

Brownian Motion and Coagulation Process

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Abstract: This review discusses the Brownian motion and coagulation/flocculation (C/F) in water/wastewater treatment. In water/wastewater treatment processes, pertinent questions relating to Brownian motion and C/F are often asked. Some of these questions are: Brownian motion and molecular agitation are favourable or not to separation processes? As high salinity (seawater) decreases disorder, increasing surface water salinity would be a convenient water treatment process or not? The processes of C/F are used to remove dissolved substances and colloids from water in order to assure efficient settling.

Keywords: Colloid, Brownian Motion, Coagulation, Flocculation, Water/Wastewater Treatment

1. Introduction

In water treatment engineering, some questions are asked: Brownian motion and molecular agitation are favourable or not to separation processes? After coagulation/flocculation (C/F) and settling, two separate phases (limpid water + mud) are present, disorder is minimised or not? Freezing decreases disorder or not? Freezing treats or not water? High salinity (seawater) decreases disorder or not? Increasing surface water salinity would be a convenient water treatment process or not? In other words, this review tries to find links between Brownian motion and coagulation.

The processes of C/F are used to remove dissolved substances and colloids from water in order to assure efficient settling [1,2].

2. Colloids

Colloidal particles are defined as aggregates of atoms and/or molecules; their density is near to water density (~1) and their diameters are small enough that gravity is not able to settle them. Consequently, they remain in suspension [3]; this

is why they are called stable dispersions [4]. Their stability originates from the reciprocal repulsion between colloids [5]. However, their stability may be disturbed by applying some chemical products. Coagulation is defined as the key unit process where such reactants are injected in order to destabilise the colloids repulsion, thus pushing them to form bonds together [6]. This chemical process is usually encountered before the unit operation of flocculation [7]. The colloids are frequently responsible of the turbidity and sometimes of the colour that make water undrinkable; consequently, these fine particles should be completely eliminated from water [8].

This section reviews some prerequisite topics, which are indispensable in the comprehension of C/F process, including behaviour and stability of colloids and Zeta potential [8,9].

2.1. Colloid Behaviour

In its great fraction, the suspended solids in surface waters are constituted with materials, such as silica, with density of 2.65 [10]. As their sizes are ranged from 0.1 to 2 mm, they may be easily removed from water by settling. On the other hand, when their diameter is less than 10^{-5} mm (10 μ m), they

require sometimes a year to settle only 1 mm. Moreover, when a particle is in this size range, we may assist to the appearance of the turbidity and/or colour of water, rendering the water unpotable. The elimination of colloids by decantation is always applicable in the case if their settling velocity is relatively rapid, i.e., some meters per hour. For these reasons, C/F process acts by disturbing the reciprocal repulsions between colloids pushing them to form bonds together and constitute agglomerates for efficient decantation [6]. Colloids may be classified in the diameter interval of nm to μm . Colloids are considered as agglomerates of some hundreds of atoms and/or molecules, even if a distinguished molecule, e.g., in the case of proteins, is big enough to be classified as a colloidal particle [4,8].

A colloidal suspension is constituted with two phases: (1) the *dispersed phase*, or the *solute*, and (2) the *dispersion medium*, or the *solvent* [4]. Each phase can possess all the three states of matter, i.e., solid, liquid, and gas. As an illustration, we may have the dispersion medium as a liquid, and the dispersed phase as a solid. This suspension is known as a *liquid sol*. Sometimes, the dispersion medium is a gas and the dispersed phase is a solid. This system is known as a *gaseous sol*, and the best illustrations are dust and smoke. Table 1 presents the various types of colloidal constitutions. In the C/F

process, in the case of water/wastewater, attention will be accorded to the solid being dissociated in water [6,11]. Sols may be classified as *lyophilic* or *lyophobic*; the first ones are those that constitute bonds with the solvent and the second ones are those that do not constitute bonds with the solvent. If the solvent is water, lyophilic and lyophobic sols are, respectively, named *hydrophilic* and *hydrophobic sols*. The affinity of the *hydrophilic sols* for water is attributed to polar functional groups that are found on their surfaces. These groups include such polar groups as $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2$. They are, respectively, named the *hydroxyl*, *carboxylic*, and *amine* groups. As established, the functional polar groups are found sticking out from the surface of the particle. Due to the affinity of these groups for water, the water is attached on the surface. This water is named *fixed water* and is attached on the surface and moves with the colloid. On the other hand, the *hydrophobic colloidal particles* do not have affinity for water; consequently, they do not contain any attached water. Habitually, inorganic colloidal particles are hydrophobic, and organic ones are hydrophilic [4]. As an illustration of an inorganic colloid is the case of clay colloids that produce turbidity in water, and an illustration of an organic colloidal particle is the colloids in domestic sewage [8].

Table 1. Types of colloids [8].

Dispersion Medium	Dispersed Phase	Common Name	Example
Solid	Solid	Solid sol	Coloured glass and gems, some alloys
Solid	Liquid	Solid emulsion	Jelly, gel, opal (SiO_2 and H_2O), pearl (CaCO_3 and H_2O)
Solid	Gas	None	Pumice, floating soap
Liquid	Solid	Liquid sol	Turbidity in water, starch suspension, ink, paint, milk of magnesia
Liquid	Gas	Foam	Whipped cream, beaten egg whites
Gas	Solid	Gaseous sol	Dust, smoke
Gas	Liquid	Gaseous emulsion	Mist, fog, cloud, spray
Gas	Gas	Not applicable	None

2.2. Zeta Potential

The repulsive property of colloids generates from the electrical forces that they possess [4]. At a near point from the colloid surface, the force is significant. It decreases near to zero at a high gap from the colloid. The electrical forces are generated because of the charges that the colloids have at their surfaces. These charges, named *primary charges*, are generated following one or both of two processes: (1) the rupture of the polar groups and (2) preferential adsorption of ions from water. The primary charges on hydrophobic colloids are attributed to preferential adsorption of ions from water [8].

The primary charges, on hydrophilic colloidal particles, are mainly attributed to the polar groups, e.g., the carboxylic and amine groups [4]. The phenomenon monitoring the charges apparition on these types of colloidal particles is shown in Fig. 1. The symbol R shows the colloidal particle entity. The colloidal particle is illustrated at the top of the drawing, without the influence of pH. By a convenient combination of the H^+ and OH^- being introduced to the suspension, the colloidal particle achieves ionisation of carboxylic and the amine groups. At this point, both ionised groups neutralise

each other and the colloid is considered as neutral. This point is well known as the *isoelectric point*, and the related ion of the colloid is named the *zwitter ion*. When pH is augmented by introducing a base, the added OH^- will neutralise the acid extremity of the zwitter ion (i.e., the NH_3^+); the zwitter ion will disappear, and the entire colloidal entity will be negatively charged. The inverse situation is correct if the pH is decreased by the introduction of H^+ ions. The injected H^+ ions neutralise the base extremity of the zwitter ion (the COO^-); the zwitter ion disappears, and the entire colloidal entity will be positively charged. From this interpretation, a hydrophilic colloid can reach a primary charge of either negative or positive as a function of the pH [12]. The first electrical charges on a colloidal particle which, as we have established, could either be classified as positive or negative, attract ions of opposite charges from the suspension. These ions with opposite charges are named *counterions*. This is phenomenon shown in Fig. 2. When the primary charges are enough large, the attracted counterions can constitute a compact layer surrounding the first charges. This layer is named the *Stern layer*. In turn, the counterions have the possibility to attract their own counterions, the *coions* of the primary charges, constituting an additional layer. Because these coions

constitute a continuous distribution of ions into the bulk of the suspension, they have tendency to be distributed; moreover, they may constitute a diffused layer. The second layer is well known as the *Gouy layer*. Consequently, the *Stern* and *Gouy* layers constitute an envelope of electric double layer surrounding the first charges. The totality of the electric charges in the Stern layer displaces with the colloidal particle; as a result, this layer is an attached layer. In the case of the

Gouy layer, a fraction of the layer may displace with the colloidal particle by shearing at a *shear plane*. There is a possibility for this layer to shear off out of the boundary of the attached Stern layer evaluated from the surface of the colloidal particle. Consequently, certain variations of the charges in the layer displace with the colloid, at the same time others do not. This plane is shown in Fig. 2 [8].

