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Review article

A review of electrocoagulation as a promising coagulation process for improved organic and inorganic matters removal by electrophoresis and electroflotation

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ABSTRACT

In drinking water treatment, coagulation is the most common process to remove particles and impurities. It is described as the process whereby particles are destabilised by dosing a chemical additive (coagulant) where charge neutralisation (CN) and sweep coagulation (SC) are the major mechanisms. Due to the encountered difficulties in natural organic matter (NOM) removal, the concept of enhanced coagulation (EnC) was introduced to increase NOM removal where CN is more accentuated. EnC must be well optimised to overcome its practical considerations such as adjusting the pH of the source water and residual metal concentration in the treated water. In the last three decades, there is new tendency to use electric field/electrochemistry in some chemical processes especially chemical coagulation (CC). Indeed, literature has proved that electrocoagulation (EC) is a promising water treatment technology. During EC process, there are two induced phenomena: electrophoresis (EP) and electroflotation (EF); separately, they are well known in electrochemistry's applications and well developed technically and mathematically. How important are these inherent phenomena in EC process efficiency, constitutes the main aim of this review. Moreover, this paper tries to discuss some aspects of coagulation/flocculation, EP, EF, and EC. Since EP depends upon DC electric field, using anode and cathode as for EC for which the anode is sacrificial, it takes place in the EC device and contributes to its performance. Indeed, the first responsible mechanism of EC performance is the migration to an oppositely charged electrode, i.e., EP, and aggregation due to CN. Hence, EP contributes essentially to EC efficiency as EF does with $H_{2(g)}$ bubbles liberation from the cathode. The EF's contribution may be increased when $O_{2(g)}$ is produced from the anode, at the same time with metal ion liberation. However, as EC process is in fact the combination of these three simultaneous processes need more mathematical, technical, and practical studies to quicken its industrial application at a large scale.

Keywords: Colloid; Coagulation; Charge neutralisation; Electrocoagulation; Electrophoresis; Electroflotation

1. Introduction

Under the proposed disinfectants/disinfection by-products (D/DBP) Rule, the US environmental protection agency (USEPA) has developed regulations for DBPs [1]. Removal of natural organic matter (NOM)—a precursor of trihalomethanes (THMs) and other DBPs – is one of the primary objectives of this rule [2] which has set a maximum contaminant level (MCL) of 80 μg L^{-1} for THMs and 60 μg L^{-1} for five haloacetic: acids (HAA5) [3]. In addition, parasitic protozoa as agents of waterborne disease are of major concerns to water utilities using surface

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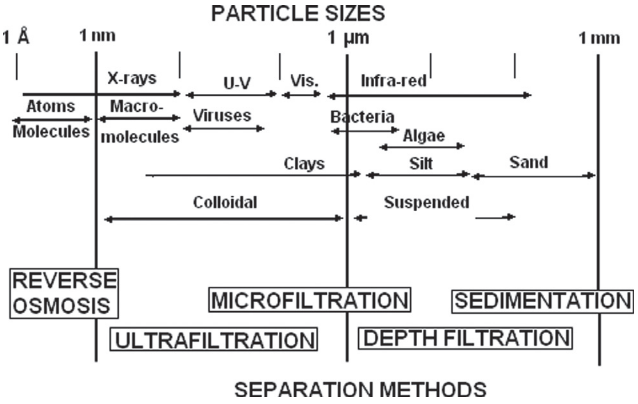

Fig. 1. Typical size ranges of particulate material and the wavelengths of different forms of electromagnetic radiation. The conventional boundary between colloidal and suspended matter is at 1 µm. Appropriate solid–liquid separation processes for different particle sizes are also shown [32].

Table 1
Water quality characteristics of olorado River water (CRW) and California State Project water (SPW) [1]

Parameter	SPW	CRW
Turbidity (NTU)	1.1–3.5	0.64–1.7
EM (µm s^{-1} V^{-1} cm)	−1.13 to −1.51	−0.84 to −1.29
pH	7.85–8.20	8.13–8.34
TOC (mg l^{-1})	3.79–3.94	2.41–2.68
THM formation potential (µg l^{-1})	378–403	100–127
Alkalinity (mg l^{-1} as $CaCO_3$)	74–75	132–135
Hardness (mg l^{-1} as $CaCO_3$)	106–112	287–293
UV absorbance at 254 nm (cm^{-1})	0.115–0.119	0.033–0.038
Bromide (mg l^{-1})	0.3	0.07

water sources. Outbreaks of giardiasis and cryptosporidiosis in the United States have increased the focus on how efficiently filtration plants remove particles (Fig. 1) in the micron size range [1]. The USEPA has developed the enhanced surface water treatment rule (ESWTR), which expands the scope of the current surface water treatment rule (SWTR) to include *Cryptosporidium* [1].

Coagulation with hydrolysing metal salt coagulants [4–6], such as alum and ferric chloride (FC) [7], followed by sedimentation and granular filtration—and chlorination: all these processes constitute the conventional water treatment technology, has traditionally been used to remove suspended particles, which cause turbidity, from source water [1,8]. enhanced coagulation (EnC) uses higher dosages of metal salt coagulant, adjusts the pH of the source water, or both to remove NOM in addition to suspended particles [9,10]. EnC has been specified by USEPA as best available technology for NOM removal. How effectively coagulation removes NOM [11,12] and particles depends on several factors, including coagulant type and dosage, particle and NOM properties, solution chemistry (e.g., pH and presence of divalent cations), and the efficiency of the subsequent solid-liquid separation processes, most notably granular (deep-bed) filtration.

EnC efficiently removes NOM from source water. However, systematic research on the simultaneous removal of particles and THM precursors by EnC is limited. In their article, Vrijenhoek et al. [1] reported results of a pilot-scale investigation of EnC for the removal of particles and THM precursors from two natural water sources, colorado river water (CRW) and california state project water (SPW) (Table 1). The implications of the results for current and pending regulations pertaining to particles and DBPs are discussed. On the basis of the results of these investigations [1], the following conclusions are drawn:

1. Effective removal of particles (residual turbidities <0.1 NTU) was achieved at alum doses of 20–60 mg l^{-1}. At these dosages, *sweep coagulation (SC)* was the predominant particle removal mechanism for both water sources. A further increase in coagulant dosage had little effect on particle removal.
2. Removal of particles (>2 µm) was generally consistent with the behaviour of turbidity reduction. Particle counting, however, provided more information on the overall efficiency of the solid-liquid separation process.
3. Optimal removal of THM precursors was obtained at pH 5.5. At this pH, humic substances (HSs) are likely to be removed by formation of insoluble aluminium-humates complexes (at a low alum dosage) and adsorption to aluminium hydroxide precipitates (at high alum dosage).
4. Total organic carbon (TOC) and UV_{254} reduction by chemical coagulation (CC) was lightly dependent on the humic fraction of NOM and thus on the source water. The ratio of UV_{254} to TOC - specific ultraviolet absorbance (SUVA) - is a good surrogate for the humic fraction of NOM.
5. SUVA decreased as THM precursors were removed with the addition of a metal salt coagulant. When the decrease in SUVA became small with continued addition of the metal salt coagulant, the removal of THM precursors improved only marginally with increasing coagulant dosage.
6. EnC does not benefit source water with low SUVA. Such water, however, may not form elevated concentrations of DBPs because of the low reactivity of the NOM (i.e., a low humic fraction in NOM).
7. Water sources with elevated Br^- concentrations (such as SPW) form a higher percentage of brominated

DBPs. The percentage of brominated THMs increases as the coagulant dosage increases because of the increase in the Br^-:TOC ratio [1].

EnC must be well optimised to overcome its practical considerations (such as EnC uses higher dosages of metal salt coagulant, adjusts the pH of the source water, or both to remove NOM in addition to suspended particles, and residual metal concentration in the treated water) [1].

In our recent paper [13], we have largely reviewed NOM removal and EnC as a link between CC and electrocoagulation (EC). Some advantages and disadvantages of each process are there discussed [13]. Table 2 presents the main mechanisms for coagulation, EnC, and EC [13]. For EC, the first mentioned mechanism is the migration to an oppositely charged electrode, i.e., electrophoresis (EP), and aggregation due to charge neutralisation (CN).

However, in the next sections we will discuss some aspects of coagulation/flocculation (C/F), EP, EC, and electroflotation (EF). How important are the two induced phenomena – EP and EF – in EC process constitutes the main aim of this review.

2. Coagulation and flocculation

Coagulation and flocculation constitute the backbone processes in most water treatment plants (WTPs) [14,15]. Their objective is to enhance the separation of particulate species in downstream processes such as sedimentation and filtration. Colloidal particles and other finely divided matter are brought together and agglomerated to form larger size particles that can subsequently be removed in a more efficient fashion. The traditional use of coagulation has been primarily for the removal of turbidity from potable water [16]. However, more recently, coagulation has been shown to be an effective process for the removal of many other contaminants that can be adsorbed by colloids such as metals, toxic organic matter (OM), viruses, and radionuclides [17]. EnC is an effective method to prepare the water for the removal of certain contaminants in order to achieve compliance with the EPA newly proposed standards. These contaminants include arsenic [18], emerging pathogens such as *Cryptosporidium* and *Giardia* [19], and humic materials [20,21]. HSs are the precursors of THMs and other DBPs formed by disinfection processes [22].

Letterman et al. [23] divided the coagulation process into three distinct and sequential steps:

1. Coagulant formation;
2. Particle destabilisation;
3. Interparticle collisions.

The first two steps are usually fast and take place in a rapid-mixing tank. The third step, interparticle collisions, is a slower process that is achieved by fluid flow and slow mixing. This is the process that causes the agglomeration of particles and it takes place in the flocculation tank. Coagulation is usually achieved through the addition of inorganic coagulants such as aluminium- or iron-based salts, and/or synthetic organic polymers commonly known as polyelectrolytes [24–26]. Coagulant aids are available to help in the destabilisation and agglomeration of difficult and slow to settle particulate material [14].

2.1. Properties of colloidal systems

Colloids are very small particles that have extremely large surface area. Colloidal particles are larger than atoms and ions but are small enough that they are usually not visible to the naked eye. 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 [17]:

1. Gravitational effects are negligible, and
2. Surface phenomena predominate.

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 [27]. The developed electrostatic repulsive forces prevent the colloids from coming together and, consequently, contribute to their dispersion and stability [28].

2.1.1. Electrokinetic properties

The electrokinetic properties of colloids can be attributed to the following three processes [17,23]:

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:

$$R\text{–}NH_3^+ \rightarrow R\text{–}NH_2 + H^+ \quad (1)$$

$$R\text{–}COOH \rightarrow R\text{–}COO^- + H^+ \quad (2)$$

The resulting charge on the surface of such particles is a function of the pH. At high pH values or low hydrogen ion concentrations, the above reactions shift to the

Table 2
Main mechanisms for coagulation, EnC, and EC [13]

Process	Main mechanisms
Coagulation (coagulant dosing)	Particles presence: 1. CN of the negatively charged colloidal particles by adsorption of positively charged coagulant species. 2. SC of colloids in precipitated $Me(OH)_3$ solids ($Al(OH)_3$, $Fe(OH)_3$). NOM presence: 1. Complexation of NOM with dissolved metal coagulant species (Al or Fe), leading to direct precipitation of a Me-NOM solid phase. 2. Complexation of NOM with dissolved coagulant species, leading to adsorption of this complexed material onto precipitated $Me(OH)_3$ solids. 3. Direct adsorption of NOM onto the surface of precipitated $Me(OH)_3$ solids. Particles and NOM presence: 1. Dissolved coagulant species present upon coagulant addition. 2. Presence of precipitated metal hydroxide solids. 3. Concentration of particles and NOM. 4. Chemical properties of these contaminants and their reactivity with dissolved coagulant species. 5. pH of coagulation, which is affected by the chemistry of the coagulant and the alkalinity of the water.
EnC (increased coagulant dosing)	Particles presence: 1. More CN of the negatively charged colloidal particles by adsorption of positively charged coagulant species. 2. More SC of colloids in precipitated $Me(OH)_3$ solids ($Al(OH)_3$, $Fe(OH)_3$). NOM presence: 1. More complexation of NOM with dissolved metal coagulant species (Al or Fe), leading to direct precipitation of a Me-NOM solid phase. 2. More complexation of NOM with dissolved coagulant species, leading to adsorption of this complexed material onto precipitated $Me(OH)_3$ solids. 3. More direct adsorption of NOM onto the surface of precipitated $Me(OH)_3$ solids. Particles and NOM presence: 1. More dissolved coagulant species present upon coagulant addition. 2. More presence of precipitated metal hydroxide solids. 3. Concentration of particles and NOM. 4. Chemical properties of these contaminants and their reactivity with dissolved coagulant species. 5. pH of coagulation, which is affected by the chemistry of the coagulant and the alkalinity of the water.

(continued)

Process	Main mechanisms
EnC (increased coagulant dosing & acidified pH)	Particles presence: 1. Most CN of the negatively charged colloidal particles by adsorption of positively charged coagulant species. 2. Less SC of colloids in precipitated $Me(OH)_3$ solids ($Al(OH)_3$, $Fe(OH)_3$). NOM presence: 1. Most complexation of NOM with dissolved metal coagulant species (Al or Fe), leading to direct precipitation of a Me-NOM solid phase. 2. Most complexation of NOM with dissolved coagulant species, leading to adsorption of this complexed material onto precipitated $Me(OH)_3$ solids. 3. Less direct adsorption of NOM onto the surface of precipitated $Me(OH)_3$ solids. Particles and NOM presence: 1. More dissolved coagulant species present upon coagulant addition. 2. Less presence of precipitated metal hydroxide solids. 3. Concentration of particles and NOM. 4. Chemical properties of these contaminants and their reactivity with dissolved coagulant species. 5. Acidified pH of coagulation, which is affected by the chemistry of the coagulant and the alkalinity of the water.
EC (coagulant dosing & electric field)	1. Migration to an oppositely charged electrode (EP) and aggregation due to CN. 2. Cation or hydroxyl ion (OH^-) forms a precipitate with the pollutant. 3. Metallic cation interacts with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation). 4. Hydroxides form larger lattice-like structures and sweeps through the water (SC). 5. Oxidation of pollutants to less toxic species. 6. Removal by EF or sedimentation and adhesion to bubbles.

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, i.e. 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 [23].

Oil droplets adsorb negative ions, preferably hydroxides (OH^-), from solution and, consequently, they develop a negative charge [27]. 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. This is known as isomorphic replacement [23]. 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. 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. Examples of such imperfection include (a) the substitution of an aluminiumion (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. [23], 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.

2.1.2. Hydration

Water molecules may also be sorbed on the surface of colloids [29], 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 (water loving) particles [30]. Colloids, that do not show affinity for water and do not have bound water films, are classified as hydrophobic (water hating) particles [31].

2.1.3. Brownian movement

Colloids exhibit a continuous random movement caused by bombardment by the water molecules in the dispersion medium. 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 [32].

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 [29]. 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. 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 [14].

2.2. Colloidal structure and stability

The stability of colloidal particulate matter is dependent on their electrokinetic property. Colloidal particles acquiring similar primary charges develop repulsive forces that keep them apart and prevent their agglomeration. The primary electrical charges could be either negative or positive. However, the majority of colloids that exist in aqueous systems are negatively charged [32]. A colloidal system as a whole does not have a net charge. Negative primary charges on colloidal particles are balanced by positive counter-ions near the solid–liquid interface and in the adjoining dispersion medium. In a similar fashion, positively charged particles are counterbalanced by negative ions present in the surrounding water. This natural inclination toward achieving electrical neutrality and counterbalance of charges results in the formation of an electric double layer around colloidal particles.

The electric double layer, which comprises the charged particle and surrounding counter-ions, is illustrated in Fig. 2. The total potential at the surface of the primary charged particle is termed the Nernst potential. The dense layer of counter-ions fixed on the surface of the primary particle is called the Stern layer. The outer limit of this layer is defined by the surface of shear that separates the mobile portion of the colloid from the surrounding mixture of diffuse ions. In an electric field, the ions within the surface of shear will move with the particle as a unit. The concentrated counter-ions within the surface of shear reduce the net charge on the particle by an amount that is usually referred to as the Stern potential. Consequently, the potential is maximum at the surface of the primary particle, the Nernst potential, that decreases rapidly through the Stern layer resulting in a net overall charge on the particle at the surface of shear called the zeta potential (ZP). This potential determines the extent of repulsion between similarly charged particles and is commonly considered to be the major cause of the stability of a colloidal system. Further away from

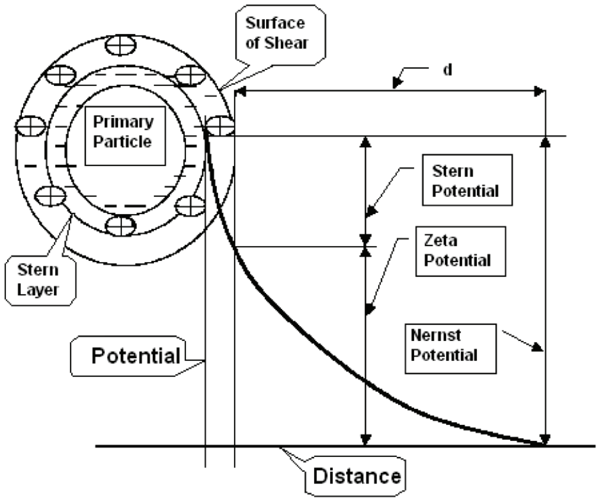

Fig. 2. The electrical potential of a negatively charged colloidal particle [14].

the surface of shear both the concentration and potential gradients continue decreasing, but at a more gradual drop, until the potential approaches the point of electrical neutrality in the surrounding solution [14].

The counter-ions of the Stern layer are concentrated in the interfacial region owing to electrostatic attraction. However, these ions tend to be more loosely attached, as they are located at distances further away from the particle surface as a result of the potential gradient. Consequently, any thermal agitation may cause these less strongly held ions to diffuse away toward the bulk of the dispersion medium. These two opposite forces, electrostatic attraction and diffusion, give rise to the distribution of the potential over distance such that the highest concentration of counter-ions occurs at the particle interface and drops gradually with increasing distance. When the dispersion medium contains low concentration of ions (low ionic strength), the diffuse layer will be spread over a wide distance, *d*, as shown in Fig. 2. On the other hand, when the dispersion medium possesses a high ionic strength, the diffuse layer would get compressed, become thinner, and eventually extend far less distance into the bulk of the solution. Detailed analysis of the theory of the double layer and stability of colloids can be found in Verwey and Overbeek [33], Morel [34], O'Melia [35], and Elimelech and O'Melia [36].

When two similar primary charge particles drift toward each other, their diffuse layers start to interact leading to the production of a repulsive electrostatic force. The resulting repulsion between the approaching particles increases as the particles get closer. Such charged particles may not be able to collide at all if their charges are high enough [35]. Ultimately, as illustrated in Fig. 3, the colloidal stability depends on the relative strength of the above electrostatic forces of repulsion and the forces of attraction.

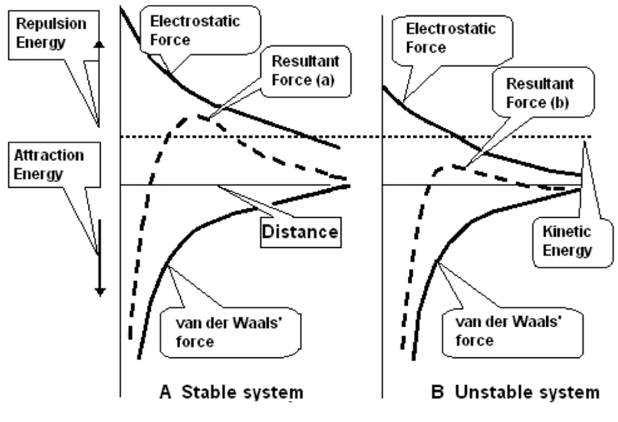

Fig. 3. Effect of interparticle forces on the stability of a colloidal system [14].

The forces of attraction are due to van der Waals' forces. All colloidal particles, irrespective of their composition, sign or magnitude of charge, or the composition of the dispersion medium, possess such attractive forces. They arise from the following:

(a) Electronegativity of some atoms is higher than for others in the same molecule.
(b) Vibration of charges within one atom creates a rapidly fluctuating dipole.
(c) Approaching particles induce vibrations in phase with each other [14].

