakage model. The broken flocs which contain positive charge will yield repulsive force between particles and reduce the efficiency of collision. That is the reason why the kaolin particles can re-grow fully in CN, but cannot in sweep condition.
4.	When HA was added into the kaolin water, kaolin particles would adsorb some of the HA. With some coagulant added, flocs were formed by HA and particles. The HA traps charges and works as polymers, which interact with charged particles by bridging flocculation, CN or other interactions. There may exist chemical bonds in the flocs because of HA and coagulant. After the breakage, chemical bonds are broken and collision efficiency decreases. The collision efficiency of small flocs would decrease with HA added. So if the HA is higher than a threshold, its reversibility decreases disregarding the coagulation mechanism in CN or *SF*.

than larger flocs. The same conclusion is made by Liu and Glasgow [101] who added that effective separation by sedimentation is best achieved by dense, compact flocs characterised by reduced interparticle distances.

5. Chemical bonds on the surface of flocs

Recently, Xiao et al. [102] employed the particle image velocimetry (PIV) system to investigate the flocculation dynamics for different flocculants in different model waters. With the PIV and image analysis, the change in particle size distribution could be well recorded. Using the sequence of flocculation, shear breakage and re-flocculation on a jar-test device together with the PIV system, the rate of floc formation, the strength of the flocs, the recovery of broken flocs, and the morphological and structural features of the flocs were characterised. The results indicated that the adsorption of HA on the particle will stabilise the particles, hence hinder the flocculation process. *SF* using a higher chemical coagulant dosage was an effective means of process enhancement for the removal of particulates and associated organic matter. The dynamics of aggregation–breakager–re-flocculation process was characterised by particle size distribution (PSD) measurement with PIV setup. The particle strength and reversibility capability were examined. Strength index showed the HA flocs have comparable strength, while recovery index indicated a less recovery capability with the increasing of HA concentration after exposure to a higher shear, especially for ferric HA flocs [102]. What is interesting here is that Xiao et al. [102] concluded that the bonds holding HA flocs together are not purely physical bonds given the limited re-growth seen.

On the other hand, Laurent et al. [103] investigated the flocs surface functional groups evolutions due to an ultrasonic treatment in respect with the mechanisms involved during sonication. They studied the activated sludge surface functional groups changes after treatment of a sample at different ultrasonic specific energies. Sludge functionality was qualitatively assessed by recording the infrared (FT-IR) spectra of centrifugation pellets. Potentiometric titration coupled with proton surface complexation modeling was used to assess the nature and quantity of ionisable functional groups present at the floc surface and in the aqueous phase. These evolutions were linked to changes of both mixed liquor biochemical composition (TSS, VSS, COD, proteins, humic like substances, polysaccharides) and physical properties (floc size and settleability). Observations carried out showed that activated sludge flocs were essentially mechanically disintegrated by ultrasonic waves: the nature of chemical bonds observed by FT-IR did not shift after ultrasonic treatment. Moreover, the total number of ionisable functional groups measured by potentiometric titrations remained constant during sonication. However, due to the solubilisation of organic components induced by cavitation process, the corresponding ionisable functional groups (carboxyl, hydroxyl, amine) were transferred from particulate to soluble fraction. Moreover, due to the variable amount of proteins, humic like substances and polysaccharides solubilised, the relative contributions of carboxyl, hydroxyl and amine groups varied at floc surface [103].

Moreover, Wen et al. [104] have efficiently removed the terephthalic acid (TA), which is a main component in alkali-decrement wastewater, using ferric chloride in high pH solutions. About 90% removal of TA is achieved at pH between 8 and 11. Especially, the removal reached 94.3% at pH 11. However, as the pH increased from pH 12 and 13, the low removal of TA were found. The increasing ferric chloride dosage had a dramatic positive impact on the achieved removal of TA. Further increase in the ferric chloride dosage did not produce better removal rate. The increase of TA concentration also led to the increase of ferric chloride dosage in order to get the same removal of TA. There was approximately a negative linear relationship between TA concentration and removal of TA. Compared with other coagulants, it can be seen that ferric chloride is more effective in a high pH solution and the amount of ferric chloride required is also less as compared with aluminum chloride, magnesium chloride and calcium chloride. Wen et al. [104] clearly showed that terephthalate anions strongly binds to positive $Fe(OH)_3$ flocs and forms insoluble complexes, probably through a mechanism involving electrostatic attraction. The electrostatic attraction may be particularly useful means of purifying wastewater in high pH solutions [104].