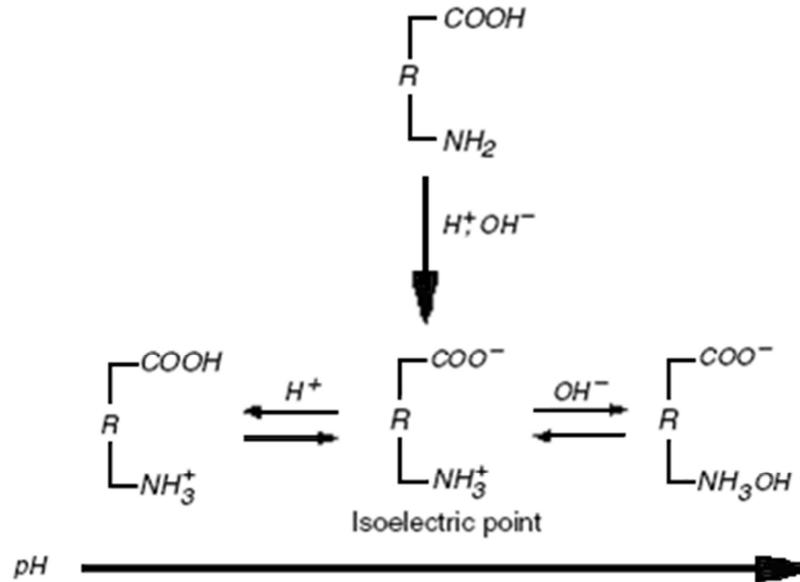


Figure 1. Initial charges of a hydrophilic colloidal particle depending on pH [8].

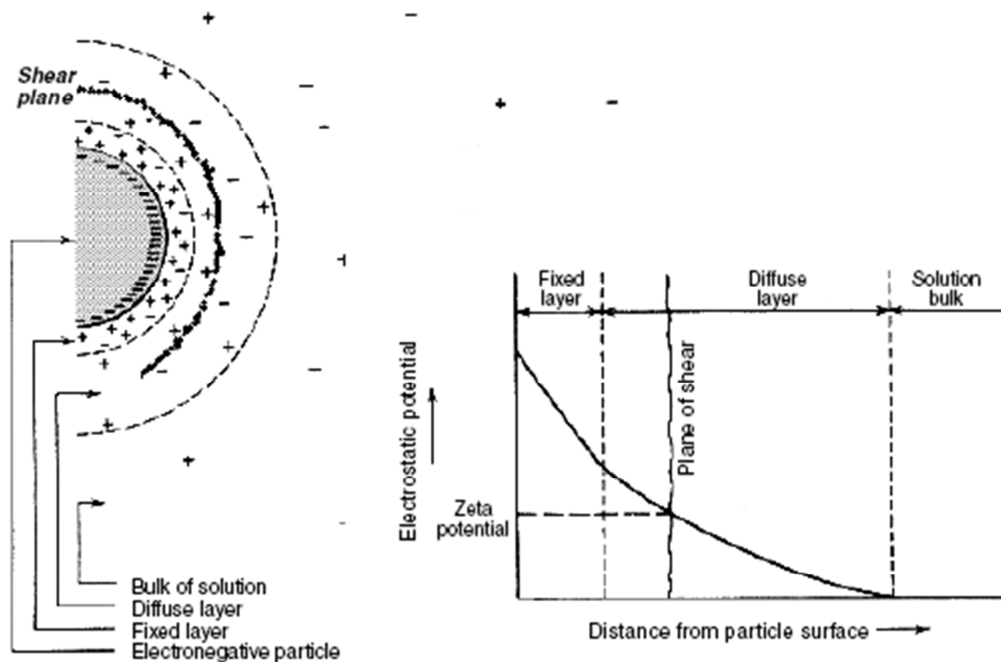


Figure 2. Charged double layer surrounding a (negatively) charged colloidal particle (left) and change of electrostatic potential as a function of distance from colloid surface (right) [8].

The electric charges possess an electrostatic potential. As shown on the right-hand side of Fig. 2, this potential is most important at the colloid surface and decreases to zero at the bulk of the suspension. The potential at a certain point from

the surface at the birth of the shear plane is named the *Zeta potential* [4]. The greater this potential, the more important is the repulsive force and the more stable the colloidal particle [8].

3. Collision Mechanisms

Colloids are brought into contact following certain manners:

- Brownian diffusion (i.e., *perikinetic* agglomeration).
- Fluid motion (i.e., *orthokinetic* agglomeration).
- Differential sedimentation [8,13,14].

These mechanisms are illustrated in Fig. 3. As seen above, all particles in water are subject to random motion as a consequence of their thermal energy. This phenomenon is well known as *Brownian motion*. Due to this fact, collisions between colloids produce *perikinetic aggregation* [15]. It is easy to evaluate the frequency of the created collisions [16]. It is evident that Brownian (perikinetic) agglomeration has not the capacity to conduct to the formation of large aggregates. This is due to the decrease in particle content and the second-order nature of the process. Practically, flocculation processes are frequently performed under conditions where the suspension is under the action of certain form of *shear*, i.e., by stirring or flow [17]. When colloids are transported thanks to suspension, they may produce a great influence on the rate of colloid collision. This phenomenon is named *orthokinetic agglomeration* [15]. In fact, the primary theoretical concept to this phenomenon was the fruit of Smoluchowski's research, at

the same time with his famous study on perikinetic agglomeration [18]. In the case of orthokinetic collisions, Smoluchowski studied the example of spherical particles in *uniform and laminar shear* [16]. Practically, such conditions are not found; however, the simple case constitutes an appropriate basic point. Fig. 4 illustrates the primary model for the Smoluchowski analysis of orthokinetic collision intensities. Two spherical colloids, of various sizes, are fixed in a uniform shear field. This signifies that the velocity of the fluid varies linearly as a function of distance in only one direction, perpendicular to the direction of flow. The rate of variation of fluid velocity in the z -direction is du/dz . This is the *shear rate* and is attributed the symbol G . The centre of one colloid, radius a_j , is assumed to be fixed in a plane where the fluid velocity is zero, and colloids above and below this plane displace along fluid streamlines with various velocities, as a function of their situation. A colloid of radius a_i will *just* be in contact with the central sphere if its centre lies on a streamline at a distance $a_i + a_j$ from the plane where $u = 0$ ($a_i + a_j$ is the *collision radius*, as in the analysis of perikinetic agglomeration) [16]. The totality of colloids at points less than the collision radius will enter in collision with the central sphere, at rates that are function of their concentration and position (and consequently velocity) [14].