The above phenomena result in an attractive force between the two oppositely oriented dipoles. The magnitude of the force varies inversely with distance between particles, increasing rapidly with decreasing distance (see Fig. 3). If particles come close enough for these forces to take over, they will adhere [14].

The other factor, in addition to van der Waals' attractive forces, tending to destabilise a colloidal system is Brownian movement [37]. This is due to the random motion of colloids brought about by their bombardment by molecules of the dispersion medium. The outcome of the movement is to impart kinetic energy to the colloidal particles. Higher energy particles moving in a random fashion tend to collide eventually [32].

Moreover, Fig. 3 illustrates the relationship of forces that exist between colloidal particles as a function of the separation distance. The net resultant force is obtained by the summation of the respective electrostatic repulsive force and van der Waals' attractive force. When the resultant repulsion energy exceeds the kinetic energy (Fig. 3A), the particles will not coagulate and the dispersion is stable. When the kinetic energy is larger than the repulsion energy (Fig. 3B), the dispersion is unstable and the particles will coagulate. Consequently, if it is required to destabilise and coagulate a stable dispersion, then the electrostatic repulsion energy between the particles must be lowered and/or the kinetic energy of the particles must be raised [14].

2.3. 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. Upon being added to the water, the action of the metal salt is complex [23,38]. It undergoes dissolution, the formation of complex highly charged hydrolysed metal coagulants (hydroxyoxides of metals), interparticle bridging, and the enmeshment of particles into flocs. Polymers work either on the basis of particle destabilisation or bridging between the particles.

The destabilisation process is achieved by the following four mechanisms of coagulation:

1. Double-layer compression.
2. Adsorption and CN [39].
3. Entrapment of particles in precipitate.
4. Adsorption and bridging between particles [40–43].

2.3.1. 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. The addition of counter-ions with higher charges, 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 (see Fig. 3) would become smaller or even would be completely eliminated, allowing the particles to approach each other and agglomerate [14].

A mathematical model that describes this coagulation mechanism is explained in detail in [33]. The prediction of this model is in agreement with what is known as the Schultze–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. Table 3 illustrates the relative effectiveness of various electrolytes in the coagulation of negatively and positively charged colloids [17]. 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.

Table 3
Relative coagulation power of electrolytes [14]

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

2.3.2. Adsorption and charge neutralisation

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 [17,23,38]. 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. 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 [44]. 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 [14]. 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 [45]. 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.

2.3.3. Entrapment of particles in precipitate

When the coagulants alum [$Al_2(SO_4)_3$] or FC ($FeCl_3$) are added in high enough concentration, they will react with water (and hydroxides (OH^-)) to form metal hydroxide precipitates, $Al(OH)_3$ or $Fe(OH)_3$ 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 SC [14,23,46].

There are three elements that influence this coagulation mechanism [14,38]:

1. Oversaturation: The rate of precipitation is a function of oversaturation with the metal hydroxide. To

obtain fast precipitation and efficient SC, high concentrations of $Al(OH)_3$ or $Fe(OH)_3$ 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 [38].

2.3.4. Adsorption and bridging between particles

Polymers destabilise colloidal particles through the formation of bridges that extend between them. 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 [14].

2.4. Time requirement for rapid-mixing in coagulation

Coagulation can be broken down into several sequential steps. Chemical reactions occur immediately after the addition of coagulants, forming active coagulant species. The active species promotes the destabilisation and the contact of suspended colloids through 'rapid-mixing'. The engineering practice of rapid-mixing has relied heavily on accumulated experiences. Since 1969 [47], a series of researches on rapid-mixing has been started. A study of rapid-mixing involves theories in coagulant chemistry, mixing, and mass transfer. Due to of such complexity, no simple and concrete guideline on the operation can be offered for the engineering design of rapid-mixing. Studies on rapid-mixing can be approached microscopically or macroscopically, depending on whether the focus is on the physical or chemical parameters [47].

From the microscopic point of view, the nature of coagulants and their coagulation mechanisms are the keys to the success of rapid-mixing. Studies have shown that the variation in hydrolysis species of coagulants dominates the coagulation mechanism. Researchers [47] employed a turbulent pipe-flow reactor to examine the influence of the hydrolysis time on particle destabilisation of alum coagulation. They found that the Al hydroxo-complex species of maximum destabilisation capacity formed within 0.1 s after chemical addition. The efficiency of coagulation decreased continuously in the first 6 s and then remained the same. In studying the rapid-mixing of alum coagulation, authors [47] discovered that rapid-mixing is significant if adsorption and CN are the principal mechanisms of the coagulation. In a study on coagulation by polymers, Amirtharajah and Jones [48] found that rapid-mixing is critical in colloid bridging.

The microscopic view of study on rapid-mixing has drawbacks such as insufficient mixing when the operation is scaled up, as well as the failure to consider the break-up of aggregates during rapid-mixing. These phenomena were also noticed by Clark and Srivastava [49] who performed a series of studies to explore the role of rapid-mixing on coagulation. In a continuous study on various sizes of mixing tanks, they found that small mixing tanks were more sensitive to experimental conditions. As a result, a feedback approach was introduced to include all of the operational parameters in rapid-mixing. Therefore, some researchers have shifted their focus towards the subsequent processes such as sedimentation and filtration to view rapid-mixing from a macroscopic point of view [47]. The idea is to monitor the turbidity of the effluent from sedimentation and filtration to reflect the efficiency of rapid-mixing. The optimal rapid-mixing condition is the one corresponding to the lowest residual turbidity. A macro-approach is more applicable in the operation of WTPs. However, no model can include all operational parameters due to the great variation in treatment units.

Other researchers focused their studies on the impact of rapid-mixing on flocculation (or slow-mixing) which is the immediate subsequent process. Researchers [47] described the effect of rapid-mixing intensity on particle aggregation in flocculation. In the study, they introduced an apparent aggregation rate (K_{app}) to evaluate the operation of rapid-mixing. Authors [47] have suggested that K_{app} is an effective index for rapid-mixing. The major disadvantage of this approach is that it is time-consuming to apply the K_{app} in water treatment works. Studies from the macro-point of view ignore important parameters such as the coagulant type and coagulation mechanisms. As a result, no general guideline for rapid-mixing can be established due to the great variation in experimental conditions.

In their study [47], Kan et al. employed a photometric dispersion analyser (PDA) to monitor clay coagulation by alum and polymeric aluminium chloride (PAC). The effect of rapid-mixing time on particle removal was studied. A standard jar test was performed to determine the degree of destabilisation of particles. Maximum ratio outputs of PDA measurements were inversely related to residual turbidities. Adequate rapid-mixing times evaluated from both PDA and mixing tests were close to each other. Studies of coagulation mechanisms at various rapid-mixing times indicated that mixing time had significant impact on CN and SC. The difference in residual turbidity can be attributed to the characteristics of microflocs. The rise in residual turbidity in SC suggested the breakage of microflocs.

2.5. Influencing factors

Many factors affect the coagulation process. In addition to mixing that is explained above, the following discussion covers the most important factors.

2.5.1. Colloid concentration

Colloidal concentration has a large impact on both the required dosage and the efficiency of the coagulation process itself. The dosage of coagulants required for the destabilisation of a colloidal dispersion is stoichiometrically related to the amount of colloidal particles present in solution [14]. However, for dilute colloidal systems, the rate of coagulation is very slow because of the small number of colloids in suspension and, therefore, not enough contact between particles is available. Under such conditions increasing the concentration of particulate matter by the addition of a coagulant aid or recycling of settled sludge would improve the coagulation rate. Application of a large coagulant dosage to a dilute colloidal suspension would result in a greater chance of restabilising the colloids.

2.5.2. Coagulant dosage

The effect of aluminium and iron coagulant dosage on coagulation, as measured by the extent of removing particles causing turbidity in water, has been studied and evaluated in great detail by O'Melia [38]. They divided the relationship into four zones starting with the first low-dosage zone and increasing the dosage progressively to the highest dosage that is applied in zone four:

Zone 1: Not enough coagulant is present for the destabilisation of the colloids.
Zone 2: Sufficient coagulant has been added to allow destabilisation to take place.
Zone 3: Excess concentration of coagulant can bring about charge reversal and restabilisation of particles.
Zone 4: Oversaturation with metal hydroxide precipitate entraps the colloidal particles and produces very effective SC.

The range of coagulant dosage that triggers the start, end, or elimination of any of the above zones is dependent on colloidal particle concentration and pH value.

2.5.3. Zeta potential

The ZP represents the net charge of colloidal particles [14]. Consequently, the higher the value of the ZP, the greater is the magnitude of the repulsive power between the particles and hence the more stable is the colloidal system. The magnitude of the ZP [50] is determined from electrophoretic measurement of particle mobility in an electric field (Fig. 4).

2.5.4. Affinity of colloids for water

Hydrophilic colloids are very stable. Because of their hydration shell, chemicals cannot readily replace sorbed water molecules and, consequently, they are difficult to coagulate and remove from suspension. The stability of hydrophilic dispersions depends more on their "love" for water than on their electrostatic charge. It has been estimated that suspensions containing such particles require 10–20 times more coagulant than what is normally needed to destabilise hydrophobic particles [51]. Typical examples are the colour-producing material – such as HSs [22] - in surface water and organic colloids present in wastewater (Fig. 5). On the other hand, examples of hydrophobic particles are metal oxides that can be easily coagulated and destabilised. However, the bulk of colloidal particles in turbid water usually exhibit a mixture of hydrophobic–hydrophilic properties resulting

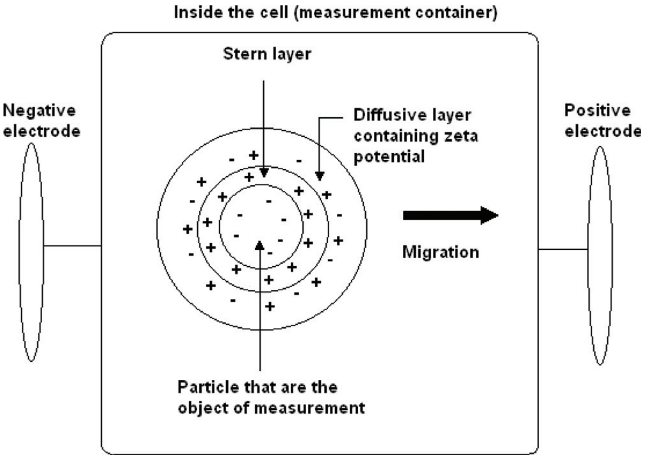

Fig. 4. ZP measurement [50].

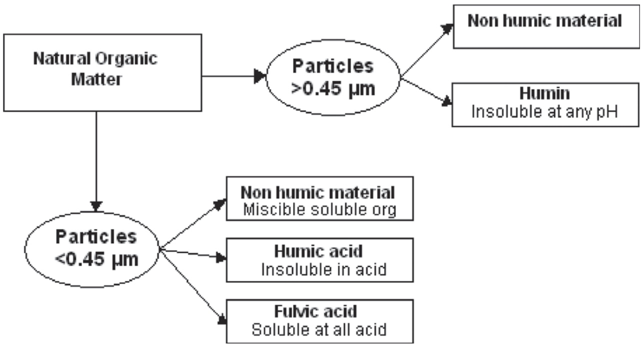

Fig. 5. Schematic presentation of the composition of NOM in water with emphasis on humic material [22].

in suspensions that are intermediate in the degree of their difficulty to coagulate [14].

2.5.5. pH value

pH is a measure of H^+ and OH^- ion concentration. The presence of these ions in the potential-determining layer may cause particle charge to be more positive or less negative at pH values below the IEP. At high pH values above the IEP the reverse effect takes place, whereby particle charge becomes more negative or less positive. The IEP is the pH value at which charge is most nearly neutralised. The IEP for aluminium hydroxide is around pH 8. It varies with the ionic strength in solution but is normally in the pH range of 7 to 9 [23].

The solubility of colloidal dispersions is affected radically by pH. $Al(OH)_3$ is amphoteric in nature and is soluble at low and high pH. The greatest adsorption occurs in the pH range where there is minimum solubility. Examples of optimum pH ranges for metallic salts are shown in Table 4 [52]. It was well reported [14] that optimal coagulation with alum takes place at pH values near 5 and 7. At these points, the positively charged aluminium hydroxide neutralises the negatively charged turbidity producing colloidal particles, resulting in zero ZP. However, in the pH range from 5 to 7 the colloidal particles are restabilised due to charge reversal brought about by excess adsorption of the positively charged aluminium hydroxide species; pH also plays a part in affecting the amount of aluminium residual in the treated water [14].

Table 4
Optimum pH values for metallic coagulants [14]

Coagulant	pH
Alum	4.0 to 7.0
Ferrous sulphate	8.5 and above
FC	3.5 to 6.5 and above 8.5
Ferric sulphate	3.5 to 7.0 and above 9.0

The influence of pH on the polymer's behaviour [53] and effectiveness in coagulation is particularly important because of the interaction between pH and the charge on the electrolyte. The extent of charge change with pH is a function of the type of active group on the polymer (carboxyl, amino, etc.) and the chemistry of those groups.

2.5.6. Anions in solution

As explained below, one of the constraints in using alum and iron as coagulants is the occurrence of charge reversal and restabilisation of colloids. However, this behaviour can be suppressed or eliminated in the presence of high concentrations of anions such as sulphate, silicate, and phosphate [54]. It was found that background concentration of SO_4^{2-} in excess of 10 to 14 mg l^{-1} has the ability to prevent restabilisation. Coagulation with alum is brought about by various species of positively charged aluminium hydroxyoxides. Aluminium hydroxide possesses its lowest charge and lowest solubility at its IEP that lies in the pH range of 7 to 9 [23]. As a result, when the alum dosage is increased within this pH range, SC takes place due to the formation of the aluminium hydroxide precipitate. However, at lower pH values (5–7), higher dosages of alum will tend to increase the positively charged alum species that get adsorbed on particles' interface leading to charge reversal and the restabilisation of the colloidal particles. Similar concepts and conclusions are applicable to iron coagulants.

2.5.7. Cations in solution

The presence of divalent cations, such as Ca^{2+} and Mg^{2+} [22], in raw water is commonly considered not only to be helpful in the coagulation of negatively charged colloidal clay particles by anionic polymers but also to be necessary. Three reasons have been suggested to be behind this beneficial effect [14]:

1. Compression of the colloidal double layer.
2. Reduction of the colloidal negative charge and minimisation of repulsive potential.
3. Reduction in the range of repulsive barrier between adsorbed polymers.

3. Three coagulation's most difficult challenges: NOM, viruses and algae

3.1. Natural organic matter removal

Waters containing low molecular weight (MW) HSs can be difficult to treat by coagulation processes [55], as the smaller molecules and uncharged species are less effectively removed [56]. The charged impurities present can be taken out by ion exchangers or adsorbents [56]. Oxidative degradation, followed by biological treatment, is an option for all organic species [57]. There is scope for a vastly improved approach to achieve more economical treatment for organics removal generally.

Impurities in source waters can be present as suspended material, like clay, silica, microbial cells or algae [58], as dissolved and colloidal NOM, and as dissolved salts. Drinking water sources typically contain 2–10 mg l^{-1} of NOM, of which only 10–30% has been identified [56]. There are many reasons why it poses a problem for the water treatment industry; among them the formation of potentially carcinogenic chlorinated hydrocarbons such as THMs when disinfection is carried out with chlorine [59]. There are also bacterial regrowth problems and aesthetic issues like colour, taste and odour [56]. As well, NOM fouls membranes [60] and adsorbents, interferes with the oxidation of dissolved iron and manganese to insoluble, easily removed forms, and acts as an electron transfer agent in the corrosion process [56].

3.1.1. Natural contaminants in water supplies

Impurities may be dissolved compounds as well as insoluble particles, and may be of organic or inorganic origin [61]. Some of the more commonly found natural components containing OM are, in decreasing order of size, zooplankton, phytoplankton, bacteria, viruses, clay-humic acid complexes, humic acids (HAs), proteins, polysaccharides, fulvic acids (FAs), and very small molecules such as fatty acids, carbohydrates, amino acids and hydrocarbons [62,63]. The organic impurities are formed by the biological degradation of organic life substances [64], and include highly coloured compounds. Inorganic salts of natural origin are also present to some degree. Ion exchange will of course adsorb predominantly dissolved and colloidal ionic matter, and not insoluble material to any extent.

Dissolved compounds, defined as that which will pass through a membrane having pores of 0.45 μm size, when measured as dissolved organic carbon (DOC), have levels in the range 0.1–115 mg l^{-1}, with 5.75 mg l^{-1} being reported as a global average for streams [56]. DOC poses a problem for the water treatment industry for a number of reasons [65]. DOC can be made up of amino acids, fatty acids, phenols, sterols, sugars, hydrocarbons, urea, porphyrins or polymers [64]. The polymers include polypeptides, lipids, polysaccharides and HSs. The variation of DOC can be from 2.2 mg l^{-1} for an oligotrophic lake, 5 mg l^{-1} for a river, 10 mg l^{-1} for a eutrophic lake, 15 mg l^{-1} for a marsh and 30 mg l^{-1} or more for bog water. The level along a river and from one river to another can range from 0.30–30.0 mg l^{-1}. The level in summer can be four times that in winter, so the variation is seasonal as well as regional. In Arizona, spring snowmelt and late summer monsoon rains give the highest DOC production [56]. The make up of the organic compounds for an average river water is 40% FAs, 10% HAs, 30% hydrophilic acids, 10% carbohydrates, 6% carboxylic acids and 4% amino acids [56]. Although HSs, encompassing fulvic and humic acids, constitute about 50% of the total DOC of a typical surface water, the proportion can be as high as 80%. HSs are unique and troublesome materials in that they have quite variable properties, in terms of acidity (pK_a 3–5), MW (several hundred to ten thousand) and molecular structure (mostly phenolic and carboxylic acid functionalities, but also alcohol, quinone, ether, ester and ketone groups). They behave as negatively charged colloids or anionic polyelectrolytes at natural pH levels and have surface-active properties, but can interact via their hydrophobic aromatic and aliphatic regions with non-polar pollutants such as pesticides and polychlorinated biphenyls. HSs are often present as stable complexes with metal ions.

3.1.2. Mechanisms of humic acids coagulation

HA is a NOM, resulting from the weathering and/or the biodegradation of dead plants and animals [64,66,67]. There is no specific molecular structure suggested for HA, but it has been noted that its functional groups such as carboxylic and phenolic acids can adsorb metal ions and influence its fate [68]. In order to reduce the concentration of HA in drinking water, coagulation is an essential method. With different coagulant (such as iron salt or aluminium salt) and dosages and different pH, HA can be removed either by complexation with the coagulant or by precipitation after being adsorbed [69–71]. Based on the stoichiometry, researchers have proposed several coagulating mechanisms for the removal of NOMs. The mechanisms of destabilisation include not only the CN and the incorporation of OM onto the iron hydroxide flocs but also the co-precipitation of the complexes of metal-OM with the metal hydroxides [66]. Van Benschoten and Edzwald [72] used the Times Spectrophotometric Analysis to predict the possible chemical formula of the complex formed after the FA reacted with the aluminium sulphate. In addition, from the kinetics point of view, Istv'an [73] showed that the hydrolysis of metal ions occurred immediately after contacting with water. Therefore, most of the iron or aluminium salts before reacting with the OM are in the form of hydroxide. In turn, some studies have found that the species, the number, and the position of the functional groups on OMs all have significant effect on coagulation [74]. By using mono- and poly-aluminium compounds as coagulants to react with FA at different pH, researchers [66] proposed the following equations:

(CN and precipitation)

$$\text{FA} + \text{monomeric Al} \rightarrow \text{FA} - \text{monomeric Al}_{(s)},\ \text{pH} = 4 \sim 5 \qquad (3)$$

$$\text{FA} + \text{polymeric Al} \rightarrow \text{FA} - \text{polymeric Al}_{(s)},\ \text{pH} = 5 \sim 6 \ \text{(adsorption)}\ \text{pH} > 7 \qquad (4)$$

$$\text{FA} + \text{Al(OH)}_{3(s)} \rightarrow \text{FA} - \text{Al(OH)}_{3(s)} \qquad (5)$$

$$\text{FA} - \text{polymeric Al}_{(s)} + \text{Al(OH)}_{3(s)} \rightarrow \text{FA} - \text{polymeric Al}_{(s)} - \text{Al(OH)}_{3(s)} \qquad (6)$$

They concluded that the coagulation mechanism and the reaction pathway of HSs are strongly kinetically affected. At low pH, the aluminium salt neutralised the charge on FA directly. Therefore, the flocs formed after the destabilisation precipitated gradually. Increasing solution pH will enhance the hydrolysis of Al-salt, and thus increase the chance to form $\text{Al(OH)}_{3(s)}$. Simultaneously, the opportunity for FA to contact with the free Al-salt decreases, so the FA is removed by adsorbing onto $\text{Al(OH)}_{3(s)}$. On the other hand, the slow hydrolysis of the pre-hydrolysed polyaluminium salt could neutralise the charge of FA before the formation of the $\text{Al(OH)}_{3(s)}$, and form the FA-polymericAl which could be removed through adsorption [66].