As mentioned above, the results obtained by Wen et al. [104] indicate that a form of CN exists between the terephthalate anions and the positive $Fe(OH)_3$ flocs (i.e., *sweep* flocs) forming insoluble complexes. To more elucidate the significance of the chemical properties of the flocs, Droppo et al. [105] worked on the effects of chemical amendments on aquatic floc structure, settling and strength.

Furthermore, Claesson et al. [106] measured the forces acting between negatively charged mica surfaces in the presence of some different cationic polyelectrolytes using a surface force apparatus. The different polyelectrolytes used have between 10 and 100% of the monomers charged. Particular emphasis has been given to the forces acting between the polyelectrolyte-coated surfaces when the ionic strength of the solution is low, that is, when electrostatic forces predominate the interaction between the surface and the polyelectrolyte. Under these conditions the most highly charged polyelectrolytes adsorb in a very flat conformation and only a weak recharging is observed even at polyelectrolyte concentrations considerably above that needed to neutralise the mica surface charge. The floc structures formed in the presence of various polyelectrolytes can to a large extent be rationalised by considering the interactions measured in the surface force apparatus provided that the difference in charge density of the mica surface and the latex surface is kept in mind [106]. Further, Xu et al. [107], who worked similarly as Wang et al. [96,97], added that the flocs generated in acidic conditions were stronger and more recoverable than those generated in alkaline conditions no matter which coagulant was used.

Finally, Zhao et al. [108] studied the growth, breakage and re-growth nature of flocs formed by titanium tetrachloride ($TiCl_4$) and PACl. Results indicated that the responses of flocs to different operating parameters depend on the coagulant used. The ability of floc to resist breakage decreased with the increase of shear force and breakage period. Floc strength properties were also measured in response to increasing shear force, with the results suggesting that the order of floc strength was $TiCl_4 > PACl$. Floc regrowth of the two coagulants after exposure to high shear was limited, and flocs formed by $TiCl_4$ displayed weaker recoverability. The flocs generated in acid conditions were more recoverable than those generated in alkaline conditions no matter which coagulant was used [108].

It seems that the results obtained by Zhao et al. [108] are opposite at those obtained by Xu et al. [107].

6. Conclusions

The following conclusions are drawn:

1. Colloids are very small particles that have extremely large surface area. They range in size from 0.001 to 10 μm resulting in a very small ratio of mass to surface area. The consequence of this smallness in size and mass and largeness in surface area is that in colloidal suspensions: (1) gravitational effects are negligible, and (2) surface phenomena predominate. Hence, during C/F process, colloids are removed by CN and *SF* mechanisms which act on the anionic charge of the colloid by its neutralisation prior to its removal by sedimentation/filtration.
2. *Sweep* flocs can be described as large aggregates of $Al(OH)_3/Fe(OH)_3$ that are formed when Al/Fe salt is added to water. It has been found that *sweep* flocs formed in any conventional water treatment process are positively charged as the PZC of $Al(OH)_3$ and $Fe(OH)_3$ is ≈8.5. The colloids of clay minerals abundantly found in the water are negatively charged; for example, the PZC of silica and kaolin is ≈2 and 4, respectively. As a result, the colloidal particles are electrostatically attached to the *sweep* flocs in the neutral pH water.
3. It was proved that breaking and re-growing the flocs may be an effective way to reduce coagulant dosage, and the decanted flocs from treated water with high dosage of coagulant can be added into raw water as coagulant.
4. The flocs generated in acidic conditions were stronger and more recoverable than those generated in alkaline conditions no matter which coagulant was used. An opposite conclusion was obtained by other workers.
5. Even if researches have greatly elucidated the growth, breaking and the re-growth of flocs, more deep understandings of CN and *SF* mechanisms remain to be achieved in order to well optimise the C/F process at the nano level.

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