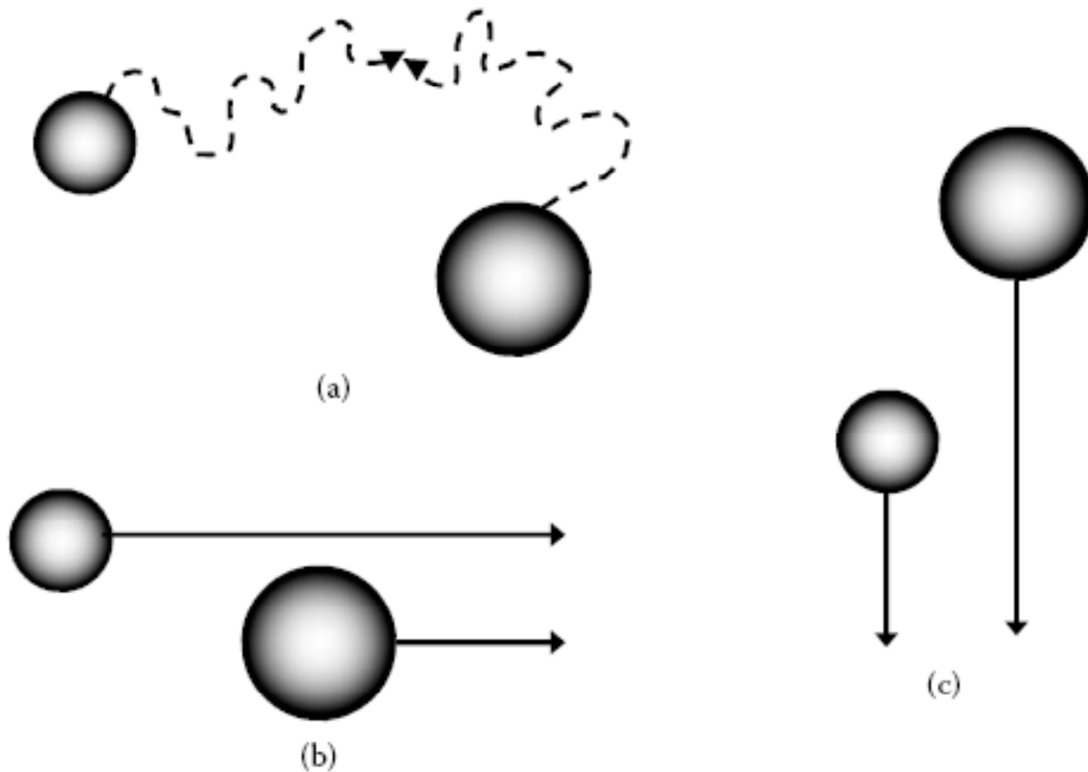


Figure 3. Particle transport conducting to collisions by (a) Brownian diffusion, (b) fluid motion, and (c) differential sedimentation [14].

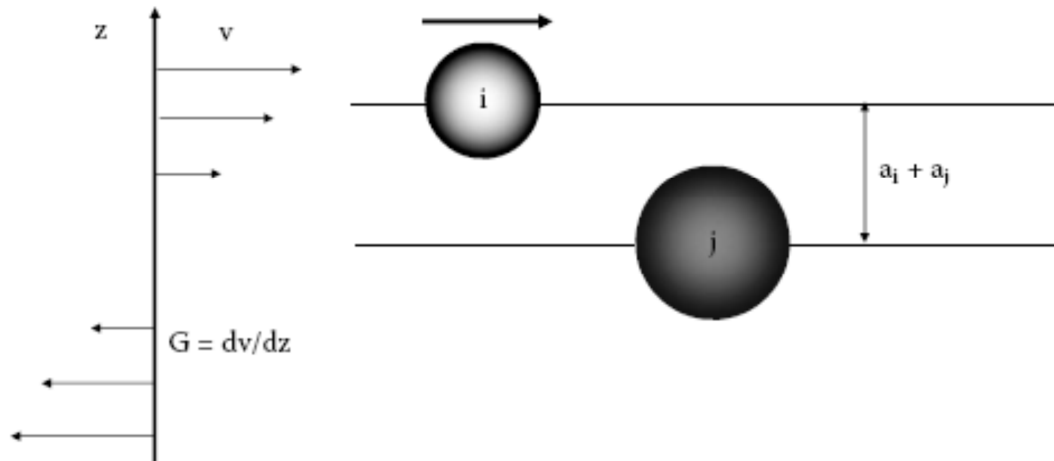


Figure 4. Model for orthokinetic agglomeration in uniform laminar shear [14].

On the other hand, there is an additional significant collision mechanism. This mechanism appears when colloids of different size (or density) are settling in water [15]. Evidently, larger and denser colloids will sediment faster and have the possibility to enter in collision with more slowly settling colloids during their settling [13,14].

4. Coagulation and Flocculation

4.1. Terminology

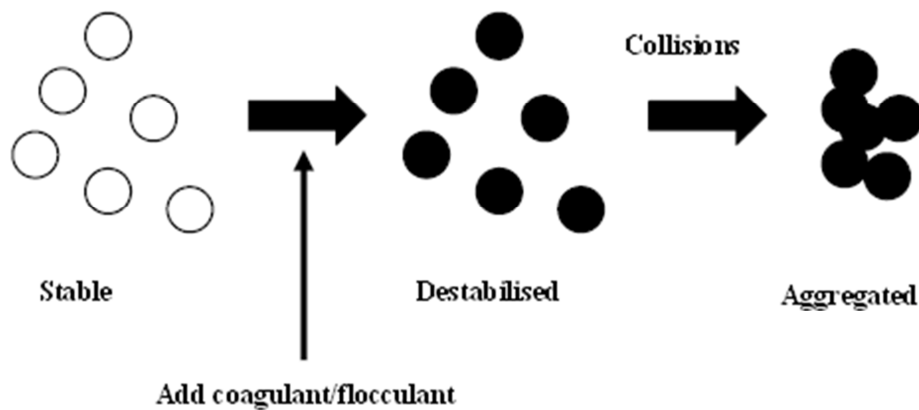


Figure 5. Destabilisation and aggregation of particles [14].

We will discuss the case of stable colloids; their stability is due to their surface charge and consequently electrical double-layer repulsion [22]. In such situation, destabilisation implicates an augmentation in ionic strength or a neutralisation of the colloid charge. Introducing salts to elevate ionic strength is not considered as a convenient choice and additional additives will be utilised, as discussed in the following paragraphs. The destabilisation stage aims to render the *collision efficiency*, α , as great as possible, in ideal conditions with $\alpha = 1$, until the point that every collision conducts to agglomeration [15]. In the case where colloids are completely destabilised, so that $\alpha = 1$, collisions are indispensable if agglomerates have to be constituted [16]. The colloid collision frequency is largely function of the particle

4.1.1. “Coagulation” and “Flocculation”

This section concerns processes in which suspended colloids constitute bigger agglomerates. These agglomerates can be eliminated with more efficiency by physical separation processes such as decantation and filtration [19-21]. Supposing that the colloids are originally stable, we may have two key steps in the agglomeration process. These fundamental stages are illustrated in Fig. 5:

- Destabilisation of colloids
- Collisions of colloids to build-up agglomerates [14].

content and of the mechanism by which collisions occur. For less concentrated water, where the frequency of the generated collisions may be insignificant, it may be easy for colloids to be completely destabilised but to demonstrate very little aggregation upon acceptable time values [16]. Due to the short-interval characteristic of interactions between particles, it is frequently easy to treat separately the destabilisation and collision phenomena [4]. That is mean that it is usually acceptable to suppose that the frequency of the generated collisions is not disturbed by interactions between colloids [14].