In their detailed study [75], Electrophoretic mobility (EM), pyrene fluorescence, surface tension measurements, transmission electron microscopy on resin-embedded samples, and X-ray microscopy (XRM) were combined to characterise the aggregates formed from humic colloids and hydrolysed-Fe species under various conditions of pH and mixing. They show that, at low coagulant concentration, the anionic humic network is reorganised upon association with cationic coagulant species to yield more compact structures (Fig. 6). In particular, spheroids about 80 nm in size are evidenced by XRM at pH 6 and 8 just below the optimal coagulant concentration. Such reorganisation of humic colloids does not yield surface-active species, and maintains negative functional groups on the outside of humic/hydrolysed-Fe complex. They also observe that the humic network remains unaffected by the association with coagulant species up to the restabilisation concentration. Upon increasing the coagulant concentration, restructuration becomes limited: indeed, the aggregation of HA with hydrolysed-Fe species can be ascribed to a competition between humic network reconformation rate and collision rate of destabilised colloids. A decrease in stirring favours the shrinkage of humic/hydrolysed-Fe complexes, which then yields a lower sediment volume. Elemental analyses also reveal that the iron coagulant species are poorly hydrolysed in the destabilisation range. This suggests that destabilisation mechanisms such as SC or adsorption onto a hydroxyde precipitate are not relevant to our case. A neutralisation/complexation destabilisation mechanism accompanied by a restructuration of flexible humic network (Fig. 6) is then proposed to occur in the range of pHs investigated [75].

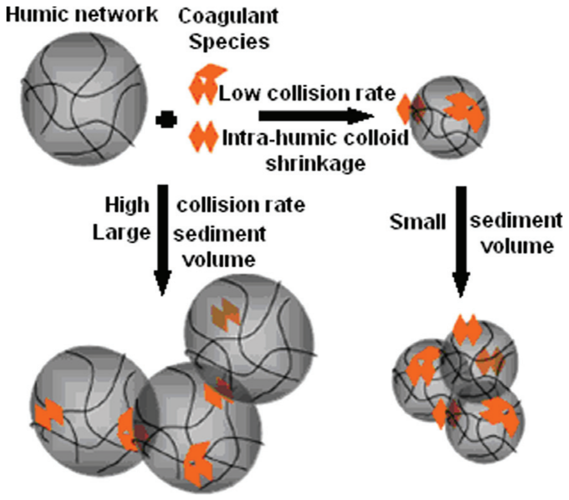

Fig. 6. Schematic illustration of HA aggregation dynamics with hydrolysed Fe coagulant species [75].

3.1.3. Synthetic polyelectrolytes in drinking water treatment

Synthetic polyelectrolytes [76] are widely used in drinking water treatment (DWT), either as flocculants in conjunction with a metal salt coagulant or, less commonly, as coagulants in their own right [77]. The global market for water treatment polymers exceeds $US 2.6 billion pa. Polyacrylamide and acrylamide copolymers are commonly used in the first mode; poly(diallyldimethylammonium chloride) (PDADMAC) is the most common polymer used in the second mode. Polyelectrolytes increase the size and strength of flocs formed by alum or iron-based coagulants [78]. When used as complete or partial replacements for inorganic coagulants they extend filter run times and yield smaller volumes of sludge. However, there is no accepted method for measuring polymer residuals in treated water. Consequently, regulation of their use is arbitrary and inconsistent [77].

Good review of organic polyelectrolytes in water treatment is given by Bolto and Gregory [53].

3.1.4. Polyaluminium chloride PAC-Al_{30} for humic acid removal

PACs are a group of highly effective coagulants in water treatment that have replaced a large part of traditional aluminous coagulants in recent years because of low dosage, high efficiency, low cost and convenient usage [79,80]. In order to improve the coagulation efficiency and to suit different conditions, many sorts of PAC with different aluminium hydrolysis ratio ($B = [OH^-]/[Al^{3+}]$) have been produced and used, and introduction of different ions, such as SO_4^{2-}, SiO_3^{2-}, Fe^{3+}, and organic polymers into PAC has also been investigated [81]. It is generally believed that $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}) is the most effective coagulation species in polyaluminium coagulants due to its strong CN capability, high structure stability and nanometre molecular diameter [82–85]. But this opinion has been challenged by the discovery of $[(AlO_4)_2Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}), the biggest and highest charged polycation ever characterised in PAC. Allouche et al. [86] and Rowsell and Nazar [87] characterised the species of Al_{30} by in situ ^{27}Al NMR measurement, and found that Al_{30} is composed of two δ-Al_{13} connected by four aluminium monomers with a molecule dimension of about 2.0 nm in length. With these excellent characters, it may be a better species than Al_{13}.

Chen et al. [88] testified that Al_{30} species can become the dominant species in polyaluminium solution when the freshly prepared polyaluminium solution is heated at 95°C for 12 hr, and the formation of Al_{30} is accelerated by the increase of total aluminium concentration. Allouche et al. [89] demonstrated that aluminium monomers are the species controlling the conversion of Al_{13} Keggin ε into Al_{30}. Phillips et al. [90] researched the rates of oxygen exchange between the Al_{30} molecule and aqueous solution. Chen et al. [91] found that PAC with a content of 76.8% of Al_{30} removes turbidity more efficiently, and has much broader effective dosage range and pH range when compared with high Al_{13} content PAC and $AlCl_3$.

However, there are few reports about the Al_{30} C/F performances for OMs. In their research, Zhang et al. [79] investigated the coagulation behaviours of PAC with a high Al_{30} content (PAC-Al_{30}) to remove HA, a group of typical organics found in source water. B value is a key parameter for PAC, which may significantly influence the hydrolytic aluminium species distribution in solution, and further affects the C/F performances, the effluent quality, and the water treatment cost. The influences of B value on the C/F performances of PAC-Al_{30} were also studied. Meanwhile, the residual aluminium concentration in the purified water was tested.

Indeed, coagulants PACs with a high Al_{30} content (PAC-Al_{30}) were prepared in laboratory, and the aluminium hydrolysis ratios ($B = [OH^-]/[Al^{3+}]$) of PAC-Al_{30} were 1.2, 1.8 and 2.4 respectively. Coagulation behaviours of PAC-Al_{30} with different B values and conventional coagulant $AlCl_3$ were compared by jar test to remove HA from water. Floc growth, CN capacity, HA removal and residual aluminium concentration in the purified water were investigated. The influences of initial pH and coagulant dosage on coagulation behaviours were considered. The results show that coagulants PAC-Al_{30} exhibit much stronger floc formation capacity, have broader effective dosage range and initial pH range, reach higher HA removal efficiency, and get lower residual aluminium concentration than $AlCl_3$ does. The C/F capacity of PAC-Al_{30} increases with the B value. The HA removal reaches 98.5% at an initial pH of 7.0 and PAC-Al_{30} ($B = 2.4$) dosage of 0.16 mmol l^{-1} (total aluminium concentration, Al_t) when the initial HA concentration is 10 mg l^{-1}; the residual aluminium in the purified water is 0.066 mg l^{-1}. Al_{30} is verified as highly efficient C/F species for HA removal [79].

3.1.5. Chitosan for humic acid coagulation and adsorption

Of all the available coagulants, aluminium sulphate and PAC are the most widely used, because they are cheap, effective and easy to handle. Most important of all, aluminium can be overdosed to ensure coagulation efficiency. However, over-use of aluminium salt coagulants elevates the aluminium concentration and turbidity in the treated water, which in turn devaluates the treatment process. Researchers [92] also reported that intake of a large quantity of aluminium salt may cause Alzheimer's disease [93,94]. The search for a better alternative to meet the increasing demand for water quality has become an important area of study. Polymers combined with alum or polymers alone have been applied in the coagulation, and gradually gained popularity in water treatments. Synthetic polyelectrolytes produce sludge of better dewatering characteristics. The sludge is smaller in volume than those from conventional alum flocculation, and facilitates filtration. However, their long-term effects on human health are not well understood.

Chitin is a cellulose-like biopolymer widely distributed in nature, especially in marine invertebrates, insects, fungi, and yeasts [95]. Its deacetylated product, chitosan, is readily soluble in acidic solutions, which makes it more available for applications [53,96,97]. Chitosan (Fig. 7) is a biodegradable, non-toxic, linear cationic polymer of high MW [98]. It was discovered [92] that chitosan was an effective agent for coagulation of suspended solids from various food processing wastes. Since chitin is the second most abundant biopolymer, the application in coagulation not only avoids the health threat from alum treatment, but also allows recycling of a large amount of crab shell. The feasibility of applying chitosan in the coagulation of colloidal particles was

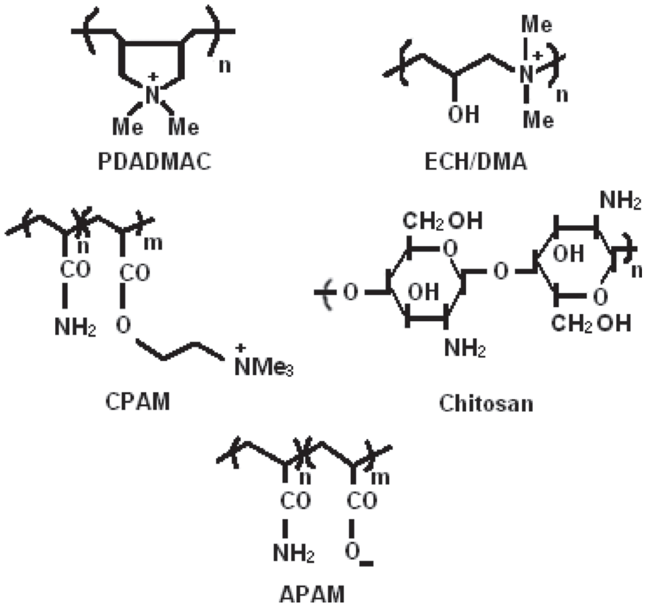

Fig. 7. Structures of the cationic polyelectrolytes polydiallyldimethyl-ammonium chloride (PDADMAC), polymers from epichlorohydrin and dimethylamine (ECH/DMA), cationic polyacrylamide (CPAM), chitosan and anionic polyacrylamide (APAM) [53].

assessed in some laboratories [92]. Pan et al. [92] found that chitosan can be a potent coagulant for surface water treatment, especially for source waters of medium and low turbidity. From various treatments of chitosan, they further recommended that the optimal pretreatment condition to prepare modified chitosan coagulant is deacetylation by 45% alkali pretreatment for 60 min and dissolution in 0.1% hydrochloric acid.

In their study [92], coagulations of synthetic and real water with the modified chitosan, mixed coagulant of chitosan and PAC at various ratios, and PAC were compared. The efficiency was evaluated by the factors of settling rate, floc diameter, and residual turbidity. Coagulation with chitosan alone required least dosage. Chitosan coagulants also produced larger floc with higher settling velocity. Satisfactory results were obtained from the mixed coagulant of chitosan/PAC = 4:1. Although low pH decreased the optimal dosage, the flocs produced were smaller with slower settling rate. Increasing the rapid mixing strength improved the coagulation only when the applied dosage was less than the optimum dosage. Studies using other particles such as kaolinite and clay indicate that the properties of particles have a significant effect on the chitosan coagulation efficiency [92].

In their study [99], activated clay was added in chitosan slurry to prepare composite beads. The adsorption isotherms and kinetics of two organic acids (tannic acid, HA) and two dyes (methylene blue, reactive dye RR222) using composite beads, activated clay, and chitosan beads were compared. With composite beads as an adsorbent, all the isotherms were better fitted by the Freundlich equation. The adsorption capacities with composite beads were generally comparable to those with chitosan beads but much larger than those with activated clay. The pseudo-first-order and pseudo-second-order equations were then screened to describe the adsorption processes. It was shown that the adsorption of larger molecules such as tannic acid (MW, 1700 g mol^{-1}), HA, and RR222 from water onto composite beads was better described by the pseudo-first-order kinetic model. The rate parameters of the intraparticle diffusion model for adsorption onto such adsorbents were also evaluated and compared to identify the adsorption mechanisms [99].

Rizzo et al. [100] attract our attention to an important fact about chitosan: due to its nature, some OM may be released during coagulation step, thus increasing the concentration of DBPs as well as the toxicity of finished water. In their paper [100], the efficiency of chitosan and conventional coagulants (alum and FC) was compared in terms of turbidity and NOM removal, as well as acute toxicity on *Daphnia magna* of coagulated and coagulated/chlorinated surface water. The coagulation experiments were carried out by jar test using low TOC and high alkalinity surface water. Turbidity and NOM removal, as well as toxicity were investigated (i) under actual conditions, (ii) for different pH (5, 6, 7) and (iii) in HA spiked surface water samples. All coagulants decreased toxicity on *D. magna* from 100% to 0% immobilisation. However, the addition of HAs affected final toxicity in different ways according to coagulant type and dose. Moreover, the chlorination step after coagulation increased toxicity too according to the coagulant type as follows: chitosan > FC > alum [100]. Good review of chitosan for C/F processes is given by Renault et al. [101].

3.1.6. Preformed polymeric iron chloride (PIC)

Conventional metal coagulants, such as polymeric and monomeric forms Al and Fe salts, are widely used in DWT, whereas alum salt is suspected harmful to human and living organisms [66]. In addition, a number of authors have reported that iron salts gave higher DOC removal than alum salts [102–104]. Consequently, increasing attention has been placed on ferric coagulants [105], especially polyferric coagulants which have a lot of advantages over monomeric forms Fe salts, such as wider working pH range, lower sensitivity to water temperature and lower residual ferric concentrations [106]. Moreover, the removal of HSs by polyferric coagulants has been a well-established option, and the mechanism involved was well understood [107]. However, the coagulation performance of metal coagulants cannot satisfy the increasing demand for OM removal, and thus numerous researchers have focused on the use of organic polymer in DWT, such as PDADMAC. Chang et al. [108] found that the PDADMAC not only removes the turbidity effectively, but also reduces the formation of THMs significantly. However, the high cost of PDMDAAC limits its comprehensive application in DWT.

Jar tests [109] were conducted using synthetic waters containing model colloids and organics to evaluate the coagulation performance of simple $FeCl_3$ and polymeric iron chloride (PIC) having various polymer yield. Coagulation of synthetic model waters with PICs of different hydrolysis ratios was compared to simple FC under varying conditions of pH and model water concentrations. The use of PICs seemed to produce similar reduction in turbidity and TOC when compared with using $FeCl_3$ as a coagulant under typical range for coagulation; however, treatable region was broadened to lower pHs for coagulation of both model waters. By eliminating the region of restabilisation of turbidity at lower pHs, an additional region for coagulation using PICs at pH 5–6 was observed. A conceptual surface charge distribution when using different coagulants was established to explain the restablisation observed in this study. The different coagulation behaviours of PICs when compared to simple $FeCl_3$ are probably due to their larger sizes and bearing lower charge density.

3.2. Viruses removal

During DWT [110], coagulation is an essential process for combining small particles into larger aggregates. Small particles in the drinking water source, such as viruses, that will not settle from suspension by gravity are destabilised and combined into larger aggregates during the coagulation process; this allows the small particles to be effectively removed by subsequent sedimentation and filtration processes. Several studies have reported the usefulness of the coagulation process for the removal of enteric viruses and bacteriophages, which are viruses that infect bacteria [111,112].

Some bacteriophages have been evaluated as possible indicators for enteric viruses. For instance, F-specific RNA bacteriophage concentrations are highly correlated with those of enteric viruses in a wide range of water environments and water treatment processes [110]. Because of their morphological similarity to hepatitis A viruses and polioviruses, F-specific RNA bacteriophage MS2 is widely used as a surrogate for pathogenic waterborne viruses in Europe and the United States [110], whereas the F-specific RNA bacteriophage Qβ tends to be used as a surrogate in Japan [113].

Previous studies have compared the behaviors of Qβ and MS2 in the physicochemical treatment process. Their behaviours are similar in the process of adsorption onto solid surfaces (such as cellulose, kaolin, carbon black and river sediment), the sandy aquifer treatment process, and the direct MF treatment process, whereas the sensitivities of Qβ and MS2 to UV radiation are significantly different [110]. The behaviours of these two bacteriophages in the coagulation process may be different as well, although these differences have not been investigated except for previous studies of our research group. If significant differences do exist, then Qβ and MS2 cannot be used as equivalent surrogates to evaluate the effectiveness of treatment processes for the removal of pathogenic waterborne viruses.

Virucidal activity during the water treatment process has been widely investigated. UV as well as disinfectants such as free chlorine, chlorine dioxide, chloramines and ozone are well known to inactivate viruses [110]. A research group has reported the virucidal activity of aluminium coagulant [114]. The plaque forming unit (PFU) method in an attempt to determine the mechanisms and kinetics of the virucidal activity of aluminium coagulant was used [110]. During coagulation of the virus suspension, although the majority of viruses were entrapped in the aluminium floc particles, some of the viruses remained suspended in the liquid phase. Not all the suspended viruses were infectious; some were likely inactivated by the virucidal activity of aluminium coagulant. Thus, virus removal during the coagulation process includes two mechanisms: entrapment in floc particles and inactivation [115]. The PFU method, however, can detect neither the viruses entrapped in the floc particles nor the inactivated viruses judging from its measurement principle. Therefore, even though the virus concentration measured by the PFU method decreases in the liquid phase during the coagulation process, it remains unclear whether the decrease results from the entrapment in floc particles, inactivation, or both [110].

3.3. Algae removal

The eutrophication of surface water is a worldwide problem, which is increasing in significance [116]. Eutrophication is caused by excessive inputs of nutrients especially phosphorus that stimulate nuisance growth of algae. The omnipresence of algae caused by the eutrophication of surface water is the current and growing problem in the production of drinking water. To control the massive growth of algae in lakes and reservoirs, the impact of some chemicals such as copper sulphate, potassium permanganate, on algae were studied. Copper sulphate [$CuSO_4$ $5H_2O$] has been used to control nuisance algae in lakes and reservoirs for more than 80 years, and is considered to be an effective algicide available. Potassium permanganate was also studied on the specific use as an algicide for reservoirs [116].

In DWT, conventional coagulation is still the main treatment process for algae removal. Massive growths of algae have caused many problems. Some algae cause uncomfortable tastes and odours, some algae cause filter clogging, some algae can penetrate the filter, leading to the deterioration of drinking water quality. Algae are also a precursor of DBPs. Algae removal from water treatment process is difficult because of their small size and the low specific gravity [116].

It was reported that pre-treatment with oxidants may enhance the coagulation process and specifically enhance the removal of algae and other particulate matters in subsequent treatment steps [117–119]. The effects of chlorine, ozone and chlorine dioxide on *Scenedesmus* sp. cultures were studied [120]. Algal cells activity and chlorophyll concentration decreased, and the concentration of dissolved organic substances increased with increasing applied oxidant concentration. It was found that pretreatment with chlorine dioxide (1, 3 or 5 mg l^{-1}) or ozone (2.6, 4.6 or 8.1 mg l^{-1}) on algal cultures enhanced algal coagulation with aluminium sulphate, while prechlorination with 10 or 20 mg l^{-1} chlorine increased the required dosage of alum by 15%. However, the negative effect of using chlorine and chlorine dioxide resulting from the formation of by-products are limiting the use of these chemicals as pre-oxidants. In addition, it was recently recognised that the ozonation of waters containing bromide may lead to the formation of bromate at a level suspected of being hazardous to health, which is a negative aspect for using ozone as a preoxidant.