In the following paragraphs, the word “aggregation” will be utilised in a large sense, to significate any phenomenon whereby colloids aggregate together [23]. We may ask the

question of other terms, particularly the largely employed words, i.e., *coagulation* and *flocculation* [24]. However, there is no wide acceptance concerning the manner, by which such words have to be utilised. Moreover, we may find at least two largely used conventions [14].

It is frequent to limit the word *coagulation* to situations where colloids are destabilised by salts or by charge neutralisation (CN) and the agglomerates (*coagula*) have tendency to be small and dense [25]. *Flocculation* is consequently limited to the examples in which polymer bridging is the key stage, agglomerates have tendency to become bigger, and more open structurally [26]. Due to the fractal nature of aggregates, it is frequent that bigger structures have tendency to be more open and less dense [27]. Therefore, the differentiation between small, compact coagula and larger, less dense flocs is an unavoidable result of the stronger interparticle binding in the case of polymers, conducting to larger agglomerates [17]. An additional complication is that *flocculation* is, in certain conditions, applied to situations where agglomeration produces in a *secondary minimum* [4]. An additional quite different adoption is frequently utilised in the field of water/wastewater technology [6]. Following this convention, *coagulation* is related to destabilisation, by the injection of convenient chemicals, and *flocculation* is related to the generation of agglomerates, frequently by certain form of fluid movement (i.e., orthokinetic aggregation) [28]. These are related to the two steps illustrated in Fig. 5 and could be considered as chemical and physical characteristics of the agglomeration phenomenon [14].

4.1.2. Destabilising Agents

Due to the first distinction established from *coagulation* and *flocculation*, the chemical products utilised to produce destabilisation of colloids may be named *coagulants* or *flocculants*, as a function of their manner of introduction and mechanism [29]. Consequently, coagulants would be inorganic salts, including those containing specifically adsorbing counterions, and flocculants would be long-chain polymers, which implicate bridging interactions [30]. Even if there are greatly several different types of destabilising chemicals, the wide proportion of those utilised practically are classified in just two categories:

- Hydrolysing metal coagulants
- Polymeric flocculants [31,32].

The type of these chemicals and their mechanism will be reviewed in the following sections [14].

4.2. Hydrolysing Metal Coagulants

The most largely utilised coagulants are based on aluminium and ferric salts, such as aluminium sulphate ("alum") and ferric chloride [33]. Initially, it was assumed that their mechanism was a consequence of the trivalent nature of the metals, producing Al^{3+} and Fe^{3+} ions in suspension, which are supposed to be very efficient in destabilising negatively charged particles [5]. In fact, this is a largely oversimplified consideration due to the fact that trivalent metal ions are easily *hydrolysed* in water, which has an important influence on their

action as coagulants [14].

4.2.1. Hydrolysis of Metal Cations

In certain conditions, metal ions in solution are found as simple hydrated cations. This is the situation for alkali metal ions such as Na^+ and K^+ . Due to the polar nature of water, such cations are *hydrated* at a certain level, which signifies they are surrounded by some water molecules fixed by electrostatic attraction between the positive metal ion and the negative (oxygen) extremities of the water molecules. It is acceptable to resonate in matter of a *primary hydration shell*, where water molecules are directly related to the central metal ion and more strongly fixed water in a secondary hydration shell. In the case of the trivalent metal ions Al^{3+} and Fe^{3+} , it is established that the primary hydration shell is constituted of six water molecules in octahedral coordination (see Fig. 6 (a)). Due to the elevated positive charge on the central metal ion, electrons tend to be drawn in the direction of the metal from the water molecules, and this may conduct to the liberation of H^+ leaving a hydroxyl group fixed and a decreased positive charge for the metal, as illustrated in Fig. 6 (b). Since the phenomenon essentially implicates the splitting of water molecules, it is named *hydrolysis*. Since hydrolysis produces the liberation of H^+ into water, it is strongly dependent of pH. Indeed, elevated pH values favour dissociation and vice versa. Moreover, as each proton is liberated, the reducing positive charge renders additional dissociation more complicated. Consequently, with augmenting pH there is a sequence of hydrolysis equilibria, which can be presented as follows [14]:

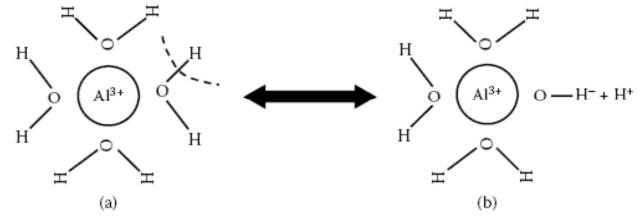
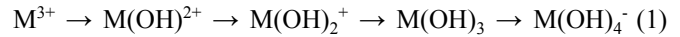
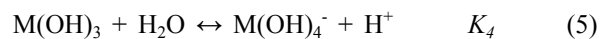
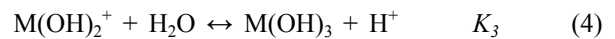
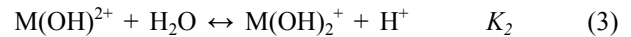
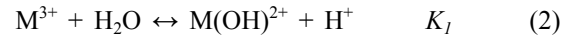


Figure 6. Hydrolysis of Al^{3+} [(a) hydrated aluminium cation, only 4 of 6 H_2O molecules shown, (b) after release of H^+ to form $Al(OH)^{2+}$] [14].

For convenience, H_2O molecules, in the hydration envelop, are not presented. Each of the steps in the hydrolysis phenomenon has a convenient equilibrium constant [14]:



These are defined in the classical method, so that in the situation of K_2 , for example:

$$K_2 = \frac{[M(OH)_2^+][H^+]}{[M(OH)^{2+}]} \quad (6)$$

where square brackets represent molar concentrations of the different species [14].

For Al and Fe(III), the uncharged hydroxide, $M(OH)_3$, has too poor solubility in water and is possibly to constitute a precipitate upon a certain interval of pH. This precipitation is crucial in the mechanism of hydrolysing metal coagulants. As well as the equilibrium constants listed earlier, a solubility constant for the metal hydroxide is also required, considering the following dissociation of the solid phase, $M(OH)_{3(s)}$:



$$K_s = [M^{3+}][OH^-]^3 \quad (8)$$

If correct equilibrium were achieved, consequently the convenient solubility constants would be those for the stable crystalline forms such as gibbsite and goethite, in the case of Al and Fe, respectively. On the other hand, these are habitually constituted slowly (usually weeks or months). Considering the point of view of coagulation process, it is much more important to deal with the solubility constants (K_{sam}) of the amorphous precipitates that generate originally. However, these values are affected with some uncertainty and only evaluated values can be presented. They are frequently at least 100-fold bigger than values for the corresponding crystalline solids; consequently, the amorphous material is soluble. Table 2 presents certain values for the hydrolysis and solubility constants for Al and Fe(III) species in water at 25°C and at zero ionic strength; consequently, they are convenient for low salt concentrations, typical of many natural waters. The constants are shown in the conventional pK form (where $pK = -\log_{10}K$). Using these pK values, it is easy to evaluate, as a function of pH, the concentrations of the various dissolved hydrolysis products in equilibrium with the amorphous hydroxide precipitate. Due to uncertainties over the solubility constants for the amorphous precipitates, the results may not be very accurate, but they present a helpful indication of the relative significance of the different species over an interval of pH values. Fig. 7 is a *speciation* diagram illustrating the results of such evaluations for Al and Fe(III), considering data

in Table 2. The total content of dissolved species, in equilibrium with the solid form, is really the solubility of the metal at a certain value of pH. From Fig. 7, it is obvious that there is a certain minimum solubility, which appears near neutral pH, for both metallic forms. It must be noted here that the minimum solubility of Fe(III) is greatly lower than that of Al and that the minimum is widely larger. Moreover, it is clear that, for of Al, the anionic form $Al(OH)_4^-$ (aluminate) is the predominant dissolved species near neutral pH. An additional manner of presenting the speciation values is to plot the mole fraction of each species as a function of the total dissolved quantity in equilibrium with the amorphous hydroxide. This has been performed in Fig. 8 for Al and Fe(III). These results illustrate great gaps between these metals. In the case of Al, the dominant species are Al^{3+} , at low pH (~ 4.5) and the aluminate ion, $Al(OH)_4^-$, at pH values more important than ~ 7 . The intermediate species make only minor roles at pH values in the interval of $\sim 4-6.5$. For Fe(III), the different species are found upon a larger pH interval (about 8 units) and each hydrolysis product is predominant at certain pH values. This is the predicted behaviour for hydrolysis of metal ions. The cause that Al species are “squeezed” into a much narrower pH interval is assumed to be the consequence of a transition from octahedral coordination in $Al^{3+} \cdot 6H_2O$ to the tetrahedral $Al(OH)_4^-$. In the situation of Fe(III), octahedral coordination is fixed throughout. Moreover, it is important to indicate that the *soluble*, uncharged $Fe(OH)_3$ is the dominant dissolved Fe species in the pH interval 7–9 (even if the real content is only $\sim 2 \times 10^{-8}$ M). The corresponding Al species, $Al(OH)_3$, is often a minor dissolved component in *relative* terms, although it is at least 10 times more soluble than $Fe(OH)_3$ [14].

Table 2. Equilibrium constants (pK values) for Al and Fe(III) hydrolysis and solubility of amorphous hydroxides (values for 25°C and zero ionic strength) [14].

	pK_1	pK_2	pK_3	pK_4	pK_{sam}
Al^{3+}	4.95	5.6	6.7	5.6	31.5
Fe^{3+}	2.2	3.5	6	10	38

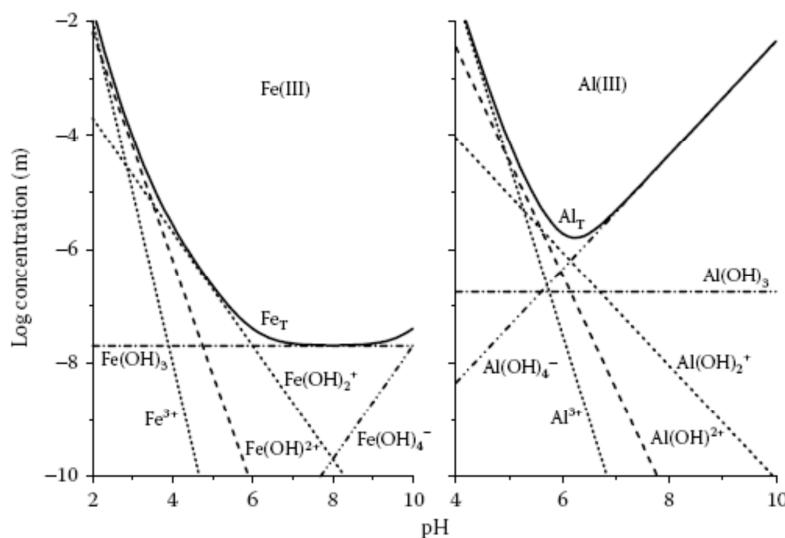


Figure 7. Speciation diagrams for Fe(III) and Al(III) (only monomeric hydrolysis products indicated) [14].

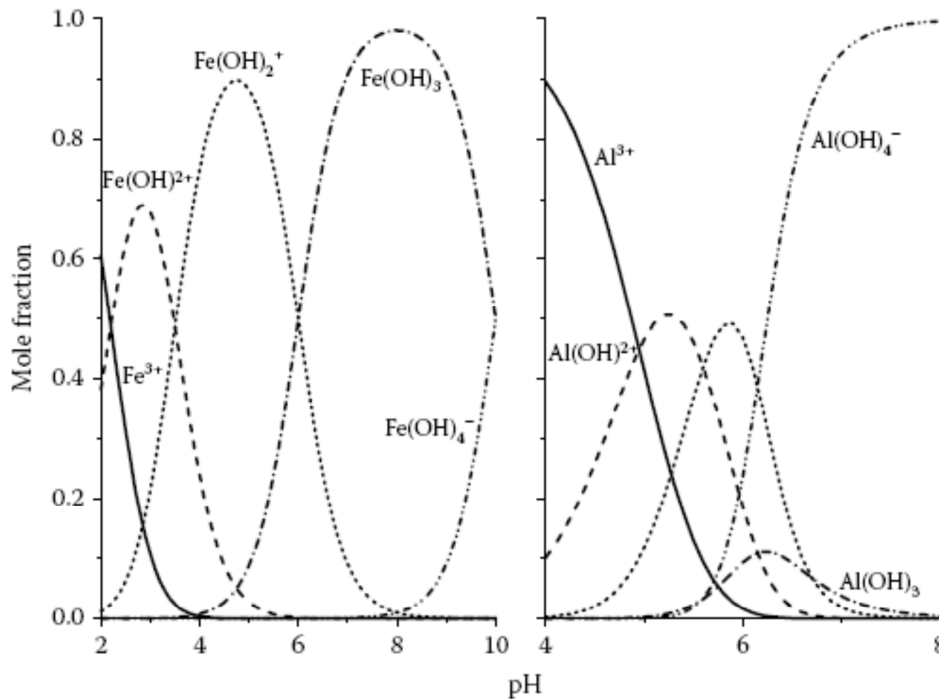


Figure 8. Proportion (mole fraction) of hydrolysed Fe(III) and Al(III) species relative to total soluble metal concentration [14].

Our review so far has not taken into consideration some difficulties. One of these difficulties is the action of different anionic species that may affect hydrolysis equilibria. As an example, it is established that fluoride constitutes strong complexes with Al and this generates most important aluminium solubility than would be expected based on the results in Fig. 8. Another remark is that only *monomeric* hydrolysis products have been taken into account, at the same time, under some conditions, *polynuclear* species can be significant. These constitute the subject of the next section [14].