Potassium permanganate has been investigated as an alternative preoxidant for the direct filtration of impounded surface water. The experiments of modified jar test apparatus and pilot plants showed that permanganate pre-treatment followed by coagulation with dual coagulants (ferric sulphate and cationic polymer) distinctly improved the particle and algae removal commonly achieved in direct filtration [121]. It is suggested that the common mechanism of algae removal by oxidant is the destruction of the algae architecture to various extent through different ways of oxidation.

Potassium ferrate [K_2FeO_4] is another strong oxidising agent, which has a strong redox potential through the entire pH range, ranging from −2.2 V in acid to −0.7 V in base [120]. Several investigations have been conducted in applying potassium ferrate as a favourable alternative disinfection to chlorine for the disinfection of water and wastewater [122–125]. It is found that ferrate(VI) ion appeared to be an effective antifoulant [116], as only short contact times were required for ferrate concentration of 10^{-5} M to control the biofilm growth. In addition, recent study found that ferrate treatment did not produce any mutagenic by-products during the treatment process [126].

On the other hand, excess growth of cyanobacteria [127] and needle-like diatoms affects the coagulation efficiency in flocculation and sedimentation processes [128,129]. A dose increase of coagulant is a tentative way to improve the coagulation efficiency, but this creates subsidiary problems, including an increased cost for the coagulant and sludge treatment.

Some researchers have reported that algogenic organic matter (AOM) is involved in the reduction of coagulation efficiency [130], and one of the inhibitory mechanisms is that AOM can form complexes with cations in coagulant, which deteriorates the coagulation ability of the coagulant [131]. It has also been reported that the formation of polynuclear mixed ligand complexes between AOM and metals in the coagulant gives rise to an increase in the dissolved and colloidal coagulants that cannot be effective in the coagulation process [132]. However, AOM that can chelate metals in the coagulant and contribute to the reduction of coagulation efficiency have yet to be identified. The identification of constituents of AOM forming complexes with coagulant could lead to the elucidation of the inhibition mechanism, which makes it possible to establish alternatives to overcome the interferences of the coagulation process caused by the excess growth of cyanobacteria [127].

4. Optimisation of the coagulation/flocculation process

The presence of unsetteable organic or mineral substances causes some problems in obtaining drinking water [133,134]. Generally, these substances are in colloid systems, i.e. the dispersed phase are about the particles of small sizes (about a few microns). The very significant specific surface area of the particles and the existence of a surface charge on these colloids explain the prevalence of surface forces over volume forces, which stabilise the systems and remove any possibility of elimination by spontaneous settling [135,136].

In some cases, the addition of mineral salts or organic compounds causes the agglomeration of these particles, allowing their elimination by decantation or filtration [137]. In most WTPs, the minimal coagulant concentration and the residual turbidity of the water are determined by the Jar-Test technique [138]. However, this often involves problems of excess or an insufficient coagulant, particularly during periods of fast variations of water quality. Understanding these phenomena requires taking into account the physical and chemical natures of the water to be treated [139]. Moreover, statistical and modelling studies have been performed which allowed the automation of the process for natural water with well-defined supplies and very different compositions [133].

It is known that the characteristics of the water are important in the particle-coagulant interaction [140]. The role of the pH is particularly significant in so far as it determines at the same time the electrical charge of organic and inorganic colloids and it is a major factor in the hydrolysis of aluminium salts [141]. According to Gregor et al. [142], pH control (adjustment to 5 or less before coagulation) improves soluble matter removal, with pH adjustment during the flocculation phases by lime addition. Moreover, several authors have studied the influence of temperature on the pH and the minimum concentration of alum and on the initial turbidity [143].

Kawamura [144] has shown the importance of the nature of clay in suspension on residual turbidity and alum levels at optimum flocculation. Moreover, the presence of HSs in natural water causes some problems, for instance brown-red colouring. According to several studies [133], for pH values between 6 and 8, their elimination depends on their adsorption on the aluminium hydroxides. Their chelating properties [133] interfere with the C/F process. According to Masion et al. [145], aluminium is poorly polymerised in flocs formed by C/F of OM. In the case of Vilgé-Ritter et al. [146], the removal of OM not only depends on the type of coagulant but also on the organic compounds: for alum, they have observed a greater efficiency at pH 7; with a good affinity of alum for polyhydroxyaromatic compounds. Polysaccharides, proteins and amino-sugars are not well coagulated by alum.

5. Application of electric field in some chemical processes

5.1. Electro-microfiltration

In order to increase the efficiency of microfiltration (MF), electro-MF has been used for the treatment of wastewater [147]. The control of membrane fouling by the application of external direct current (DC) electric fields has been studied in several applications, and in some cases a clear enhancement has been achieved. This treatment technology has been found to be capable of reducing the formation of filter cake and increasing the flux of filtrate [147]. MF enhanced by electric fields provides a very efficient technique for the removal from water of hydrophobically modified water soluble polymer. An electrically enhanced crossflow MF (EECMF) was used for the treatment of oxide-CMP (chemical mechanical polishing) wastewater [147]. However, there are few case studies of applications as pre-treatment step in wastewater treatment. It is also reported that electric fields treatment as non-thermal process are being developed to inactivate pathogenic microorganisms in food industry [147]. In addition, it was effective to remove nitrate ion by forming insoluble complex salt under electric fields [147].

Kim et al. [147] have evaluated the effect of electric fields application for the reduction of membrane fouling, the inactivation of microorganisms and the enhancement of particle coagulation. It was found that electric fields treatment prior to MF showed in large quantity of cumulative permeates than those in non-electric fields. This is attributed to the promotion of particle coagulation and interaction between particle and membrane surface. The number of active bacteria was reduced by electric fields treatment. This may be a positive result for the prevention of membrane biofouling as well as microbial inactivation. Coagulant dosage could also be saved about 75% compared with non-electric fields in terms of the 95% turbidity removal at 10 (kV cm^{-1}). Therefore, it is expected to improve the efficiency and the economics of the process by providing electric fields for wastewater treatment [147].

5.2. Phase equilibria modification by electric fields

The tendency of electrification of some unit operations is well pronounced. Indeed, the use of electric fields to favourably manipulate the thermodynamic and transport properties of mixtures, so that higher separation efficiencies can be achieved, is well proved [148]. The main focus was to understand and quantify the influence of electric fields on vapour-liquid, liquid-liquid, and solid-liquid systems, which have applications in solvent extraction, sorption, distillation, and vapour stripping. Such processes are widely used for treatment of wastes and sites contaminated with heavy metals, radionuclides, and organic solvents. Particular examples of applications of vapour-liquid-equilibria modification can be found in the separation of volatile organic compounds by either vapour stripping or distillation. Improvements can also be made in liquid-liquid extraction processes of Sr, Tc, and Cs by both thermodynamic and transport enhancements. Enhanced separations of metal ions by sorption can be used to remove such metal ions as Cs, Sr, Co, Pu, Cr, Cd, and Hg from aqueous solutions. Several discoveries have been made regarding the application of electric fields to modify equilibrium and enhance transport in multiphase systems. Technologies, such as electroextraction and electrosorption, have been identified for further research and development activities because they offer several benefits for tank waste treatment and environmental cleanup efforts. In electroextraction, electric fields are applied to solvent extraction systems to improve transport of chemical species and phase separation. A novel means for inducing phase inversion in a liquid dispersion that provides the opportunity for increased performance and improved process control has been devised. In electrosorption, an electric field is employed to enhance the capacity and kinetics of sorption of metal ions and anions by sorbents of high electrical conductivity and porosity. This process can be used in situ for groundwater treatment, and the sorbent can be readily regenerated by simply removing the electric field [148].

More details about electroextraction and electrosorption may be found elsewhere [148].

6. Electrophoresis

The scientist beginning a study of a material of biological origin or of a biological process is often faced with the problem of having to separate and examine the properties of molecules of high MW such as proteins and enzymes, nucleic acids, and complex lipids and carbohydrates. In almost all cases it is also necessary to cause a little damage as possible to the molecules so that their properties are not changed significantly. Thus current separation methods usually lean heavily on physical processes which cause the minimum disturbance to both the physical and chemical properties of the molecules and which result in the maximum retention of any biological activity which the molecule may possess [149].

Within the fields of protein and nucleic acid chemistry the vast majority of separation methods fall into three broad categories, namely those based on (1) size differences, those based on (2) differences in the electrical charge carried by the molecules, and those based on (3) some specific biological or chemical property of the molecules under investigation. It must be stressed at the outset that it is not always possible or necessary that these categories should be completely distinguished from one another. For example some separations based primarily on charge differences are influenced to some extent by size differences. However, separation methods which are based mainly on size differences, such as gel filtration, ultrafiltration, and the use of ultracentrifuges, and also methods based on some specific property of the molecules, such as affinity chromatography, immunoadsorption, precipitation procedures, etc., fall outside the scope of this review and will not be considered further [149].

The two general areas covered by separations based completely or largely on charge differences between molecules include those using ion-exchange media and those using the various forms of EP. The former can be used for both analytical and preparative work and may be comparatively readily scaled up to the industrial scale. Although the different methods of electrophoretic separation have their own particular advantages and disadvantages, at present they are all confined to the analytical or small-scale preparative range. At the analytical level electrophoretic methods can be unrivalled for resolution and sensitivity [149].

6.1. Basic principles of electrophoresis

The term EP is used to describe the migration of a charged particle under the influence of an electric field [150]. Under conditions of constant velocity the driving force on the particle is the product of the effective charge on the particle Q and the potential gradient E, and this is balanced by the frictional resistance f of the medium. In free solution this obeys Stokes' law so that

$$f = 6\pi r v \eta \tag{7}$$

where r is the radius of the particle moving with velocity v through a medium of viscosity η. However, Stokes' law in not obeyed strictly in gels, and f then depends on a number of factors which include gel density and particle size [151].

The EM m is defined as the distance d travelled in time t by the particle under the influence of the potential gradient E so that

$$m = d/tE \quad \text{or} \quad m = v/E \tag{8}$$

Thus measured migration distances are proportional to EMs but direct comparisons between different experiments can only be made if the products tE are equal in all cases. It also follows that, ideally, if all other conditions are equal a second experiment run at double the potential gradient (voltage) for half the time would result in the particle migrating the same distance d as in the first experiment. However, this relation is only approximately true and it is influenced by a number of factors including particularly the effects of the extra heat generated by increasing current. Nevertheless, a quick calculation of volts multiplied by time can be a useful rough practical guide when seeking an idea of how altering either of these two factors will influence the course of an electrophoretic separation [149].

The potential gradient E also corresponds to the ration of the current density J to the specific conductivity κ, so the velocity of the charged particles can also be expressed as

$$v = Em = mJ/\kappa \tag{9}$$

Most of the large molecules with which we will be concerned possess both anionic and cationic groupings as part of their structure and hence are termed zwitterions. Since the dissociation constants (p*K* values) of these groups will differ widely, the net charge on such a molecule will depend upon the pH of its environment so that pH will also influence the mobility of the molecule. The ionic strength determines the electrokinetic potential which reduces the net charge of the effective charge and it is found that the mobility of the charged particle is approximately inversely proportional to the square root of the ionic strength. Low ionic strengths permit high rates of migration, while high ionic strengths give slower rates but in practice sharper zones of separation than low ionic strength buffers [151].

Unfortunately, the higher the ionic strength of the buffer the greater the conductivity and the greater the amount of heat generated. Increasing temperature causes an increase in the rates of diffusion of the ions and also an increase in the ionic mobility amounting to about 2.4 per cent per degree Celsius rise in temperature. At the same time the viscosity of the medium falls with rising temperature. Thus the electrical resistance decreases and at a constant voltage the current will rise increasing the heat output still further. The choice of buffer strength then may be seen to be crucial since it effectively determines the amount of electrical power which can be applied to the system. Too high a power input results in excessive heat generation which may lead to an unacceptable rate of evaporation of solvent from the medium, and in free-solution systems can result in convection currents and a mixing of separated zones. In cases which are rather sensitive to heat there may even be a denaturation of proteins or a loss of enzymic activity. In contrast, too low a power input may overcome any heating problem but can also lead to poor separations as a result of the increased amount of diffusion that may occur in the running time is too long [149].

The removal of heat generated by the passage of the electrical current is one of the major problems for most forms of EP since cooling inevitably results in the formation of a temperature gradient between those parts of the medium that are better cooled than others. Because of the factors discussed above, any temperature gradient or temperature difference will lead to distortions in the bands of the separated molecules due to variations in the rates of migration through the medium. In the forms of EP carried out in cylindrical tubes or in slabs cooling is more effective at the outer edge of the medium than in the middle and curved band results [149].

We can see then that the basic concept of EP is a very simple one but that the progress of the charged particle or ion through the medium is influenced by an almost bewilderingly large number of factors. However, it is precisely because of these various influences, that the principle can be turned to good use by the investigator. For example, if size was not a factor there would be no separation between a large particle with a particular charge and a small one with a similar charge. Likewise, a non-homogeneous supporting matrix is deliberately introduced in the technique of gradient gel EP to aid separation, while an equalisation of the charges of cationic and anionic groups to give molecules with no net charge is the basic requirement for isoelectric focusing [149].

EP utilises a difference in movement of species in a separation channel or space for their spatial separation [152]. A basic partial differential equation that results from the balance laws of continuous processes in separation sciences is the nonlinear conservation law or the continuity equation. Attempts at its analytical solution in EP go back to Kohlrausch's days. Recently, Gaš [152] (i) has reviewed derivation of conservation functions from the conservation law as appeared chronologically, (ii) deals with theory of moving boundary equations and, mainly, (iii) presents the linear theory of eigenmobilities. It shows that a basic solution of the linearised continuity equations is a set of travelling waves. In particular cases the continuity equation can have a resonance solution that leads in practice to schizophrenic dispersion of peaks or a chaotic solution, which causes oscillation of electrolyte solutions [152].

Apparatus for conducting EP, such as that illustrated in Fig. 8 [150], is remarkably simple and low cost. The gel medium, which is supported on glass plates, is inserted into a Plexiglass chamber. Two buffer reservoirs make contact at each end of the gel. Electrodes immersed in the buffers complete the electrical circuit between the gel and power supply. Many samples can be separated simultaneously, since it is possible to use a multilane gel. One or two lanes are frequently reserved for standard mixtures to calibrate the electropherogram. Calibration is usually based on molecular size or in isoelectric focusing [150].

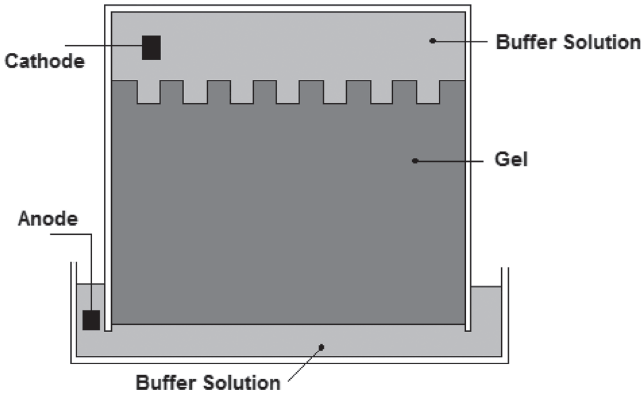

Fig. 8. Drawing of an apparatus for slab-gel EP [150].

6.2. Dynamic computer simulations of electrophoresis

In the seventies and early eighties, computers became available and researchers began to develop simulation models for EP. These efforts were driven by the interest of exploring the dynamics of electrophoretic processes [153], including those associated with zone EP (ZEP), moving boundary EP (MBEP), and thereby identifying the underlying chemical and physical processes involved in the separation of charged compounds in solution under the influence of a DC electric field. The models are based upon equations derived from the transport concepts in solution together with user-inputted conditions, such as concentrations, mobilities, diffusion coefficients, p*K* values, electric field strength or current density, column length and its segmentation, and chip EP [154–159].

6.3. Electrophoresis is an induced phenomenon in electrocoagulation process

From the above short description, we can conclude that EP – effective method of separation – since it depends upon DC electric field using two electrodes (anode (+) and cathode (–)) as for EC - for which the anode is sacrificial – take place in the EC device. However:

1. In EC process, we have not to separate the molecules of high MW such as proteins and enzymes, nucleic acids, and complex lipids and carbohydrates, we have to remove NOM (HSs) and OMs from water.
2. In EP process, within the fields of protein and nucleic acid chemistry the vast majority of separation methods fall into three broad categories, namely those based on (1) size differences, those based on (2) differences in the electrical charge carried by the molecules, and those based on (3) some specific biological or chemical property of the molecules under investigation. In EC process, we have also these separation methods which are more complicated with metal ion liberation from the anode and hydrogen liberation from the cathode.
3. The term EP is used to describe the migration of a charged particle under the influence of an electric field. The term EC is used to describe the in situ production of Al^{3+}/Fe^{2+} instead of aluminium/iron salt adding as in the case of conventional coagulation where the migration of a charged particle under the influence of an electric field take more place.

6.4. Indecisiveness of electrophoretic mobility determination in evaluating Fe(III) coagulation performance

Coagulation using a hydrolysable metal salt (HMS) like FC is an important process for removing particles in water industry [160]. The removal of particles in an HMS coagulation is thought to occur via two primary mechanisms: CN and SC [161]. Dosed HMS can be quickly and evenly distributed into water during the first stage of a coagulation process, rapid mixing. Many hydrolysed species are formed very quickly upon HMS addition. Most of these species are positively charged and believed to lower the repulsive forces between the negatively charged particles by CN. The second stage, flocculation, is to agglomerate particles by chemically joining or bridging them together. SC occurs in which voluminous flocs are formed. The water is clarified when flocs that contain particles are separated from water [160].

In the field of coagulation, EM is utilised to characterise the electrostatic charge of particles and to judge whether the particles are destabilised. Most particles in a natural aqueous system are negatively charged, reflected as negative EM [23]. During Fe(III) coagulation, the negatively charged particles are neutralised by positively charged Fe(III) hydrolysis species. As a consequence, the negative EM of particles shifts towards a more positive direction. Many studies have been conducted to establish the relationship between the particle removal efficiency and the changes in the EM, such as sign reversal [160,162]. These studies indicate that an effective Fe(III) coagulation performance is produced when the suspension EM is close to zero. An ineffective coagulation process is usually attributed to the restabilisation of particles in the case of excessive coagulant dosage marked by a highly positive EM, or stabilisation in the case of underdose reflected as a highly negative EM [160,162]. However, there are also some conflicting views. Letterman et al. [23] pointed out that, when an HMS is used, it is inconsistent and difficult to interpret coagulation behaviour through EM or ZP measurement in certain cases [23]. Furthermore, when flocs are formed, some particles can be enmeshed by flocs. Whether the SC efficiency depends on suspension EM is a question to date.

In their study [160], the significance of EM determination in evaluating Fe(III) coagulation performance was questioned. It was found that SC, an important coagulation mechanism for particle removal, was independent of the surface charge of particles reflected as EM; there was no decisive relationship between coagulation performance and suspension EM. The coagulation behaviour cannot be simply predicted on the basis of EM measurement. A highly positive EM or a highly negative EM did not contradict the fast growth of flocs or high turbidity removal efficiency. A good coagulation performance was not necessarily produced when EM was about zero. As long as the solution pH and Fe(III) concentration favoured the formation and fast growth

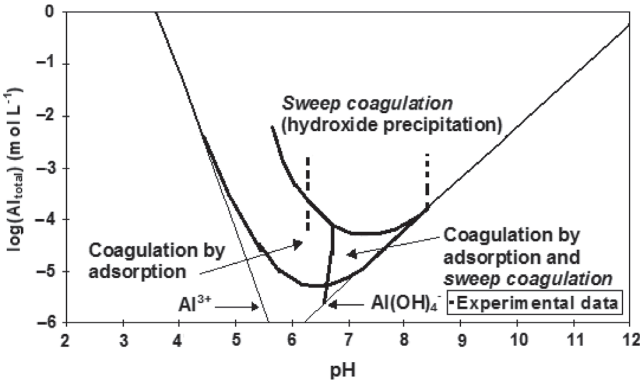

Fig. 9. Coagulation diagram for alum [133].

of ferric hydroxide precipitate, Fe(III) coagulation performed well regardless of the suspension EM. Without flocs, coagulation through CN proceeded slowly and particle removal efficiency was low. Therefore, suspension EM or the surface charge of particles becomes less insignificant if a fast coagulation process and high particle removal efficiency are required. In the studies of the particle aggregation without voluminous flocs enmeshing particles, the EM would still be a useful parameter because in this case particle aggregation is mainly induced by the double layer compression and/or CN.