4.2.2. Polynuclear Hydrolysis Products

In addition to the monomeric hydrolysis products discussed previously, there are several possible *polynuclear* forms that may be significant. For Al these include $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_3(\text{OH})_4^{5+}$ [25], and there are similar forms for Fe(III) [34]. On the other hand, these may be unimportant at the low contents of the metals habitually utilised in coagulation [35]. Practically, only the monomeric products and the hydroxide precipitate may be significant. Polynuclear hydrolysis forms can be produced in some circumstances. The best encountered of these is $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ or “ Al_{13} ,” which can be produced by certain neutralisation of aluminium salt solutions or by many different manners [25]. This tridecamer has the so-named keggin structure, consisting of a central tetrahedral AlO_4^{5-} unit surrounded by 12 Al octahedra with shared extremities. The tetrahedral and octahedral Al sites can be without difficulty distinguished in the ^{27}Al NMR spectrum. Under convenient conditions, Al_{13} constitutes rapidly and essentially irreversibly, remaining stable in aqueous solutions for long time. The tridecamer is assumed present largely in the natural aquatic medium (e.g., in acid forest soil water). Using

coagulation data, additional polynuclear forms, such as the octamer, $\text{Al}_8(\text{OH})_{20}^{4+}$, have been suggested [36]. In fact, there is no clear prove for the octamer and it is not likely to be important practically. There are several commercial chemicals based on prehydrolysed metal salts. For aluminium, a frequent example is the class of materials known as *polyaluminium chloride* (PACl), which may be formed by controlled neutralisation of aluminium chloride solutions [37]. It is possible that several of such chemicals contain significant contents of the tridecamer Al_{13} . For aluminium sulphate, it is hard to produce prehydrolysed species with elevated degrees of neutralisation since sulphate promotes hydroxide precipitation. The presence of small contents of dissolved silica can importantly ameliorate the stability, and the resulting chemical is named *polyaluminosilicate-sulphate* [14]. There are corresponding products containing polymerised iron species [38], even if these are not as largely utilised as PACl [39].

4.2.3. Action of Hydrolysing Coagulants

In fact, there are mainly two significant manners, in which hydrolysing coagulants may destabilise and coagulate particles with negative charge [14]. At low contents and upon appropriate pH values, cationic hydrolysis reactants may adsorb and neutralise the colloid charge, consequently producing destabilisation and coagulation [36]. At more important concentrations of metallic salt, hydroxide precipitation appears and this has a great action — forming the so-called *sweep flocculation* (SF) [40].

4.2.4. Charge Neutralisation (CN) by Adsorbed Species

At low contents of metal, only soluble species are detected (see Fig. 7). It is usually assumed that hydrolysed cationic species such as Al(OH)^{2+} are more easily fixed on negative

surfaces than the free metal ion and so may efficiently neutralise surface charge. In a general manner, CN with aluminium salts appears at low metal contents, habitually of the order of a few micromoles/L at \sim pH 7. It is known that, for many inorganic suspensions at pH 6, the quantity of Al required to neutralise the surface charge is near 5 μ moles per m^2 of particle surface (\sim 130 μg Al per m^2). In fact, even at very low metal contents, the solubility of the amorphous hydroxide may be surmounted. In addition, in the area of neutral pH, cationic hydrolysis reactants represent only a small proportion of the total soluble metal, particularly for Al (Fig. 8). The fact that CN is frequently detected in such examples assumes that the efficient species might be colloidal hydroxide particles [12]. In the case of aluminium hydroxide, the point of zero charge is near pH 8; consequently, the precipitate particles should be positively charged at lower pH values. For ferric hydroxide, the point of zero charge is lower, near pH 7. Moreover, when the bulk solubility is not surmounted, it is likely that certain form of *surface precipitation* will appear because of nucleation at the surface. Really, it is not easy to differentiate between surface precipitation and the fixation of colloidal hydroxide particles that have been precipitated in solution [12]. A combination of these effects may be most possible practically and constitutes the basis of the *precipitation charge neutralisation (PCN)* model, which is shown schematically in Fig. 9. Whatever the precise nature of the charge-neutralising species, they are possible to be apt of charge reversal at higher dosages; in other words, this fact signifies that there will be a characteristic *optimum dosage* at which coagulation is most performant [36]. At higher dosages, particles become positively charged and *re stabilised*. The optimum dosage must be function of the particle concentration; however, practically the value is frequently low. In some cases, the optimum dosage interval can be limited; consequently, precise dosing control is required. Another disadvantage of relying on CN is that, for low particle concentrations, the collision rate and consequently the agglomeration rate will be low, and long periods may be required to give significantly large flocs [17]. Neutralising surface charge, by small-adsorbed species, does nothing to increase the collision rate, even if, of course, the collision *efficiency* can be importantly improved [14].

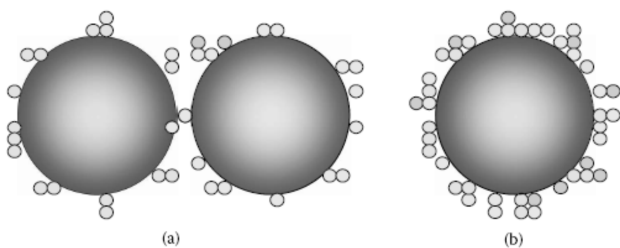


Figure 9. Precipitation charge neutralisation (PCN) model, showing (a) CN and (b) charge reversal (restabilisation) of particles by precipitated hydroxide colloids [14].

Some of the advantages announced for prehydrolysed coagulants are assumed to be a consequence of the presence of highly charged cationic species, such as $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$. The

fact that this ion carries 7 positive charges assumes that it would be very strongly adsorbed on negative surfaces and would be efficient in neutralising particle charge. If we assume that species such as Al_{13} can be more performant in charge neutralisation, it will be difficult to see how, at the optimum dosage, the coagulation rate could be more important than with other adsorbing cationic species [14].

4.2.5. “Sweep” Flocculation

Practically in water/wastewater treatment operations, metal coagulants are injected at dosages much higher than the solubility of the amorphous hydroxide and extensive precipitation appears. For some causes, that are not completely accepted, this can produce much more efficient separation than simple CN. The most possible interpretation is that the initial colloids are fixed, in a certain manner, into the growing hydroxide precipitate and are consequently eliminated from water. This enmeshment of particles is usually assumed as a “sweeping” action — consequently the term “sweep flocculation” (*SF*) [17]. The hydroxide precipitate could be considered as “bridging” particles together and consequently “*SF*” might be the more convenient term from one point of consideration [17,41]. In addition, in water/wastewater treatment, the formation of large hydroxide agglomerates needs some form of agitation; consequently, orthokinetic collisions are important, and this once again encourages the utilisation of the term “flocculation” [42]. The agglomerates constituted because of hydroxide precipitation are largely known as “flocs” [17]. However, it is confusing that the additives utilised are widely known as “coagulants” [14].

Moreover, *SF* usually conducts to faster aggregation than CN and produces stronger and larger flocs [17]. It is easy to understand the reason for the higher aggregation rate [14]. The generation of a hydroxide precipitate produces a big augmentation in the efficient particle concentration and consequently a most important collision rate, following Smoluchowski theory [15]. Hydroxide precipitates are constituted from large numbers of colloids, which constitute very soon after injection [12]. The agglomeration of these colloids produces low-density flocs, with a relatively big volume [23]. Following the theory of orthokinetic aggregation, the rate is directly proportional to the volume fraction of suspended particles, and this can be largely augmented by hydroxide precipitation [43]. This is the principal explanation why *SF* is so much more efficient than CN [44]. The flocs formed under “sweep” conditions are also stronger and consequently grow larger for the same shear conditions [23]. A great advantage of *SF* is the fact that it does not much depend on the nature of the colloids to be eliminated, whether bacteria, clays, oxides, or others [44]. For relatively less concentrated suspensions, the optimum coagulant injection is that which produces the most rapid hydroxide precipitation and is not practically function of the nature and concentration of suspended particles. The large volume associated with hydroxide flocs conducts to an important practical problem — the production of large quantities of sludge that requires to be

removed of in certain mannert [23]. In a water treatment plant, most of the sludge generated is in bonds with metal hydroxide rather than the impurities eliminated from water. Even if there is habitually no important restabilisation in the case of *SF* and consequently no sharp optimum dosage region, overdosing is best avoided to limit the volume of sludge generated [37].

The mechanism of prehydrolysed coagulants, such as PACl, at typical injections also very possibly implicates hydroxide precipitation and *SF*, even if this point has not been widely studied [17,37]. There is prove that the nature of the precipitate differs from that produced with “alum” [14].

4.2.6. Overview

When hydrolysing coagulant is increased to a suspension of negatively charged colloids, four distinct zones are distinguished:

Zone 1: Very low dosage; colloids remain negative and consequently stable,

Zone 2: Dosage sufficient to produce CN and consequently coagulation,

Zone 3: Higher dosage generating charge reversal and restabilisation,

Zone 4: Still higher dosage producing hydroxide precipitation and *SF* [14].

Fig. 10 illustrates the results of a standard *jar test* manner, habitually utilised in water treatment plants. In this manner, a suspension is injected with various quantities of coagulant under standard mixing and decantation conditions [13]. Habitually, there is a brief *rapid mix* time instantaneously after injection. This is followed by a longer time of *slow stirring*

during which flocs may be generated because of orthokinetic aggregation [17]. Then, these flocs are authorised to settle for a standard time, after which a sample of the supernatant water is aspirated and its turbidity is evaluated [23]. This *residual turbidity* produces a good information of the intensity of elimination during decantation and consequently of the efficiency of the C/F process [13]. Fig. 10 illustrates that, at very low coagulant injection, the remaining turbidity is high, showing little or no sedimentation (*Zone 1*). As the dose is elevated, there is a narrow interval (*Zone 2*) where there is an important reduction in remaining turbidity. This is the area of CN by adsorbed species, and it is frequently found that the colloid charge (as measured, for instance, by electrophoretic mobility [45,46] or streaming current [47]) is near zero. At higher injections, remaining turbidity is once again high, showing restabilisation of the colloids because of excess adsorption and charge reversal (*Zone 3*). Finally, at still higher dosages, there is a significant removal in remaining turbidity due to hydroxide precipitation and *SF* (*Zone 4*). It should be indicated that the remaining turbidity in *Zone 4* is lower than that in *Zone 2*, illustrating that *SF* produces larger, faster-settling flocs than those generated by CN [23]. In addition, as mentioned above, there is no restabilisation after *Zone 4*. The behaviour illustrated in Fig. 10 is typical of aluminium salts near pH 7 [17]. With these conditions, the hydroxide precipitate is positively charged. At pH values near to the isoelectric point (around pH 8), *Zone 2* may not be clear and only *SF* is functioning [14].

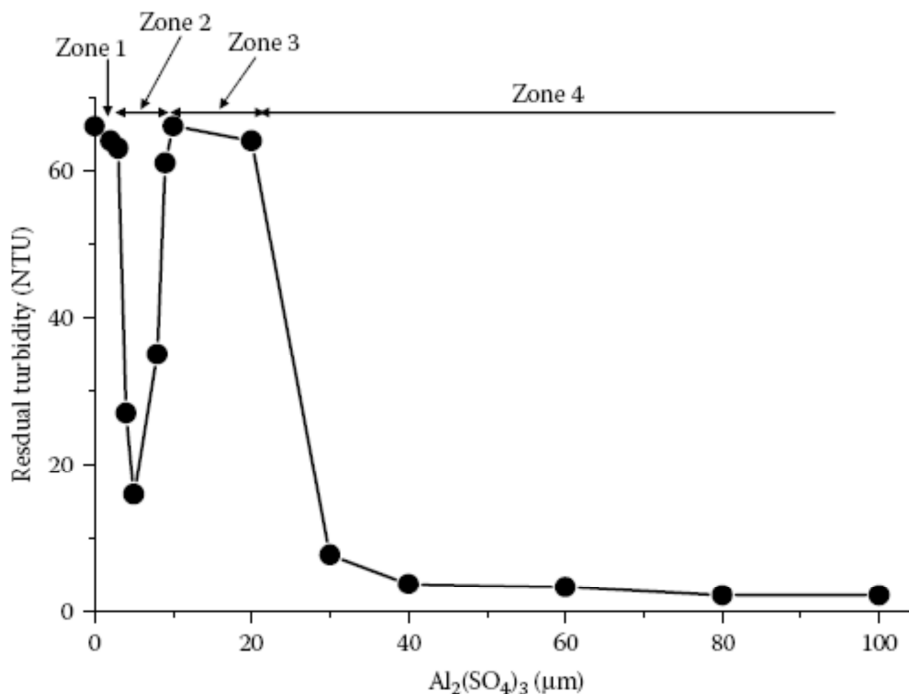


Figure 10. Residual turbidity of kaolin suspensions after coagulation with aluminium sulphate over an interval of doses at pH 7 [14].

4.2.7. Practical Aspects

Many important factors can importantly influence the

efficiency of hydrolysing coagulants [17]. These comprise the effects of different anions and the effect of temperature [45]. Several frequent anions can constitute complexes with

aluminium and iron (III) and can importantly influence hydroxide precipitation. An important illustration is sulphate, which is naturally present in water and may be introduced as aluminium or ferric sulphate during water treatment. Sulphate coordinates moderately strongly with Al, but the important influence is on the precipitation process. On the positive effect of the isoelectric point of aluminium hydroxide (i.e., below about pH 8), sulphate can adsorb on the precipitate and decrease its positive charge. This signifies that the colloidal precipitate can agglomerate more rapidly to generate large hydroxide flocs [14,48].

Temperature has influences that are practically significant [49]. Particularly, at rather low temperatures, conventional aluminium coagulants have tendency to achieve less well for different causes [45]. Some prehydrolysed coagulants seem to be less influenced by low temperatures and are usually proposed for applications in cold areas [45]. Another

advantage of prehydrolysed coagulants, such as PACl, is that, at efficient injections, they form less sludge than simple metal salts [37]. This may be partly attributed to the fact that they can be efficient at lower dosages [50]. Hydroxide flocs, as generated under *SF*, have tendency to be weak and are easily disrupted under high shear conditions [17]. In addition, the breakage can be irreversible at a certain level; consequently, flocs do not easily reform when the shear rate is decreased [14].

4.3. Flocculation Processes

The principal needs for efficient flocculation are as follows:

- Rapid mixing of coagulants (Fig. 11).
- Opportunity for collisions of destabilised particles and so flocculation [14].

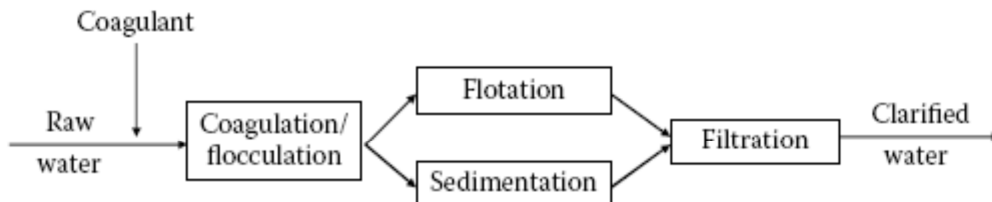


Figure 11. Typical order of processes for particle separation in a water treatment plant [14].