Furthermore, by monitoring the floc growth rate and suspension EM, the floc formation region was constructed within the solubility diagram of ferric in equilibrium with amorphous $Fe(OH)_{3(am)}$. It was found that CN and restabilisation also existed within the floc formation region. CN and *SC* usually occurred sequentially (Fig. 9) during Fe(III) coagulation if flocs were formed [160].

7. Electrocoagulation

EC [163] is a process consisting of creating metallic hydroxide flocs within the water by electrodissolution the soluble anodes, usually made of iron or aluminium [164]. The difference between EC and CC is mainly in the way of which iron/aluminium ions are delivered [165]. In EC, coagulation and precipitation are not conducted by delivering chemicals – called coagulants – to the system, but via electrodes in the reactor [166,167].

EC is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges [168]. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralised and several particles combine into larger and separable agglomerates [169]. Electrode assembly is the heart of the treatment facility [170]. Therefore, the appropriate selection of its materials is very important. The most common electrode materials for EC are aluminium and iron. They are cheap, readily available, and proven effective [171].

The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the EC process. EC has occurred in three steps: in first step, coagulant has formed because of oxidation of anode; in second step, pollutants have destabilised; and in last step, destabilised matters have united [172,173].

As seen above, CC results from two basic mechanisms; perikinetic or electrokinetic coagulation in which the ZP is reduced by ions or colloids of opposite charge to a level below the van der Waals attractive forces and orthokinetic coagulation, in which the micelles aggregate and form clums which agglomerate the colloidal particles [162, 163].

7.1. The pH as a key parameter in coagulation and electrocoagulation

In both coagulation processes (chemical and electrochemical) it is common the use of aluminium or iron reagents as coagulants [30,174,175].When these reagents are added to the wastewater, different hydrolysis species are formed. According to literature [133,176], the main parameters influencing the speciation are the pH and the metal concentration (Fig. 9). In this context, it is widely reported the formation of monomeric hydroxometallic ions that coexist with the metallic hydroxide precipitates. The aluminium hydroxide precipitate presents a minimum solubility in the region of pH 6 and the chemistry of monomeric ions is complex and it influences significantly on the coagulation process. On the contrary, ferric hydroxide precipitate shows a much lower solubility over a rather broad pH range and this limits the influence of the monomeric species on the coagulation results [177]. As well, in addition to these species, it is reported the formation of polymeric hydroxometallic ions, especially under high metal concentrations [178,179]. All these hydrolysis metal species can interact with different types of pollutants, achieving their removal from the wastewaters. These interaction processes are strongly related to the metal speciation, and they can be summarised into three main types:

- The metallic ionic monomeric species can neutralise the charge of the pollutants by adsorption on their surfaces (or by binding to their ionised groups).
- The metallic ionic polymeric species can bind to several particles (or molecules) of pollutant at a time.

- The pollutants can be enmeshed into growing metallic hydroxide precipitates, or can be adsorbed onto their surfaces [180].

7.2. Electrocoagulation and electroflotation for wastewater treatment

Among the electrochemical technologies [181–183], EC and EF may be effective substitutions for conventional coagulation and flotation in a wastewater treatment process [162,184]. EC/EF has been reported to successfully treat wastewater of different kinds, containing oil [171,185,186], fluoride [187], arsenic [188], dyes [189–192], suspended particles [193–195], surfactants [196,197], HA [198], chromium ions [199], phosphate [172], microorganisms [200] and so on. As mentioned above, EC is an electrochemical technology of treating polluted water whereby sacrificial anodes dissolve due to an applied potential, thus producing active coagulant precursors. EC is a complicated process with a multitude of mechanisms operating synergistically to remove the pollutants in wastewaters. It offers the possibility of anodic oxidation and in situ generation of active adsorbents (such as hydrous ferric oxides, hydroxides of aluminium). At the same time cathodic reactions occur and the evolution of hydrogen gas is involved, causing flotation of the absorbents. Good reviews of EC were given by Chen [201], Mollah et al. [202], and Holt et al. [203]. In the EC cell, the electrochemical reactions with metal Al as electrodes are as follows [163,181,204–206]:

At the cathode:

$$3H_2O + 3e^- \rightarrow (3/2)H_{2(g)} + 3OH^-_{(aq)}, \quad \text{for flotation} \tag{10}$$

$$2Al_{(s)} + 6H_2O + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4\,(aq)} + 3H_{2(g)} \tag{11}$$

At the anode:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-, \quad \text{for CN} \tag{12}$$

$$2H_2O \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \quad \text{for flotation} \tag{13}$$

In the solution:

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)} \quad \text{for SC (at acid pH)} \tag{14}$$

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} \quad \text{for SC (at alkaline pH)} \tag{15}$$

Reactions (11) and (15) may be more pronounced when pH is alkaline and Reaction (14) will be at acid conditions [207]. The Al^{3+} ions generated immediately hydrolyse to produce corresponding hydroxides and/or polyhydroxides in adequate pH. The Al hydroxides and polyhydroxides from the electrochemical dissolution were reported to have stronger affinity to capture the pollutants in the wastewater, causing more coagulation than those from the conventional Al coagulants. Additionally, the gas bubbles that evolve due to the water electrolysis (EL) can cause flotation of the pollutants and the coagulated materials. Therefore, EF may also play an important part in an EC cell. Although the $Al(OH)_3$ produced by the anodic Al dissolution is thought more active to coagulate the pollutants in wastewater, the passivation of Al anodes and impermeable film formed on cathodes may interfere with the performance of EC and EF [203]. The formation of an inhibiting layer on the Al electrode surface prevents Al dissolution and electron transfer, limiting Al^{3+} to the solution. As a result, the EC system is usually designed to operate in a condition of high voltage, usually higher than 10 V, to break down the inhibiting layer. The energy consumption is thus high and the electrodes are likely to be destroyed when using a high voltage for the long-term operation [181].

For iron electrodes, a study on mechanism of EC with Fe electrodes in idealised conditions is presented in our paper [208].

7.3. Electrocoagulation for virus removal

Zhu et al. [209] studied virus removal by iron EC followed by MF in water treatment using the MS2 bacteriophage as a tracer virus. In the absence of EC, MF alone achieved less than a 0.5-log removal of MS2 virus, but, as the iron-coagulant dosage increased, the log virus removal increased dramatically. More than 4-log virus removal, as required by the Surface Water Treatment Rule, was achieved with 6–9 mg $Fe^{3+}\ l^{-1}$. The experimental data indicated that at lower iron dosages and pH (< ~8 mg Fe l^{-1} and pH 6.3 and 7.3) negatively charged MS2 viruses first adsorbed onto the positively charged iron hydroxide floc particles before being removed by MF. At higher iron dosages and pH (> ~9 mg Fe l^{-1} and pH 8.3), virus removal was attributed predominantly to SC and subsequent removal by MF. Additionally, the experimental data showed no obvious influence of ionic strength in the natural water range of 10^{-7}–10^{-2} M on MS2 virus removal by EC-MF. Finally, EC pretreatment significantly outperformed CC pretreatment for virus removal. The proposed mechanism for this improved performance by EC is that locally higher iron and virus concentrations and locally lower pH near the anode improved MS2 SC by iron flocs as well as adsorption of MS2 viruses onto the iron floc particles [209].

8. Electrolysis

8.1. Introduction

The word "lysis" means to dissolve or break apart, so the word "electrolysis" (EL) literally means to break substances apart by using electricity [210]. Michael Faraday first formulated the principle of EL in 1820. The process occurs in an electrolyte, a watery solution or a salt melting that gives the ions a possibility to transfer between two electrodes. The electrolyte is the connection between the two electrodes, which are also connected to a DC. If you apply an electrical current, the positive ions migrate to the cathode while the negative ions will migrate to the anode. At the electrodes, the cations will be reduced and the anions will be oxidised. EL is the chemical decomposition and/or dissociation of organic and inorganic substances by an electrical current. The electrolytic cell contains an anode and a cathode, where separate oxidation and reduction reactions occur [210].

In the anode, there are the following oxidation reactions:

$$\mathrm{Me_1(insoluble)} = \mathrm{Me_1^{\mathit{m}+}(soluble)} + me^- \qquad (16a)$$

$$4\mathrm{OH^-_{(aq)}} = 2\mathrm{H_2O} + \mathrm{O_{2(g)}} + 4e^- \qquad (16b)$$

$$2\mathrm{Cl^-_{(aq)}} = \mathrm{Cl_{2(g)}} + 2e^- \qquad (16c)$$

Where Me_1 is metal in the anode. The electrode metal enters into the reaction, losing a flow of electrons to the electrode.

In the cathode, the following reduction reactions occur:

$$\mathrm{Me_2^{\mathit{m}+}(soluble)} + me^- = \mathrm{Me_2(insoluble)} \qquad (17a)$$

$$2\mathrm{H^+_{(aq)}} + 2e^- = \mathrm{H_{2(g)}} \qquad (17b)$$

Where Me_2^{m+} is the soluble ion in the solution.

Hydrogen gas produced at the cathode creates turbulence in the system, which can enhance the mixing. The gas also serves to transport the insoluble coagulated particles to the surface of the solution. Thus, a floating layer is formed at the liquid surface consisting of both hydrogen bubbles and entrapped suspended matter [210].

For an individual electrode, the net current flowing through the wire to the electrode is the difference between the anodic and cathodic currents developed by the electrode reactions at the electrode interface. The utilisation of electrolytic precipitation for isolating a number of elements from aqueous solution has been practiced by analytical chemists since the 19th century [211]. The principles can be grouped into two basic categories: (a) EL at constant applied cell potential for the deposition of certain elements, and (b) EL at variable potential to maintain convenient current through the cell for the deposition of a large group of elements. It is obvious that such techniques can be applied to the area of wastewater treatment for the removal of undesirable elements. In addition to the dissolution of anodic metals or generation of oxygen, other strong oxidising agents, e.g., chlorine, can be generated in the anode if the appropriate types of electrolyte are present in solution. For the generation of chlorine, high levels of chlorine are needed for the process to be economically feasible.

Electrochemical methods for treatment of wastewaters are not a new concept; as early as 1887, Eugene Hermite [210] described a method of treating sewage by electrolysing after mixing with seawater. He found that in addition to deodorising and disinfecting effects, $Mg(OH)_2$ was produced as a flocculant in the process, which helped to lower sewage solids effectively.

A series of techniques was then developed. Most of these required the use of sacrificial electrodes such as iron or aluminium to aid in sludge flocculation and the addition of chloride for the generation of chlorine for disinfection. Several studies utilising such methods have been described in the literature and in patents, most of which are similar in principle with minor modifications in the process or design of the electrode [210]. There has been a strong emphasis on development of electrochemical processes for wastewater treatment. Although the economic advantage of these processes over conventional secondary-tertiary processes has not been fully demonstrated, some studies show that EL is a promising method [212,213].

Earlier electrolytic wastewater treatment had been directed toward the generation of $C1_2$ or O_3 for the deodorisation and disinfection of wastewater, or toward controlling part of another treatment process [214]. Most electrolytic odour control systems destroy malodorous emissions by oxidation. Ozone, although not strictly an electrolytic process in the usual sense, nevertheless must be produced at the treatment site by electrical means. The process, using a high-voltage alternating current (AC) silent discharge in air or oxygen gas, can eliminate shipping of dangerous materials. The large-scale use of EL to treat sewage was demonstrated in a coastal area (Guernsey, England) as shown in Fig. 10 [210]. The plant, which was constructed by CJB Process Ltd. in 1965, disinfected raw sewage with

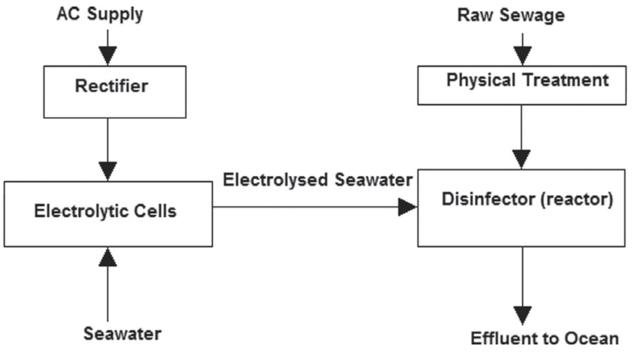

Fig. 10. Simplified flow sheet of processes used in CJB Guernsey plant [210].

Table 5
List of important chemical reactions in EC [210]

Location	Reaction[a]
Anode	$4OH^-_{(aq)} = 2H_2O + O_{2(g)} + 4e^-$ $2Cl^-_{(aq)} = Cl_{2(g)} + 2e^-$ $Al_{(s)} = Al^{3+}_{(aq)} + 3e^-$ (when Al is applied) $Fe_{(s)} = Fe^{2+}_{(aq)} + 2e^-$ (when Fe is applied)
Cathode	$2H^+_{(aq)} + 2e^- = H_{2(g)}$ $O_{2(g)} + 2H_2O + 4e^- = 4OH^-_{(aq)}$
Solution phase	$nAl^{3+}_{(aq)} + mOH^-_{(aq)} = Al_n(OH)_m{}^{3n-m}_{(aq)}$ (when Al is applied) $Al^{3+}_{(aq)} + OH^-_{(aq)} = Al(OH)_{3(s)}$ (when Al is applied) $iFe^{2+}_{(aq)} + jOH^-_{(aq)} + kH_2O = Fe_i(H_2O)_k(OH)_j{}^{2i-j}_{(aq)}$ (when Fe is applied) $4Fe^{2+}_{(aq)} + 10H_2O + O_{2(g)} = 4Fe(OH)_{3(s)} + 8H^+_{(aq)}$ (when Fe is applied) $Fe^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2(g)} = Fe^{3+}_{(aq)} + 2H_2O$ (when Fe is applied) $iFe^{3+}_{(aq)} + jOH^-_{(aq)} + kH_2O = Fe_i(H_2O)_k(OH)_j{}^{3i-j}$ (when Fe is applied)

[a] i, j, k, m, and $n = 0, 1, 2, \ldots$.

a dose of electrolysed seawater that contained disinfectant (Cl_2) due to the reduction in the anode (Table 5) by the DC. CJB claimed that further improvement at Guernsey had halved the total processing time from 60 to 30 min, and reduced production costs to 2–3 cents per 3.78 m^3. The method, which had been used in operations on a much smaller scale at Sorrento, Italy, two years before the Guernsey plant, was shown to yield a final effluent that was aesthetically, hygienically; and economically acceptable.

In the United States, an EC cell utilising a metallic sacrificial anode as the generating source of coagulant was used by the General Electric Company as part of a shipboard waste-treatment system. Electrolytic waste treatments have been demonstrated over a considerable range of sizes and with various types of wastewaters in 1972. A similar approach was recently intensively studied by researchers such as Chen et al. [215]. The EC approach is used for treatment of food wastewater. These systems with increasing frequency may prove to be the optimum processing method where electric power is available and particularly where space and safety are prime considerations. Where electrolytes are neither present in nor available for addition to wastewaters, EL may be severely handicapped by the high electrical resistance of water.

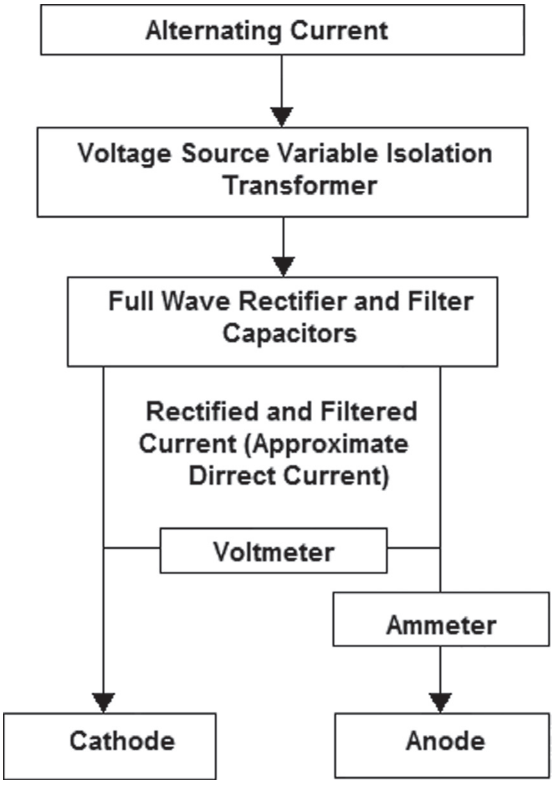

Fig. 11. Schematic of typical electrolytic cell [210].

8.2. Mechanisms of electrolysis

Electrochemical processes take place in an interfacial region between an electrode and an electrolyte where the mode of electric conduction changes from electronic to ionic. A schematic diagram of a typical EL cell is shown in Fig. 11. The kinds of reactions that predominate depend on the direction of current flow. The majority of the chemical reactions that have been useful for wastewater treatment occur at the anode, where chemical oxidation takes place. In most instances, the main cathode reactions produce hydrogen in water-disinfection applications more often a hazard than a desideratum. If heavy metal ions are present in wastewater, they may also be deposited on the cathode by the EL current. A process utilising this principle has been reported for recovery of metals from waste solutions [216]. The more toxic forms of chromium, i.e., Cr(VI), can be reduced to Cr(III) at a cathode, which is subsequently precipitated as $Cr(OH)_{3(s)}$ and removed from the waste stream. Copper ion in wastewater can be reduced to its elemental form in the cathode, which can be reused.

Under normal circumstances the cathodic removal efficiency for very low concentrations of trace metals would be extremely low. The most important use of cathodic reactions in water purification is the raising of pH by the hydrogen ion removal. High pH precipitates $Mg(OH)_{2(s)}$ in waters containing magnesium and facilitates the removal of insoluble phosphates and carbonates, as well as the removal of soluble phosphate and ammonia as $Mg(NH_4)PO_{4(s)}$. It is useful to consider the anodic reactions for wastewater treatment as following:

Sacrificial anodes: Metal ions are generated in the aqueous phase directly from the electrode material. The most useful appear to be Fe^{2+}/Fe^{3+} and Al^{3+}. The majority of the current is generated at the electrode surface by the loss of electrons in oxidising and dissolving the anode metal. The fate of the metal ions after dissolution depends on concentrations of the anion species. Both Fe^{3+} and Al^{3+} are precipitated as metal hydroxides in neutral solutions to produce flocs for flocculating suspended solids [215]. Direct reaction may also remove nutrients (e.g., phosphate) as insoluble precipitates [210].

Inert electrodes: The participants in the anode reactions all come from the solution as the anode material remains essentially unchanged. The reactions might include the oxidation of reduced metals, such as Fe(II) to Fe(III), or the discharge of negative ions, such as Cl^- or OH^-. The overall result of the discharge of Cl^- ions is usually the hydrolysis of $Cl_{2(g)}$ in the water. The discharge of OH^- usually results in the release of oxygen at the anode, a reaction that is, of course, favoured by high pH. The production of oxygen (or ozone) at the anode will tend to lower the pH in the anode region just as, conversely, the production of $H_{2(g)}$ at a cathode raises the pH in that region [210].

8.3. Organic and suspended solids removal

The effective oxidation of organic removal in various waste streams by the EL has been reported [202,203]. It can be used for treatment of industrial wastewaters, landfill leachate, and domestic sewage. Successful examples include colour removal and food wastewater treatment. Specific organic compounds such as phenols, tannic acid, lignin, EDTA, and aniline can be destructed by the approach [210].

8.4. Disinfection

It is normally required that the effluents after secondary biological treatment be disinfected before being discharged into nearby waters. Chlorination is the major method of disinfection [210]. Other methods such as UV radiation and ozonation are still more expensive or less convenient than chlorination for the disinfection of the effluents. It has been reported that the EL can kill a large spectrum of microorganisms including bacteria and algae [217–219].

During the process, the effluents flow through the contactors equipped with electrodes on which DC is charged. The effluent quality, nature of the electrodes, energy input, and other operational conditions influence the effectiveness of the process. It has been reported [210] that the process can generate a high disinfection efficiency within a short contact time for the secondary wastewater effluents and surface waters. Higher killing is normally observed in saline waters owing to the high content of chloride ions. The microbial killing is attributed to various functions, including electrochlorination, destruction caused by the electric field, and inactivation by strongly oxidative but short-lived intermediate radicals. The disinfection of microorganisms is due to oxidative stress and cell death caused by electrochemically generated oxidants, irreversible permeabilisation of cell membranes by the applied electric field, and electrochemical oxidation of vital cellular constituents during exposure to electric current or induced electric fields [217–219].

Electrochlorination refers to the production of common disinfectant chemicals such as Cl_2 and NaClO in saline waters during the EL process. Chlorine gas produced at the anode causes the disinfection of wastewaters, oxidation of OM, and bleaching of smaller degradation products. The following equations typify the reactions for this process:

$$2Cl^-_{(aq)} = Cl_{2(g)} + 2e^- \tag{16c}$$

$$Cl_{2(g)} + H_2O = HOCl_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \tag{18a}$$

$$HOCl_{(aq)} = H^+_{(aq)} + OCl^-_{(aq)} \tag{18b}$$

In dilute solutions and at pH levels above 4, the reaction showed in Eq. (18a) shifts to the right. The reaction shown in Eq. (18b) is also a function of pH and shifts to the right at pH > 7.5. The disinfection efficiency is generally close to 100% for total coliform groups after a detention time of 30 min or longer with a sewage-to-seawater ratio of 9:1. However, the ratio varies depending on sewage strength. In order to determine how much electrolysed seawater should be used, it is necessary to install an active-chlorine analyser that effectively measures the strength of the sewage [210].

Electrochlorination for disinfection has long been recognised. Other mechanisms also contribute to the killing. An electric field can cause the inactivation and destruction of microorganisms by a series of electrochemical reactions inside the cells and by electromechanical compression of the cell membrane. A series of short-lived and energy-rich free radicals generated during EL such as $OH^{\bullet}$ and $ClO_2^{-\bullet}$ plays a critical role in the killing. They are very unstable and difficult to detect; however, they are extremely reactive bactericidal agents and can provide nearly instant killing action. Chlorine ions in the saline solution can function as a catalyst to facilitate the generation of the short-lived free radicals and extend significantly their functional life by a factor as high as 10 [210]. As a result, the efficiency of microbial destruction is dramatically improved. Considering the short contact time and relatively low chlorine produced, it is quite unlikely that the main killing is chlorination. Therefore, Cl^- may act as a catalyst in the formation of free radicals, rather than as a precursor to $Cl_{2(g)}$ production.

A laboratory-scale EL disinfector was used for the disinfection of saline primary and secondary effluent (with a salinity content of around 8% and a chloride content of 4,800–5,000 mg l^{-1}), and freshwater secondary effluent (with a chloride content of 110–130 mg l^{-1}) [210]. A killing efficiency of 99.9% on total coliform bacteria was achieved when the contact time of less than 10 and 20 s and the power consumption of 0.006 and 0.08 kWh m^{-3}, for the saline secondary effluent and the saline primary effluent, respectively. However, a similar degree of effectiveness for freshwater sewage effluent was not observed, even with a longer contact time and higher power input.

Few such studies have been conducted with viruses (such as [209]). It is expected that viruses are more resistant to electrochemical inactivation than bacteria. For example, bacteriophage, one of important viruses in water treatment, is not enveloped with a membrane and would be immune to inactivation processes involving irreversible membrane permeabilisation. Even enveloped viruses are more resistant than bacteria due to their smaller size. In addition, viruses tend to be more resistant to commercially used chemical disinfectants (e.g., chlorine) than vegetative bacteria. Drees et al. [220] reported that bacteriophages survived short exposures to various current magnitudes in an electrochemical cell better than bacteria at both low and high population density [220]. The inactivation rate of bacteria exposed to a low current magnitude (5 mA) for an extended time ranged from 2.1 to 4.3 times greater than that of bacteriophages, indicating that bacteria are more sensitive to EL than bacteriophages. It was found that electrochemically generated oxidants were a major cause of inactivation within the electrochemical cell.

Since viruses are more resistant than bacteria to the electrochemical inactivation, use of this technology in fields that affect human health (such as drinking water disinfection) must ensure the destruction of viruses, not just bacteria, in order to consider the treated medium safe. Another disadvantage of its application for water disinfection is the formation of undesirable DBPs. These compounds are not only formed in the disinfection, but also in its application for OM if the chloride ions are present in the solution. The by-products include chloroform, chloromethane, bromodichloromethane, and 1,1,1–trichloroethane; they are suspected human carcinogens. Careful control and management are therefore important [210].

9. Electroflotation

9.1. From flotation to electroflotation

Recently, the technique of flotation has emerged as a unit process for effluent treatment [221]. The adsorbing colloid flotation, in particular, has been shown to be a powerful technique for the removal of traces of toxic metals from effluents, on both laboratory and pilot plant scale. The technique of adsorbing colloid flotation involves the preparation of a suitable colloid, like $Fe(OH)_3$, $Al(OH)_3$, HgS, etc., in the effluent in order to adsorb the toxic metal ions on the surface and then effect the solid-liquid separation by flotation after adding a suitably chosen surfactant. One of the major hindrances for the scale up of this technique is the high cost of the surfactants. It has been argued that the use of a surfactant with a proper charge, i.e., opposite to the surface charge on the colloid, is essential to affect such a flotation. There are two theoretical models which have been suggested to describe the process of flotation. According to the first model, the surfactant is first adsorbed at the gas-water interface charging electrically the bubble surface with a charge opposite to that of the colloid, so that the colloid is attracted to the rising bubble. The second model assumes that the surfactant is first adsorbed on the colloid surface, making the surface hydrophobic, and thus forcing the colloid to the surface of the rising bubble. However, in practice both mechanisms operate [221].

Manohar et al. [221] have shown that the EF of colloidal $Fe(OH)_3$ does not require any surfactant and that the flotation efficiency is independent of the surface charge of the colloid. It is further shown - using powdered activated carbon - that coagulation is the sufficient condition for flotation provided that there are a large number of small bubbles. A formula for flotation efficiency based on the coagulation theory is derived and it is shown that this model qualitatively describes all the observed aspects of flotation.

9.2. Electroflotation for oil field effluent water treatment

EF [222] is a simple process that floats pollutants to the surface of a water body by tiny bubbles EL. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively. The EF technique depends upon generation of hydrogen and oxygen gases during EL of water. Gas bubbles formed on electrode surface contact with oil drops; then the attached oil–gas combinations rise up to the surface where oil may be removed by any skimming method.

EF technique has three principal advantages:

- First, dispersed gas bubbles formed from EL are extremely fine and uniform (with average bubble diameter around 20 µm).
- Second, varying current density gives the possibility of varying any gas bubble concentrations in the flotation medium, thereby increasing the probabilities of bubble-oil drop collision. Third, selection of appropriate electrode surface and solution conditions permits one to obtain optimum results for a specified separation process [223].

Bande et al. [222] studied the separation of finely dispersed oil from oil–water emulsion which was carried out in an EF cell which has a set of perforated aluminium electrodes. The effects of operating parameters on the performance of batch cell were examined. The parameters investigated are pH, voltage, oil concentration, flotation time, and salinity. The batch experiments have been conducted to optimise electrical input in the effluent. It was observed that at 5.0 V and 0.4 A current is optimum and for this condition the energy consumption was 0.67 kWh m^{-3}. The optimal treatment time was observed at 20 min. Also oil removal efficiency is 90% at pH 4.72 in 30 min treatment time for 50 mg l^{-1} concentration of oil and 94.44% of oil removed within 30 min at 4 mg l^{-1} of salinity. It has also been observed that decrease in salinity and increase in oil content of the effluent enhances the efficiency of the EF process.

10. Conclusion

1. The difference between EC and CC is mainly in the way of which aluminium/iron ions are delivered. In EC, coagulation and precipitation are not conducted by delivering chemicals – called coagulants – to the system, but via electrodes in the reactor.
2. EC is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralised and several particles combine into larger and separable agglomerates.
3. Since EP depends upon DC electric field, using anode (+) and cathode (–) as for EC for which the anode is sacrificial, it takes place in the EC device and contributes to its performance. Indeed, the first responsible mechanism of EC performance is the migration to an oppositely charged electrode, i.e., EP, and aggregation due to CN. Hence, EP contributes essentially to EC efficiency as EF does with $H_{2(g)}$ bubbles liberation from the cathode. The EF's contribution may be increased when $O_{2(g)}$ is produced from the anode, at the same time with metal ion liberation.

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References

[1] E.M. Vrijenhoek, A.E. Childress, M. Elimelech, T.S. Tanaka and M.D. Beuhler, Removing particles and THM precursors by enhanced coagulation, J. AWWA, 90 (1998) 139–150.

[2] Federal Register, Revisions to the Interim Enhanced Surface Water Treatment Rule (IESWTR), the Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1DBPR), and Revisions to State Primacy Requirements To Implement the Safe Drinking Water Act (SDWA) Amendments, 66(10), January 16 2001.

[3] P. Bose and D.A. Reckhow, The effect of ozonation on natural organic matter removal by alum coagulation, Water Res., 41 (2007) 1516–1524.

[4] J. Bratby, Coagulation and flocculation in water and wastewater treatment, 2nd Ed., IWA Publishing, London, England, 2006.

[5] M. Yan, D. Wang, J. Qu, W. He and C.W.K. Chow, Relative importance of hydrolyzed Al(III) species (Al_a, Al_b, and Al_c) during coagulation with polyaluminum chloride: A case study with the typical micro-polluted source waters, J. Colloid Inter. Sci., 316 (2007) 482–489.

[6] M.I. Aguilar, J. Sáez, M. Lloréns, A. Soler and J.F. Ortuño, Nutrient removal and sludge production in the coagulation–flocculation process, Water Res., 36 (2002) 2910–2919.

[7] A.A. Tatsi, A.I. Zouboulis, K.A. Matis and P. Samaras, Coagulation–flocculation pretreatment of sanitary landfill leachates, Chemosphere, 53 (2003) 737–744.

[8] L. Hailong, W. Dongsheng, W. Min, T. Hongxiao and Y. Min, Effect of pre-ozonation on coagulation with IPF–PACls: Role of coagulant speciation, Colloids Surf. A: Physicochem. Eng. Aspects, 294 (2007) 111–116.

[9] C. Ye, D. Wang, B. Shi, J. Yu, J. Qu, M. Edwards and H. Tang, Alkalinity effect of coagulation with polyaluminum chlorides: Role of electrostatic patch, Colloids Surf. A: Physicochem. Eng. Aspects, 294 (2007) 163–173.

[10] S. Song, A. Lopez-Valdivieso, D.J. Hernandez-Campos, C. Peng, M.G. Monroy-Fernandez and I. Razo-Soto, Arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite, Water Res., 40 (2006) 364–372.

[11] S.R. Gray, C.B. Ritchie, T. Tran and B.A. Bolto, Effect of NOM characteristics and membrane type on microfiltration performance, Water Res., 41 (2007) 3833–3841.

[12] B. Bolto, D. Dixon, R. Eldridge and S. King, Removal of THM precursors by coagulation or ion exchange, Water Res., 36 (2002) 5066–5073.

[13] (a) D. Ghernaout, B. Ghernaout and A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation, Desalination Water Treat., 2 (2009) 203–222.
(b) D. Belhout, D. Ghernaout, S. Djezzar-Douakh and A. Kellil, Electrocoagulation of a raw water of Ghrib Dam (Algeria) in batch using aluminium and iron electrodes, Desalination Water Treat., 16 (2010) 1–9.
(c) D. Ghernaout and B. Ghernaout, From chemical disinfection to electrodisinfection: The obligatory itinerary? Desalination Water Treat., 16 (2010) 156–175.
(d) A. Saiba, S. Kourdali, B. Ghernaout and D. Ghernaout, In Desalination, from 1987 to 2009, the birth of a new seawater pretreatment process: Electrocoagulation–an overview, Desalination Water Treat., 16 (2010) 201–217.

[14] N.K. Shammas, Coagulation and flocculation (ch. 4), From: Handbook of environmental engineering, Vol. 3: Physicochemical treatment processes, L.K. Wang, Y.-T. Hung and N.K. Shammas (Eds.), The Humana Press Inc., Totowa, New Jersey, USA, 2005.

[15] A.I. Zouboulis, P.A. Moussas and F. Vasilakou, Polyferric sulphate: Preparation, characterisation and application in coagulation experiments, J. Hazard. Mater., 155 (2008) 459–468.

[16] J.-W. Lee, S.-P. Choi, R. Thiruvenkatachari, W.-G. Shim and H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, Dyes Pigments, 69 (2006) 196–203.

[17] C.N. Sawyer, P.L. McCarty and G.E. Parkin, Chemistry for environmental engineering, 4th Ed., McGraw-Hill, New York, USA, 1994.

[18] USEPA (US Environmental Protection Agency), Arsenic removal from drinking water by coagulation/filtration and lime softening plants, National Service Center for Environmental Publications, Cincinnati, Ohio, USA, 2000.

[19] S.A. Cleary, Sustainable drinking water treatment for small communities using multistage slow sand filtration, MSc. thesis, University of Waterloo, Ontario, Canada, 2005.

[20] USEPA, Enhanced coagulation and enhanced precipitative softening guidance manual, EPA/815/R–99/012, National Service Center for Environmental Publications, Cincinnati, Ohio, 1999.

[21] T. Carroll, S. King, S.R. Gray, B.A. Bolto and N.A. Booker, The fouling of microfiltration membranes by NOM after coagulation treatment, Water Res., 34 (2000) 2861–2868.

[22] (a) R. Jansen, Ozonation of humic substances in a membrane contactor, mass transfer, product characterization and biodegradability, Ph.D. thesis, University of Twente, The Netherlands, 2005.
(b) E. Oguz, A. Tortum and B. Keskinler, Determination of the apparent rate constants of the degradation of humic substances by ozonation and modeling of the removal of humic substances from the aqueous solutions with neural network, J. Hazard. Mater., 157 (2008) 455–463.

[23] R.D. Letterman, A. Amirtharajah and C.R. O'Melia, Coagulation and flocculation (ch. 6), In: Water quality and treatment, A handbook of community water supplies, AWWA, R.D. Letterman (Tech. Ed.), 5th Ed., McGraw-Hill, New York, USA, 1999.

[24] S. Takahide, Kurita handbook of water treatment, 2nd English Ed., Tokyo, Japan, 1999.

[25] P. Jarvis, B. Jefferson and S.A. Parsons, Floc structural characteristics using conventional coagulation for a high doc, low alkalinity surface water source, Water Res., 40 (2006) 2727–2737.

[26] N. Graham, F. Gang, G. Fowler and M. Watts, Characterisation and coagulation performance of a tannin-based cationic polymer: A preliminary assessment, Colloids Surf. A: Physicochem. Eng. Aspects, 327 (2008) 9–16.

[27] T.D. Reynolds, Unit Operations and processes in environmental engineering, Brooks/Cole Engineering Division, Monterey, California, USA, 1982.

[28] A.W.C. van der Helm, Integrated modeling of ozonation for optimization of drinking water treatment, Ph.D thesis, Water Management Academic Press, Delft, the Netherlands, 2007.

[29] D. Grolimund, K. Barmettler and M. Borkovec, Colloid facilitated transport in natural porous media: Fundamental phenomena and modelling, In: Colloidal transport in porous media, F.H. Frimmel, F. von der Kammer and H.-C. Flemming (Eds.), Springer, 2007.

[30] M.H. Al-Malack, N.S. Abuzaid and A.H. El-Mubarak, Coagulation of polymeric wastewater discharged by a chemical factory, Water Res., 33 (1999) 521–529.

[31] Y.H. Choi, H.S. Kim and J.H. Kweon, Role of hydrophobic natural organic matter flocs on the fouling in coagulation-membrane processes, Sep. Purif. Technol., 62 (2008) 529–534.

[32] M. Elimelech, J. Gregory, X. Jia and R.A. Williams, Particle deposition & aggregation, measurement, modelling and simulation, Colloid and surface engineering series, 2nd Ed., Butterworth-Heinemann, Oxford, England, 1998.

[33] E.J.W. Verwey and J.Th.G. Overbeek, Theory of the stability of lyophobic colloids, Elsevier, Amsterdam, 1948.

[34] F.M.M. Morel, Principles of aquatic chemistry, Wiley-Interscience, New York, USA, 1983.

[35] C.R. O'Melia, In: Aquatic chemical kinetics, W. Stumm (Ed.), Wiley-Interscience, New York, USA, 1990.

[36] M. Elimelech and C.R. O'Melia, Kinetics of deposition of colloidal particles in porous media, Environ. Sci. Technol., 24 (1990) 1528–1536.

[37] X. Xu, S. Yu, W. Shi, Z. Jiang and C. Wu, Effect of acid medium on the coagulation efficiency of polysilicate-ferric (PSF)—A new kind of inorganic polymer coagulant, Sep. Purif. Technol., 66 (2009) 486–491.

[38] C.R. O'Melia, In: Physicochemical processes for water quality control, W.J. Webber, Jr. (Ed.), Wiley-Interscience, New York, USA, 1972.

[39] N. Hilal, M. Al-Abri, A. Moran and H. Al-Hinai, Effects of heavy metals and polyelectrolytes in humic substance coagulation under saline conditions, Desalination, 220 (2008) 85–95.

[40] (a) A.-V. Jung, V. Chanudet, J. Ghanbaja, B.S. Lartiges and J.-L. Bersillon, Coagulation of humic substances and dissolved organic matter with a ferric salt: An electron energy loss spectroscopy investigation, Water Res., 39 (2005) 3849–3862.
(b) H. Ødegaard, B. Eikebrokk and R. Storhaug, Processes for the removal of humic substances from water – An overview based on Norwegian experiences, Water Sci. Technol., 40 (1999) 37–46.
(c) H. Ødegaard, S. Østerhus, E. Melin and B. Eikebrokk, NOM removal technologies – Norwegian experiences, Drink. Water Eng. Sci., 3 (2010) 1–9.

[41] X. Wu, X. Ge, D. Wang and H. Tang, Distinct coagulation mechanism and model between alum and high Al_{13}-PACl, Colloids Surf. A: Physicochem. Eng. Aspects, 305 (2007) 89–96.

[42] J.-L. Lin, C. Huang, C.-J. M. Chin and J.R. Pan, Coagulation dynamics of fractal flocs induced by enmeshment and electrostatic patch mechanisms, Water Res., 42 (2008) 4457–4466.

[43] E.L. Sharp, S.A. Parsons and B. Jefferson, The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts, Environ. Poll., 140 (2006) 436–443.

[44] A. Cornelissen, M.G. Burnett, R.D. McCall and D.T. Goddard, The structure of hydrous flocs prepared by batch and continuous flow water treatment systems and obtained by optical, electron and atomic force microscopy, Water Sci. Technol., 36 (1997) 41–48.

[45] P.J. Delphos and G.M. Wesner, Mixing, coagulation, and flocculation (ch. 6), In: Water treatment plant design, AWWA, ASCE, E.E. Baruth (Ed.), 4th Ed., McGraw-Hill Handbooks, New York, USA, 2004.

[46] F. Xiao, J. Ma, P. Yi and J.-C.H. Huang, Effects of low temperature on coagulation of kaolinite suspensions, Water Res., 42 (2008) 2983–2992.

[47] C. Kan, C. Huang and J.R. Pan, Time requirement for rapid-mixing in coagulation, Colloids Surf. A: Physicochem. Eng. Aspects, 203 (2002) 1–9.