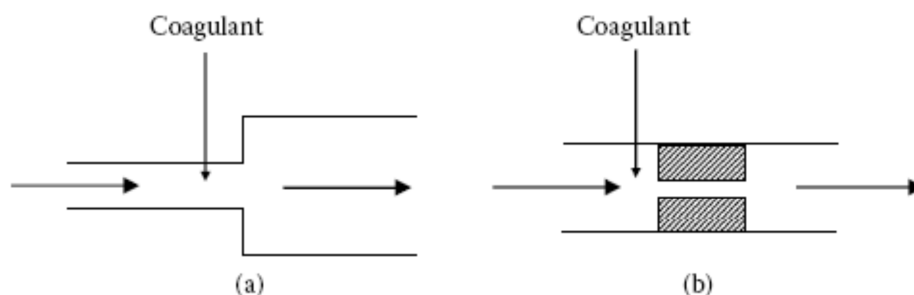


Figure 12. Rapid mixing of coagulant by “in-pipe” methods [(a) widening pipe; (b) narrowing pipe] [14] Even if rapid mixing has long been established to have significant actions on flocculation phenomena and has been examined in some detail, it is possible that many examples of poor efficiency of practical flocculation units can be related to poor mixing [14,28].

For the second step, some form of fluid motion has to be formed, which may be by mechanical stirring or flow (or both) [14,51].

4.3.1. Rapid Mixing

Mixing is necessary to help coagulant addition to disturb stability in the colloidal system [5]. For particles to aggregate they must collide, and mixing develops collision [15]. Brownian movement, the random motion affected to small particles by bombardment by individual water molecules, is always detected as a natural mixing force [52]. Nevertheless, additional mixing energy is required [53]. High intensity mixing, which distributes the coagulant and generates rapid collisions, is most performant [16]. The frequency and number of particle collisions are also significant in coagulation [15]. In a low turbidity water, the introduction of solids such as clay or the recycle of previously settled solids may be indispensable

to augment the number of particle collisions [16]. Rapid mixing (sometimes called “flash mixing”) is required to distribute the coagulant species among the particles in as short a period as possible [53]. In the case of coagulants that adsorb on particles and neutralise their charge, this can be significant [54]. Poor mixing can conduct to local overdosing of coagulant and consequently restabilisation of some particles [53]. For this cause, a short time of intense, turbulent mixing is preferable [55]. The high shear rates related to rapid mixing can also have an important role in the transport of coagulant species and can augment the rate of adsorption [53]. In the case of hydrolysing metal coagulants, upon conditions where hydroxide precipitation and *SF* are significant, the action of rapid mixing is not so obvious [44]. Nevertheless, it is established that hydrolysis rates are rapid and it is possible that rapid mixing conditions have some action in determining the

relative rates of key processes such as adsorption and the formation of precipitates [52]. In principle, rapid mixing requires to be strong but of short period (i.e., few seconds) [53]. Otherwise, the nature of flocs generated subsequently can be influenced [23]. Prolonged times of intense mixing can conduct to the growth of small, compact flocs that grow slowly when the shear rate is decreased [55]. Rapid mixing may be realised in a flow-through stirred tank (a “backmix” reactor), even if this is an inefficient mixing device due to short-circuiting of flow [53]. It is not easy to achieve total and homogeneous distribution of introduced coagulant in a short period (i.e., less than one second) [54]. It is more frequent to inject coagulant at a point where there are turbulent conditions due to flow. This point may be in a channel — for example, where water flows over a weir — or in some kind of “in-pipe” mixer [56]. The latter way can implicate injecting coagulant at a point where the pipe either widens or narrows, as illustrated schematically in Fig. 12 [14].

4.3.2. Floc Formation

Frequently, growth of large flocs needs the application of velocity gradients or shear [57]. The major effects on flocculation rate are the particle (floc) size and content and the effective shear rate, G [58]. Higher shear rates generate improved particle collision rate but may decrease collision efficiency and provoke certain floc breakage [17]. A helpful compromise is a process known as *taper flocculation*, in which the effective shear rate is initially high, producing a rapid flocculation rate, and then progressively decreased so that large flocs can generate [23]. Practically, application of shear implicates the introduction of energy [59]. This can be realised in two manners: *mechanical* or *hydraulic*. Mechanical devices are typified by flow-through stirred tanks of different types, often known as *paddle flocculators* [60]. The paddles may rotate about vertical or horizontal axes, but in all conditions the power input to the water is a function of the drag force on the paddle and the rotation speed. The power introduction to the water could be theoretically evaluated, but it is not too hard to evaluate [14].

4.4. Enhanced Coagulation

Halogenated organics are generated if natural organic matter (NOM) enters in reaction with free chlorine or free bromine [61]. Free chlorine is frequently added to water directly as a primary or secondary disinfectant [62]. Free bromine is produced from the oxidation by chlorine of the bromide ion in the source water. Factors influencing the generation of these halogenated disinfection by-products (DBPs) comprise type and concentration of NOM, chlorine form and dose, time, bromide ion concentration, pH, organic nitrogen concentration, and temperature [63–65]. Because water treatment plants have been asked to control for total trihalomethans in the past, water treatment operators are likely familiar with some of the requirements that the Disinfectant/Disinfection By-Product (D/DBP) Rule implicate [66]. The main points of the DBP Rule and some of the main changes water supply systems are asked to satisfy with are published in literature [28]. Nevertheless, The D/DBP

Rule imposes the utilisation of enhanced coagulation (EC) treatment for the removal of DBP precursors for surface water systems that have decantation capabilities [67]. The enhanced process implicates changes to the existing coagulation process such as augmenting the coagulant injection, decreasing the pH, or both sometimes [68–77].

Some authors [28] conducted bench, pilot, and demonstration scale studies to investigate arsenate removals during EC. The EC conditions in these researches comprised an augmentation of alum and ferric chloride coagulant injection from 10 to 30 mg L⁻¹, a reduction of a pH from 7 to 5.5, or both [28]. Results from these investigations established the following:

1. More than 90% arsenate removal can be realised upon EC conditions. Arsenate reductions above 90% were easily realised upon all conditions when ferric chloride was utilised.
2. EC using ferric salts is more performant for arsenic removal than EC using alum. With an influent arsenic content of 5 µg L⁻¹, ferric chloride realised 96% arsenate reduction with an injection of 10 mg L⁻¹ and no acid introduction. When alum was utilised, 90% arsenate reduction could not be realised without decreasing the pH.
3. Reducing pH during EC increased arsenic removal by alum coagulation. With ferric coagulation, pH does not play an important role between 5.5 and 7.0 [28].

Nevertheless, post-treatment pH adjustment may be needed for corrosion control when the process is realised at a low pH [28].

5. Conclusions

The main conclusions can be summarised as follow:

1. Brownian movement, the random motion related to small particles by bombardment by individual water molecules, is always present as a natural mixing force. Even if rapid mixing has long been established to have great roles on flocculation phenomena and has been investigated at a certain level, it is possible that many examples of poor efficiency of practical flocculation units can be related to poor mixing.
2. *SF* conducts to faster agglomeration than *CN* and produces stronger and larger flocs: the generation of a hydroxide precipitate produces a big augmentation in the efficient particle concentration and so a greater collision rate. Hydroxide precipitates are generated from large numbers of colloids, which constitute very soon after injection. The flocs generated upon “*sweep*” conditions are also stronger and hence grow larger for the same shear conditions.

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