[48] A. Amirtharajah and S.C. Jones, In: H.H. Hermann, E. Hoffmann and H. Odegaard (Eds.), Chemical water and wastewater

treatment IV, Proceedings of 7th Gothenburg Symposium, 23–25 September 1996, Springer, Edinburgh, Scotland, 1996, p. 23.

[49] M.M. Clark and R.M. Srivastava, Selection and design of mixing processes for coagulation, AWWARF Press, Denver, Colorado, USA, 1994.

[50] E. Berdal, Carrier water for coagulation, MSc. thesis, School of applied science, Cranfield University, England, 2007.

[51] M.J. Hammer, Water and Wastewater Technology, John Wiley & Sons, New York, USA, 1986.

[52] T.J. McGhee, Water Supply and Sewerage, 6th Ed., McGraw-Hill, New York, USA, 1991.

[53] B. Bolto and J. Gregory, Organic polyelectrolytes in water treatment, Water Res., 41 (2007) 2301–2324.

[54] J.-P. Boisvert, T.C. To, A. Berrak and C. Jolicoeur, Phosphate adsorption in flocculation processes of aluminium sulphate and polyalumium-silicate-sulphate, Water Res., 31 (1997) 1939–1946.

[55] J.K. Edzwald, Coagulation in drinking water treatment: particles, organics and coagulants, Water Sci. Technol., 27 (1993) 21–35.

[56] B. Bolto, D. Dixon and R. Eldridge, Ion exchange for the removal of natural organic matter, React. Funct. Polym., 60 (2004) 171–182.

[57] W. Stumm, Chemistry of the solid–water interface, Wiley, New York, USA, 1992.

[58] J.-J. Chen, H.-H. Yeh and I-C. Tseng, Effect of ozone and permanganate on algae coagulation removal – Pilot and bench scale tests, Chemosphere, 74 (2009) 840–846.

[59] H. Wong, K.M. Mok and X.J. Fan, Natural organic matter and formation of trihalomethanes in two water treatment processes, Desalination, 210 (2007) 44–51.

[60] N. Hilal, G. Busca, F. Talens-Alesson and B.P. Atkin, Treatment of waste coolants by coagulation and membrane filtration, Chem. Eng. Process., 43 (2004) 811–821.

[61] B.A. Bolto, Soluble polymers in water purification, Prog. Polym. Sci., 20 (1995) 987–1041.

[62] S.-J. Park and T.-I. Yoon, Effects of iron species and inert minerals on coagulation and direct filtration for humic acid removal, Desalination, 239 (2009) 146–158.

[63] U. Iriarte-Velasco, J.I. Álvarez-Uriarte and J.R. González-Velasco, Removal and structural changes in natural organic matter in a Spanish water treatment plant using nascent chlorine, Sep. Purif. Technol., 57 (2007) 152–160.

[64] E.M. Thurman, Organic geochemistry of natural water, Boston, MA: Nijhoff, Boston, USA, 1985.

[65] C.W.K. Chow, J.A. van Leeuwen, R. Fabris and M. Drikas, Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon, Desalination, 245 (2009) 120–134.

[66] W.P. Cheng and F.H. Chi, A study of coagulation mechanisms of polyferric sulphate reacting with humic acid using a fluorescence-quenching method, Water Res., 36 (2002) 4583–4591.

[67] S. Chang and R.A. Berner, Humic substance formation via the oxidative weathering of coal, Environ. Sci. Technol., 32 (1998) 2883–2886.

[68] F.J. Stevenson, Humus chemistry: genesis, composition, reactions, Wiley/Interscience, New York, USA, 1994.

[69] S.W. Krasner and G. Amy, Jar test evaluations of enhanced coagulation, J. AWWA, 87 (1995) 93–107.

[70] K.E. Dennett, A. Amirtharajah, T.F. Moran and J.P. Gould, Coagulation: its effect on organic matter, J. AWWA, 88 (1996) 129–142.

[71] C.R. Evanko and D.A. Dzombak, Influence of structural features on sorption of non-analogue organic acid to goethite, Environ. Sci. Technol., 32 (1998) 2846–2855.

[72] J.E. Van Benschoten and J.K. Edzwald, Chemical aspects of coagulation using aluminum chlorides, Water Res., 24 (1990) 1527–1537.

[73] L. Istv'an, On the type of bond developing between the aluminum and iron (III) hydroxide and organic substances, Water Sci. Technol., 27 (1993) 242–252.

[74] M.J. Semmens and K. Ayers, Removal of trace organics by coagulation from Mississippi water, J. AWWA, 77 (1985) 79–84.

[75] J.-M. Siéliéchi, B.S. Lartiges, G.J. Kayem, S. Hupont, C. Frochot, J. Thieme, J. Ghanbaja, J.B. d'Espinose de la Caillerie, O. Barrès, R. Kamga, P. Levitz and L.J. Michot, Changes in humic acid conformation during coagulation with ferric chloride: Implications for drinking water treatment, Water Res., 42 (2008) 2111–2123.

[76] B. Bolto, D. Dixon, R. Eldridge and S. King, Cationic polymer and clay or metal oxide combinations for natural organic matter removal, Water Res., 35 (2001) 2669–2676.

[77] N.S.C. Becker, D.M. Bennett, B.A. Bolto, D.R. Dixon, R.J. Eldridged, N.P. Le and C.S. Rye, Detection of polyelectrolytes at trace levels in water by fluorescent tagging, Reactive Functional Polym., 60 (2004) 183–193.

[78] M.I. Aguilar, J. Sáez, M. Lloréns, A. Soler, J.F. Ortuño, V. Meseguer and A. Fuentes, Improvement of coagulation–flocculation process using anionic polyacrylamide as coagulant aid, Chemosphere, 58 (2005) 47–56.

[79] P. Zhang, Z. Wu, G. Zhang, G. Zeng, H. Zhang, J. Li, X. Song and J. Dong, Coagulation characteristics of polyaluminum chlorides PAC-Al_{30} on humic acid removal from water, Sep. Purif. Technol., 63 (2008) 642–647.

[80] B. Shi, G. Li, D. Wang, C. Feng and H. Tang, Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species, J. Hazard. Mater., 143 (2007) 567–574.

[81] P. Zhang, H.H. Hahn, E. Hoffmann and G. Zeng, Influence of some additives to aluminium species distribution in aluminium coagulants, Chemosphere, 57 (2004) 1489–1494.

[82] N. Pasrthasarathy and J. Buffle, Study of polymeric aluminum (III) hydroxide solutions for application in wastewater treatment: properties of the polymer and optimal conditions preparation, Water Res., 19 (1985) 25–36.

[83] C.Z. Hu, H.J. Liu, J.H. Qu, D.S. Wang and J. Ru, Coagulation behavior of aluminium salts in eutrophic water: significance of Al_{13} species and pH control, Environ. Sci. Technol., 40 (2006) 325–331.

[84] (a) B.-Y. Gao, Y.-B. Chu, Q.-Y. Yue, B.-J. Wang and S.-G. Wang, Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al_{13} content, J. Environ. Manage, 76 (2005) 143–147.
(b) J. Wei, B. Gao, Q. Yue and Y. Wang, Effect of dosing method on color removal performance and flocculation dynamics of polyferric-organic polymer dual-coagulant in synthetic dyeing solution, Chem. Eng. J., 151 (2009) 176–182.

[85] U. Nowostawska, S.G. Sander, K.M. McGrath and K.A. Hunter, Effects of coagulants on the surface forces of colloidal alumina under water treatment conditions, Colloids Surf. A: Physicochem. Eng. Aspects, 266 (2005) 214–222.

[86] L. Allouche, C. Gérardin, T. Loiseau, G. Férey and F. Taulelle, Al_{30}: a giant aluminum polycation, Angew. Chem. Int. Edit., 39 (2000) 511–514.

[87] J. Rowsell and L.F. Nazar, Speciation and thermal transformation in alumina sols: structures of the polyhydroxyoxoaluminum cluster $[Al_2O_8(OH)_{56}(H_2O)_{26}]^{18+}$ and its δ-Keggin moieté, J. Am. Chem. Soc., 122 (2000) 3777–3778.

[88] Z.Y. Chen, Z.K. Luan, J.H. Fan, Z.G. Zhang, X.J. Peng and B. Fan, Effect of thermal treatment on the formation and transformation of Keggin Al_{13} and Al_{30} species in hydrolytic aluminium solutions, Colloids Surf. A, 292 (2007) 110–118.

[89] L. Allouche and F. Taulelle, Conversion of Al_{13} Keggin ε into Al_{30}: a reaction controlled by aluminium monomers, Inorg. Chem. Commun., 6 (2003) 1167–1170.

[90] B.L. Phillips, A. Lee and W.H. Casey, Rates of oxygen exchange between the $Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}{}^{18+}{}_{(aq)}$ (Al_{30}) molecule and aqueous solution, Geochim. Cosmochim. Acta, 67 (2003) 2725–2733.

[91] Z.Y. Chen, B. Fan, X.J. Peng, Z.G. Zhang, J.H. Fan and Z.K. Luan, Evaluation of Al_{30} polynuclear species in polyaluminum solutions as coagulant for water treatment, Chemosphere, 64 (2006) 912–918.

[92] J.R. Pan, C. Huang, S. Chen and Y.-C. Chung, Evaluation of a modified chitosan biopolymer for coagulation, Colloids Surf. A: Physicochem. Eng. Aspects, 147 (1999) 359–364.

[93] M. Kang, H. Chen, Y. Sato, T. Kamei and Y. Magara, Rapid and economical indicator for evaluating arsenic removal with

minimum aluminum residual during coagulation process, Water Res., 37 (2003) 4599–4604.

[94] S. Katayon, M.J. Megat Mohd Noor, M. Asma, L.A. Abdul Ghani, A.M. Thamer, I. Azni, J. Ahmad, B.C. Khor and A.M. Suleyman, Effects of storage conditions of *Moringa oleifera* seeds on its performance in coagulation, Biores. Technol., 97 (2006) 1455–1460.

[95] C.K.S. Pillai, W. Paul and C.P. Sharma, Chitin and chitosan polymers: Chemistry, solubility and fiber formation, Progress Polym. Sci., 34 (2009) 641–678.

[96] T. Chatterjee, S. Chatterjee and S.H. Woo, Enhanced coagulation of bentonite particles in water by a modified chitosan biopolymer, Chem. Eng. J., 148 (2009) 414–419.

[97] A. Szyguła, E. Guibal, M.A. Palacín, M. Ruiz and A.M. Sastre, Removal of an anionic dye (Acid Blue 92) by coagulation–flocculation using chitosan, J. Environ. Manage, 90 (2009) 2979–2986.

[98] C. Huang, S. Chen and J.R. Pan, Optimal condition for modification of chitosan: A biopolymer for coagulation of colloidal particles, Water Res., 34 (2000) 1057–1062.

[99] M.-Y. Chang and R.-S. Juang, Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, J. Colloid Interfac. Sci., 278 (2004) 18–25.

[100] L. Rizzo, A. Di Gennaro, M. Gallo and V. Belgiorno, Coagulation/chlorination of surface water: A comparison between chitosan and metal salts, Sep. Purif. Technol., 62 (2008) 79–85.

[101] F. Renault, B. Sancey, P.-M. Badot and G. Crini, Chitosan for coagulation/flocculation processes – An eco-friendly approach, Europ. Polym. J., 45 (2009) 1337–1348.

[102] K. Bell-Ajy, M. Abbaszadegan, E. Ibrahim, D. Verges and M. LeChevallier, Conventional and optimized coagulation for NOM removal, J. AWWA, 92 (2000) 44–58.

[103] J.K. Edzwald and J.E. Tobiason, Enhanced coagulation: US requirements and a broader view, Water Sci. Technol., 40 (1999) 63–70.

[104] J. Haberkamp, A.S. Ruhl, M. Ernst and M. Jekel, Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration, Water Res., 41 (2007) 3794–3802.

[105] Y. Zeng and J. Park, Characterization and coagulation performance of a novel inorganic polymer coagulant—Poly-zinc-silicate-sulfate, Colloids Surf. A: Physicochem. Eng. Aspects, 334 (2009) 147–154.

[106] B.Y. Gao and Q.Y. Yue, Effect of SO_4^{2-}/Al^{3+} ratio and OH^-/Al^{3+} value on the characterization of coagulant poly-aluminum-chloride-sulfate (PACS) and its coagulation performance in water treatment, Chemosphere, 61 (2005) 579–584.

[107] W.P. Cheng, Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution, Chemosphere, 47 (2002) 963–969.

[108] E.E. Chang, P.C. Chaing, S.H. Chao and C.H. Liang, Effects of polydiallyldimethyl ammonium chloride coagulant on formation of chlorinated by products in drinking water, Chemosphere, 39 (1999) 1333–1346.

[109] T.-K. Liu and C.-J.M. Chin, Improved coagulation performance using preformed polymeric iron chloride (PICl), Colloids Surf. A: Physicochem. Eng. Aspects, 339 (2009) 192–198.

[110] N. Shirasaki, T. Matsushita, Y. Matsui, T. Urasaki and K. Ohno, Comparison of behaviors of two surrogates for pathogenic waterborne viruses, bacteriophages $Q\beta$ and MS2, during the aluminum coagulation process, Water Res., 43 (2009) 605–612.

[111] M.D. Guy, J.D. Mclver and M.J. Lewis, The removal of virus by a pilot treatment plant, Water Res., 11 (1977) 421–428.

[112] A.H. Havelaar, M.V. Olphen and J.F. Schijven, Removal and inactivation of viruses by drinking water treatment processes under full-scale conditions, Water Sci. Technol., 31 (1995) 55–62.

[113] M. Otaki, K. Yano and S. Ohgaki, Virus removal in a membrane separation process, Water Sci. Technol., 37 (1998) 107–116.

[114] T. Matsushita, Y. Matsui and T. Inoue, Irreversible and reversible adhesions between virus particles and hydrolyzing precipitating aluminum: a function of coagulation, Water Sci. Technol., 50 (2004) 201–206.

[115] B. Zhu, D.A. Clifford and S. Chellam, Virus removal by iron coagulation–microfiltration, Water Res., 39 (2005) 5153–5161.

[116] (a) J. Ma and W. Liu, Effectiveness and mechanism of potassium ferrate(VI) preoxidation for algae removal by coagulation, Water Res., 36 (2002) 871–878.
(b) B. Ghernaout, D. Ghernaout and A. Saiba, Algae and cyanotoxins removal by coagulation/flocculation: A review, Desalination Water Treat., 20 (2010) 133–143.

[117] J. Ma, N. Graham and G.B. Li, Effectiveness of permanganate preoxidation in enhancing the coagulation of surface waters-Laboratory case studies, J. Water SRT-Aqua, 46 (1997) 1–11.

[118] J. Ma and G.B. Li, Laboratory and full-scale plant studies of permanganate oxidation as an aid to the coagulation, Water Sci. Technol., 27 (1993) 47–54.

[119] J. Ma, G. Li, Z.L. Chen, X.G. Xu and G.Q. Cai, Enhanced coagulation of surface waters with high organic content by permanganate preoxidation, IAWQ/IWSA Joint Specialized Conference, Particle Removal from Dams & Reservoirs, 15–18, February, 2000, Durban, South Africa, 2000.

[120] A. Sukenik, B. Teltch, A.W. Wachs, G. Shelef, I. Nir and D. Levanon, Effect of oxidants on microalgal coagulation, Water Res., 21 (1987) 533–539.

[121] B. Fetrusevski, A.N. Van Breemen and G. Alaerts, Effect of permanganate pre-treatment and coagulation with dual coagulants on algae removal in direct filtration, J. Water SRT-Aqua, 45 (1996) 316–326.

[122] M.B. Gilbert, T.D. Waite and C. Hare, An investigation of the applicability of ferrate ion for disinfection, J. AWWA, 68 (1976) 495–497.

[123] T. Schink and T.D. Waite, Inactivation of f2 virus with ferrate(VI), Water Res., 14 (1980) 1705–1717.

[124] J.-Q. Jiang, S. Wang and A. Panagoulopoulos, The role of potassium ferrate(VI) in the inactivation of *Escherichia coli* and in the reduction of COD for water remediation, Desalination, 210 (2007) 266–273.

[125] (a) J.-Q. Jiang, S. Wang and A. Panagoulopoulos, The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment, Chemosphere, 63 (2006) 212–219.
(b) M. Alsheyab, J.-Q. Jiang and C. Stanford, On-line production of ferrate with an electrochemical method and its potential application for wastewater treatment – A review, J. Environ. Manage, 90 (2009) 1350–1356.

[126] (a) S.J. Decula, A.C. Chao and C. Smallwood, Ames test of ferrate treated water, J. Environ. Eng., 109 (1983) 1159–1167.
(b) D. Ghernaout and M.W. Naceur, Ferrate(VI): In situ generation and water treatment–A review, Desalination Water Treat. (in press).

[127] T. Takaara, D. Sano, H. Konno and T. Omura, Cellular proteins of *Microcystis aeruginosa* inhibiting coagulation with polyaluminum chloride, Water Res., 41 (2007) 1653–1658.

[128] G. Zhang, P. Zhang, B. Wang and H. Liu, Ultrasonic frequency effects on the removal of *Microcystis aeruginosa*, Ultrason. Sonochem., 13 (2006) 446–450.

[129] H.B. Jun, Y.L. Lee, B.D. Lee and D.R.U. Knappe, Effectiveness of coagulants and coagulant aids for the removal of filter-clogging Synedra, J. Water Supply: Res. Technol., 50 (2001) 135–148.

[130] W.P. Cheng and F.H. Chi, Influence of eutrophication on the coagulation efficiency in reservoir water, Chemosphere, 53 (2003) 773–778.

[131] H. Bernhardt, H. Shell, O. Hoyer and B. Lusse, Influence of algogenic organic substances on flocculation and filtration, Water Inst. S. Afr., 1 (1991) 41–57.

[132] H. Bernhardt, O. Hoyer, B. Lusse and H. Shell, Investigations on the influence of algal-derived organic substances on flocculation and filtration, In: P.M. Huck and P. Toft (Eds.), Treatment of drinking water of organic contaminants, Pergamon Press, London, England, pp. 185–216, 1987.

[133] M. Franceschi, A Girou, A.M. Carro-Diaz, M.T. Maurette and E. Puech-Costes, Optimisation of the coagulation-flocculation process of raw water by optimal design method, Water Res., 36 (2002) 3561–3572.

[134] S. Ghafari, H. Abdul Azizb, M.H. Isa and A.A. Zinatizadeh, Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using

poly-aluminum chloride (PAC) and alum, J. Hazard. Mater., 163 (2009) 650–656.

[135] J. Gregory, Stability and flocculation of colloidal particles, Effluents Water J., 17 (1977) 515–521.

[136] W.J. Masschelein, Processus unitaire du traitement de l'eau potable, Editions Tec & Doc, Lavoisier, Paris, France, 1996.

[137] G. Li and J. Gregory, Flocculation and sedimentation of high turbidity waters, Water Res., 25 (1991) 1137–1143.

[138] B. Dempsey, Removal of naturally occurring compounds by coagulation and sedimentation, Crit. Rev. Environ. Control., 14 (1984) 311–331.

[139] S.K. Dentel and J.M. Gosset, Coagulation of organic suspensions with aluminium salts, J. Water Pollut. Con. F., 59 (1987) 101–108.

[140] P. Dolejs, Treatment of the low alkalinity humic waters with partially neutralized aluminium sulphate, Environ. Technol. Lett., 10 (1989) 41–48.

[141] A. Amirtarajah and S.L. Trusler, Destabilisation of particles by turbulent rapid mixing, J. Environ. Eng., 112 (1986) 1085–1108.

[142] J.E. Gregor, C.J. Nokes and E. Fenton, Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation, Water Res., 31 (1997) 2949–2958.

[143] J.K. Morris and W.R. Knocke, Temperature effects on the use of metal-ion coagulant for water treatment, J. AWWA, 76 (1983) 74–79.

[144] S. Kawamura, Application of colloidal titration technic to flocculation control, J. AWWA, 68 (1976) 328–336.

[145] A. Masion, A. Vilgé-Ritter, J. Rose, W.E.E. Stone, B.J. Teppen, D. Rybacki and J.J. Bottero, Coagulation-flocculation of natural organic matter with Al salts: speciation and structure of aggregates, Environ. Sci. Technol., 34 (2000) 3242–3246.

[146] A. Vilgé-Ritter, A. Masion, T. Boulangé, D. Rybacki and J.J. Bottero, Removal of natural organic matter by coagulation-flocculation: a pyrolysis-GC-MS study, Environ. Sci. Technol., 33 (1999) 3027–3032.

[147] J.-O. Kim, J.-T. Jung, I.-T. Yeom and G.-H. Aoh, Electric fields treatment for the reduction of membrane fouling, the inactivation of bacteria and the enhancement of particle coagulation, Desalination, 202 (2006) 31–37.

[148] C. Tsouris, V.M. Shah, K.D. Blankenship, D.W. DePaoli, J. Dong, M.Z.-C. Hu, S.Z. Yiacoumi, W.-T. Shin, T.-Y. Ying and K.-L. Yang, Phase equilibria modification by electric fields, Final Report, U.S. Dept. of Energy, Office of Environmental Management Science Program, Oak Ridge National Lab., Project N.: 55119, Project duration: 10/1/96–3/31/00, (2000), (http://www.osti.gov/em52/final_reports/55119.pdf, consulted 31/07/09).

[149] A.T. Andrews, Electrophoresis, theory, techniques, and biochemical and clinical application, 2nd Ed., Oxford Science Publications, Clarendon Press, Oxford, England, 1985.

[150] R. Weinberger, Practical capillary electrophoresis, 2nd Ed., AP, New York, USA, 2000.

[151] H.R. Maurer, Disc electrophoresis and related techniques of polyacrylamide gel electrophoresis, 2nd Ed., Walter de Gruyter, Berlin, New York, 1971.

[152] B. Gaš, Theory of electrophoresis: Fate of one equation, Electrophoresis, 30 (2009) S7–S15.

[153] P. Gebauer and P. Bo ek, Electrophoretic sample stacking, Electrophoresis, 30 (2009) S27–S33.

[154] W. Thormann, J. Caslavska, M.C. Breadmore and R.A. Mosher, Dynamic computer simulations of electrophoresis: Three decades of active research, Electrophoresis, 30 (2009) S16–S26.

[155] N.H.H. Heegaard, Affinity in electrophoresis, Electrophoresis, 30 (2009) S229–S239.

[156] F. Foret, Capillary electrophoresis of small ions using complex formation and indirect detection, Electrophoresis, 30 (2009) S34–S39.

[157] V. Kašička, From micro to macro: Conversion of capillary electrophoretic separations of biomolecules and bioparticles to preparative free-flow electrophoresis scale, Electrophoresis, 30 (2009) S40–S52.

[158] C. Johns, M.C. Breadmore, M. Macka, M. Ryvolová and P.R. Haddad, Recent significant developments in detection and method development for the determination of inorganic ions by CE, Electrophoresis, 30 (2009) S53–S67.

[159] E. Kenndler, Organic solvents in CE, Electrophoresis, 30 (2009) S101–S111.

[160] F. Xiao, X. Zhang and J. Ma, Indecisiveness of electrophoretic mobility determination in evaluating Fe(III) coagulation performance, Sep. Purif. Technol., 68 (2009) 273–278.

[161] A. Amirtharajah and K.M. Mills, Rapid-mix design for mechanisms of alum flocculation, J. AWWA, 74 (1982) 210–216.

[162] P.K. Holt, G.W. Barton, M. Wark and C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A: Physicochem. Eng. Aspects, 211 (2002) 233–248.

[163] (a) A.E. Yilmaz, R. Boncukcuoğlu and M.M. Kocakerim, A quantitative comparison between electrocoagulation and chemical coagulation for boron removal from boron-containing solution, J. Hazard. Mater., 149 (2007) 475–481.
(b) Y. Cengeloglu, G. Arslan, A. Tor, I. Kocak and N. Dursun, Removal of boron from water by using reverse osmosis, Sep. Purif. Technol., 64 (2008) 141–146.
(c) G. Sayiner, F. Kandemirli and A. Dimoglo, Evaluation of boron removal by electrocoagulation using iron and aluminum electrodes, Desalination, 230 (2008) 205–212.

[164] (a) A.S. Koparal, The removal of salinity from produced formation by conventional and electrochemical methods, Fresen. Environ. Bull., 12A (2002) 1071–1077.
(b) S. Yi, Y. Ma, X. Wang and Y. Jia, Green chemistry: Pretreatment of seawater by a one-step electrochemical method, Desalination, 239 (2009) 247–256.
(c) D. Ghernaout, B. Ghernaout and M.W. Naceur, Embodying the chemical water treatment in the green chemistry—A review, Desalination (2011), doi:10.1016/j.desal.2011.01.032.

[165] J.C. Donini, J. Kan, J. Szynkarczuk, T.A. Hassan and K.L. Kar, The operating cost of electrocoagulation, Can. J. Chem. Eng., 72 (1994) 1007–1012.

[166] Y.Ş. Yildiz, A.S. Koparal, Ş. Irdemez and B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater., B 139 (2007) 373–380.

[167] M. Eyvaz, M. Kirlaroglu, T.S. Aktas and E. Yuksel, The effects of alternating current electrocoagulation on dye removal from aqueous solutions, Chem. Eng. J., 153 (2009) 16–22.

[168] P. Cañizares, F. Martínez, C. Jiménez, C. Sáez and M.A. Rodrigo, Coagulation and electrocoagulation of oil-in-water emulsions, J. Hazard. Mater., 151 (2008) 44–51.

[169] Ú.B. Öğütveren and S. Koparal, Electrocoagulation for oil–water emulsion treatment, J. Environ. Sci. Heal, A, 32 (1997) 2507–2520.

[170] T. Zayas, V. Rómero, L. Salgado, M. Meraz and U. Morales, Applicability of coagulation/flocculation and electrochemical processes to the purification of biologically treated vinasse effluent, Sep. Purif. Technol., 57 (2007) 270–276.

[171] G.H. Chen, X.M. Chen and P.L. Yue, Electrocoagulation and electroflotation of restaurant wastewater, J. Environ. Eng. ASCE, 126 (2000) 858–863.

[172] (a) Ş. İrdemez, N. Demircioğlu and Y.Ş Yildiz, The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, J. Hazard. Mater. B, 137 (2006) 1231–1235.
(b) S. Vasudevan, J. Lakshmi, J. Jayaraj and G. Sozhan, Remediation of phosphate-contaminated water by electrocoagulation with aluminium, aluminium alloy and mild steel anodes, J. Hazard. Mater., 164 (2009) 1480–1486.

[173] C.-H. Huang, L. Chen and C.-L. Yang, Effect of anions on electrochemical coagulation for cadmium removal, Sep. Purif. Technol., 65 (2009) 137–146.

[174] L.G. Torres, J. Jaimes, P. Mijaylova, E. Ramírez and B. Jiménez, Coagulation–flocculation pretreatment of high-load chemical–pharmaceutical industry wastewater: mixing aspects, Water Sci. Technol., 36 (1997) 255–262.

[175] A.A. Hafiz, H.M. El-Din and A.M. Badawi, Chemical destabilization of oil-in-water emulsion by novel polymerized diethanolamines, J. Colloid Interface Sci., 284 (2005) 167–175.

[176] J. Duan and J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci., 100–102 (2003) 475–502.

[177] J. Gregory and J. Duan, Hydrolyzing metal salts as coagulants, Pure Appl. Chem., 73 (2001) 2017–2026.

[178] J.Y. Bottero, J.M. Cases, F. Fiessinger and J.E. Poirier, Studies of hydrolyzed aluminium chloride solutions. 1. Nature of aluminum species and composition of aqueous solutions, J. Phys. Chem., 84 (1980) 2933–2939.

[179] J.Y. Bottero, D. Tchoubar, J.M. Caw and F. Fiessinger, Investigation of the hydrolysis of aqueous solutions of aluminum chloride. 2. Nature and structure by small-angle X-ray scattering, J. Phys. Chem., 86 (1982) 3667–3673.

[180] P. Cañizares, C. Jiménez, F. Martínez, M.A. Rodrigo and C. Sáez, The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters, J. Hazard. Mater., 163 (2009) 158–164.

[181] C.-T. Wang, W.-L. Chou and Y.-M. Kuo, Removal of COD from laundry wastewater by electrocoagulation/electroflotation, J. Hazard. Mater., 164 (2009) 81–86.

[182] (a) F.R. Espinoza-Quiñones, M.M.T. Fornari, A.N. Módenes, S.M. Palácio, F.G. da Silva Jr., N. Szymanski, A.D. Kroumov and D.E.G. Trigueros, Pollutant removal from tannery effluent by electrocoagulation, Chem. Eng. J., 151 (2009) 59–65.
(b) İ.A. Şengil, S. Kulaç and M. Özacar, Treatment of tannery liming drum wastewater by electrocoagulation, J. Hazard. Mater., 167 (2009) 940–946.
(c) E. Yüksel, İ.A. Şengil and M. Özacar, The removal of sodium dodecyl sulfate in synthetic wastewater by peroxi-electrocoagulation method, Chem. Eng. J., 152 (2009) 347–353.

[183] (a) I. Zongo, A.H. Maiga, J. Wéthé, G. Valentin, J.-P. Leclerc, G. Paternotte and F. Lapicque, Electrocoagulation for the treatment of textile wastewaters with Al or Fe electrodes: Compared variations of COD levels, turbidity and absorbance, J. Hazard. Mater., 169 (2009) 70–76.
(b) W. Chou, C. Wang and S. Chang, Study of COD and turbidity removal from real oxide-CMP wastewater by iron electrocoagulation and the evaluation of specific energy consumption, J. Hazard. Mater., 168 (2009) 1200–1207.
(c) A. Aouni, C. Fersi, M. Ben Sik Ali and M. Dhahbi, Treatment of textile wastewater by a hybrid electrocoagulation/nanofiltration process, J. Hazard. Mater., 168 (2009) 868–874.
(d) K.S. Parama Kalyani, N. Balasubramanian and C. Srinivasakannan, Decolorization and COD reduction of paper industrial effluent using electro-coagulation, Chem. Eng. J., 151 (2009) 97–104.

[184] (a) Y.O.A. Fouad, A.H. Konsowa, H.A. Farag and G.H. Sedahmed, Performance of an electrocoagulation cell with horizontally oriented electrodes in oil separation compared to a cell with vertical electrodes, Chem. Eng. J., 145 (2009) 436–440.
(b) M. Zaied and N. Bellakhal, Electrocoagulation treatment of black liquor from paper industry, J. Hazard. Mater., 163 (2009) 995–1000.
(c) S. Hammami, A. Ouejhani, N. Bellakhal and M. Dachraoui, Application of Doehlert matrix to determine the optimal conditions of electrochemical treatment of tannery effluents, J. Hazard. Mater., 163 (2009) 251–258.

[185] L.M. Balmer and A.W. Foulds, Separation oil from oil-in water emulsions by electroflocculation/electroflotation, Filtr. Sep., 23 (1986) 366–369.

[186] (a) X. Xu and X. Zhu, Treatment of refectory oily wastewater by electro-coagulation process, Chemosphere, 56 (2004) 889–894.
(b) U.T. Un, A.S. Koparal and U.B. Ogutveren, Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes, J. Environ. Manage, 90 (2009) 428–433.

[187] (a) N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib and B. Bariou, Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, Water Res., 32 (1998) 1604–1612.
(b) C.Y. Hu, S.L. Lo and W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res., 37 (2003) 4513–4523.
(c) M.M. Emamjomeh and M. Sivakumar, Fluoride removal by a continuous flow electrocoagulation reactor, J. Environ. Manage, 90 (2009) 1204–1212.
(d) D. Ghosh, C.R. Medhi and M.K. Purkait, Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections, Chemosphere, 73 (2008) 1393–1400.

[188] P.R. Kumar, S. Chaudhari, K.C. Khilar and S.P. Mahajan, Removal of arsenic from water by electrocoagulation, Chemosphere, 55 (2004) 1245–1252.

[189] (a) J.S. Do and M.L. Chen, Decolourization of dye-containing solutions by electrocoagulation, J. Appl. Electrochem., 24 (1994) 785–790.
(b) I. Kabdaşli, B. Vardar, I. Arslan-Alaton and O. Tünay, Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation, Chem. Eng. J., 148 (2009) 89–96.
(c) I. Linares-Hernández, C. Barrera-Díaz, G. Roa-Morales, B. Bilyeu and F. Ureña-Núñez, Influence of the anodic material on electrocoagulation performance, Chem. Eng. J., 148 (2009) 97–105.
(d) İ.A. Şengil and M. Özacar, The decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes, J. Hazard. Mater., 161 (2009) 1369–1376.

[190] M. Kobya, O.T. Can and M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, J. Hazard. Mater., B100 (2003) 163–178.

[191] N. Daneshvar, H. Ashassi-Sorkhabi and A. Tizpar, Decolorization of orange II by electrocoagulation method, Sep. Purif. Technol., 31 (2003) 153–162.

[192] Z. Zaroual, M. Azzi, N. Saib and E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, J. Hazard. Mater., B131 (2006) 73–78.

[193] O. Larue, E. Vorobiev and C.V.B. Durand, Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions, Sep. Purif. Technol., 31 (2003) 177–192.

[194] N.S. Abuzaid, A.A. Bukhari and Z.M. Al-Hamouz, Ground water coagulation using soluble stainless steel electrodes, Adv. Environ. Res., 6 (2002) 325–333.

[195] D. Ghernaout, B. Ghernaout and A. Boucherit, Effect of pH on electrocoagulation of bentonite suspensions in batch using iron electrodes, J. Disper Sci. Technol., 29 (2008) 1272–1275.

[196] J. Ge, J. Qu, P. Lei and H. Liu, New bipolar electrocoagulation–electroflotation process for the treatment of laundry wastewater, Sep. Purif. Technol., 36 (2004) 33–39.

[197] E. Önder, A.S. Koparal and .B. Ö ütveren, An alternative method for the removal of surfactants from water: Electrochemical coagulation, Sep. Purif. Technol., 52 (2007) 527–532.

[198] (a) D. Ghernaout, B. Ghernaout, A. Saiba, A. Boucherit and A. Kellil, Removal of humic acids by continuous electromagnetic treatment followed by electrocoagulation in batch using aluminium electrodes, Desalination, 239 (2009) 295–308.
(b) D. Ghernaout, A. Mariche, B. Ghernaout and A. Kellil, Electromagnetic treatment-doubled electrocoagulation of humic acid in continuous mode using response surface method for its optimisation and application on two surface waters, Desalination Water Treat., 22 (2010) 311–329.

[199] (a) P. Gao, X. Chen, F. Shen and G. Chen, Removal of chromium(VI) from wastewater by combined electrocoagulation–electroflotation without a filter, Sep. Purif. Technol., 43 (2005) 117–123.
(b) I. Zongo, J.-P. Leclerc, H.A. Maïga, J. Wéthé and F. Lapicque, Removal of hexavalent chromium from industrial wastewater by electrocoagulation: A comprehensive comparison of aluminium and iron electrodes, Sep. Purif. Technol., 66 (2009) 159–166.

[200] D. Ghernaout, A. Badis, B. Ghernaout and A. Kellil, Application of electrocoagulation in *Escherichia Coli* culture and two surface waters, Desalination, 219 (2008) 118–125.

[201] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

[202] M.Y.A. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Porga and D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater., B114 (2004) 199–210.

[203] P.K. Holt, G.W. Barton and C.A. Mitchell, The future for electrocoagulation as a localized water treatment technology, Chemosphere, 59 (2005) 355–367.

[204] T. Picard, G. Cathalifaud-Feuillade, M. Mazet and C. Vandensteendam, Cathodic dissolution in the electrocoagulation process using aluminium electrodes, J. Environ. Monitor., 2 (2000) 77–80.

[205] J. Labanowski, Matière organique naturelle et anthropique: vers une meilleure compréhension de sa réactivité et de sa caractérisation, Doctorate thesis, University of Limoges, France (2004).

[206] D. Ghernaout, Élimination des substances humiques et des germes indicateurs de contamination bactériologique par électrocoagulation assistée d'un traitement magnétique de l'eau, Doctorate thesis, University of Blida, Algeria (2008).

[207] A.P. Buzzini, L.J. Patrizzi, A.J. Motheo and E.C. Pires, Preliminary evaluation of the electrochemical and chemical coagulation processes in the post-treatment of effluent from an upflow anaerobic sludge blanket (UASB) reactor, J. Environ. Manage, 85 (2007) 847–857.

[208] D. Ghernaout, B. Ghernaout, A. Boucherit, M.W. Naceur, A. Khelifa and A. Kellil, Study on mechanism of electrocoagulation with iron electrodes in idealised conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes, Desalination Water Treat., 8 (2009) 91–99.

[209] B. Zhu, D.A. Clifford and S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes, Water Res., 39 (2005) 3098–3108.

[210] (a) J.P. Chen, S.-Y. Chang and Y.-T. Hung, Electrolysis (ch.10), From: Handbook of environmental engineering, Vol. 3: Physicochemical treatment processes, L.K. Wang, Y.-T. Hung and N.K. Shammas (Eds.), The Humana Press Inc., Totowa, New Jersey, USA, 2005.
(b) D. Ghernaout and B. Ghernaout, On the controversial effect of sodium sulphate as supporting electrolyte on electrocoagulation process: A review, Desalination Water Treat. (in press).

[211] (a) J.J. Lingane, Electroanalytical chemistry, 2nd Ed., Wiley-Interscience, New York, USA, 1996.
(b) D. Ghernaout, M.W. Naceur and A. Aouabed, On the dependence of chlorine by-products generated species formation of the electrode material and applied charge during electrochemical water treatment, Desalination 270 (2011) 9–22.

[212] S.E. Sadek, An electrochemica1 method for removal of phosphates from wastewaters, Water Pollution Control Research Series No. 17010–01/70, US Department of the Interior, Federal Water Quality Administration, 1970.

[213] C.P.C. Poon, Electrochemical process of sewage treatment, Purdue Univ. Engineering Bulletin, Proc. 28th Industrial Waste Conference, Part I, Engineering Extension Series, pp. 281–292, May, 1973.

[214] C. Nebel, P.C. Unangst and R.D. Gottschling, Ozone disinfection of combined industrial and municipal secondary effluents, Part I—Laboratory Studies, Purdue Univ. Engineering Bulletin, Proc. 27th Industrial Waste Conference, Part II, Engineering Extension Series No.141, pp. 1039–1055, May, 1972.

[215] X. Chen, G.C. Chen and P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Separ. Purif. Technol., 19 (2000) 65–76.

[216] L.L. Lim, Removal and recovery of heavy metal ions, B. Eng Thesis, National University of Singapore, 2002.

[217] P. Drogui, S. Elmaleh, M. Rumeau, C. Bernard and A. Rambaud, Oxidising and disinfecting by hydrogen peroxide produced in a two-electrode cell, Water Res., 35 (2001) 3235–3241.

[218] C. Feng, K. Suzuki, S. Zhao, N. Sugiura, S. Shimada and T. Maekawa, Water disinfection by electrochemical treatment, Boiresource. Technol., 94 (2004) 21–25.

[219] M.I. Kerwick, S.M. Reddy, A.H.L. Chamberlain and D.M. Holt, Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection?, Electro. Acta, 50 (2005) 5270–5277.

[220] K.P. Drees, M. Abbaszadegan and R.M. Maier, Comparative electrochemical inactivation of bacteria and bacteriophage, Water Res., 37 (2003) 2291–2300.

[221] C. Manohar, V.K. Kelkar and J.V. Yakhmi, Electroflotation of colloids without surfactants, J. Colloid Interf. Sci., 89 (1982) 54–60.

[222] R.M. Bande, B. Prasad, I.M. Mishra and K.L. Wasewar, Oil field effluent water treatment for safe disposal by electroflotation, Chem. Eng. J., 137 (2008) 503–509.

[223] A.Y. Hosny, Separating oil from oil–water emulsions by electroflotation technique, Sep. Purif. Technol., 6 (1996) 9–17.