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Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation

Djamel Ghernaout[a*], Badiaa Ghernaout[b], Amara Kellil[a]

[a]*Chemical Engineering Department, Saad Dahlab University of Blida, Blida 09000, Algeria*
Tel./Fax: +213 (25) 43 36 31; email: djamel_andalus@yahoo.fr
[b]*Algerian Waters, Medea Area, Medea 26000, Algeria*

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ABSTRACT

Although coagulation has historically been used for turbidity removal, drinking water regulations have emerged in recent years expanding the use of this process beyond its traditional role to include disinfection by-products (DBP) precursors removal. Effective removal of DBP precursors is the one of the major challenges in modern drinking water treatment. DBP precursors are present in all surface water supplies existing as natural organic matter (NOM), and this type of precursors can be characterised by the following measurements of dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}), specific ultraviolet absorbance (SUVA), and disinfection by-products formation potential (DBPFP). The effort to remove DBP precursors results in reduction of DBP formation in potable water. However, scientists discovered that chlorination of organic matter in raw water resulted in formation of DBPs. Because of concerns over the health effects of these organic by-products, several industrial countries have established limits for DBP in drinking water. The most known chlorination by-products are trihalomethanes (THM) and haloacetic acids (HAA). The US Environmental Protection Agency (USEPA) regulated THM and HAA in drinking water at the limit of 80 and 60 $\mu g\ L^{-1}$, respectively, while recently, the European Union countries regulated THM in their water at the limit of 100 $\mu g\ L^{-1}$. The USEPA has identified enhanced coagulation (EnC) as a best available technology (BAT) for reducing DBP precursors in conventional water treatment plants. Their removal by EnC depends on a variety of factors, including but not limited to, pH, alkalinity, coagulant type and dosage, and the type and concentration of NOM. Finally, electrocoagulation (EC) presents a robust novel and innovative alternative in which a sacrificial metal anode doses water electrochemically. This has the major advantage of providing active cations required for coagulation, without increasing the salinity of the water. EC is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from the water. EC has the potential to remove efficiently DBP precursors which are essentially negative dissolved species by cationic charge neutralisation/electrical field oxidation/metal hydroxides adsorption. This paper tries briefly to describe NOM removal by coagulation, EnC and EC and shows that EC seems *a priori* to be the next future process step from coagulation passage via EnC process. However, the application of EnC to maximise removal of organics may not necessarily result in attainment of stringent levels of THMs in drinking water where chlorine is used as disinfectant. This is due to the concentration of residual DOM that is recalcitrant to removal by coagulation. This problem does not occur when the EC process is used, since disinfection is assured by EC itself. Consequently, more studies on application of EC as a substitute of chemical coagulation/disinfection at an industrial level must be done with NOM characterisation to optimise this process.

Keywords: Natural organic matter; Water treatment; Coagulation; Enhanced Coagulation; Electrocoagulation

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*Corresponding author.

1. Introduction

Natural organic matter (NOM) in water is a major concern and should be removed from drinking water for a number of reasons, including that NOM: affects organoleptic properties of water (colour, taste and odour); reacts with most disinfectants used in water treatment, thus reducing their disinfection power; influences disinfectant demand, and disinfection process design, operation and maintenance; produces disinfection by-products (DBPs) of various kinds; affects stability and removal of inorganic particles; influences heavily on coagulant demand; may control coagulation conditions and coagulation performance; affects corrosion processes; affects biostability and biological regrowth in distribution systems; forms complexes with and increase mobility of most chemical substances found in nature; fouls membranes; reduces adsorption capacity of granular activated carbon (GAC)/powder activated carbon (PAC) by pore blocking; competes with taste and odour for adsorption sites in GAC/PAC [1–5].

NOM of microbial, animal and vegetable origin in reservoir catchments is the key factor influencing most, if not all water treatment processes. With respect to coagulation process operation NOM is a key parameter because it will control coagulation processes in most cases. The character of the NOM and its involvement in water treatment processes requires greater understanding for determination of improved removal processes and interactions with other water contaminants. Contrary to conventional coagulation processes aimed primarily at turbidity removal, enhanced coagulation (EnC) implies the use of elevated coagulant dosages and strict control of pH. The implications of this shift in treatment target and operating conditions includes elevated sludge production rates, increased solids load to subsequent separation processes (i.e. settling, flotation and/or filtration units), use of inorganic acids for pH-control, increased focus on operation and optimisation issues, possible conflicts in optimum conditions for various target parameters like turbidity, NOM and micro organisms. In addition, coagulated NOM will form loose flocs and lead to early filter breakthroughs, i.e. shortened filter runs compared with conventional coagulation and filtration processes for the removal of turbidity [1]. Therefore, NOM is a key target parameter in water treatment process.

2. Natural organic matter

NOM in water contains a heterotrophic mixture of hydrophobic and hydrophilic organic compounds with a wide range of molecular weights, including non-homogeneous organic compounds such as humic substances (HS), amino acids, sugars, aliphatic and aromatic acids. NOM can be broadly divided into two fractions: HS and non-humic substances (non-HS), which include carbohydrates, lipids, and amino acids. HS are considered resistant to bacterial degradation, whereas non-HS are biodegradable and often referred as biodegradable organic matter (BOM). NOM is divided in dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC is defined operationally as material that passes a 0.2- or 0.45-μm filter. DOC consists of truly dissolved substances and macromolecules with colloid-like properties (e.g. HS). POC is defined as material that is captured by a 0.2- or 0.45- μm filter. POC consists of larger particles like algae, bacteria, particulate detritus, and organic matter (OM) within flocs. In addition, POC includes inorganic particles covered by NOM [1].

Visible and ultraviolet absorbance has been widely used to characterise raw waters in general. Because of the good correlation to DOC, colour and UV-absorption (UV-abs) are also used as surrogate parameters to DOC. Total and DOC is measured indirectly from the CO_2 produced by UV-oxididation or combustion of the OM in a water sample. Specific UV absorbance (SUVA or $SUVA_{254}$), is defined as the UV absorbance at 254 nm (m^{-1}) divided by the concentration of DOC ($mg\ C\ L^{-1}$). The unit of SUVA is commonly expressed as $L\ mgC^{-1}\ m^{-1}$. SUVA correlates well with the aromaticity and the hydrophobicity of the organic carbon. High hydrophobicity is associated with good treatability by coagulation. Therefore, SUVA can be used to indicate raw water treatability by coagulation and to predict the removal of organic carbon by coagulation [1].

NOM may have distinctive characteristics associated with its origins (vegetation, soil, wastewater, agricultural return). For example, dissolved organic matter (DOM) from aquatic algae has a relatively large nitrogen content and low aromatic carbon and phenolic contents. On the other hand, terrestrially derived DOM has relatively low nitrogen content but large amounts of aromatic carbon and phenolic compounds. Thus, the aromatic content, which is believed to be a major reactive component, varies with different sources. The contribution of each carbon source is seasonally dependent, and the hydrological and biogeochemical processes involved in physical mixing and in the carbon cycles can alter the chemical composition and the physical structure of DOM. Changing climatic conditions (e.g. global warming and more intensive rain events) may increase the volume of the DOM reservoir (e.g. increased amount of litter), the biodegradation rates and also the volumetric transport of DOC from a watershed to a water source. As a result, the concentration of NOM/DOM in drinking water sources may increase, in accordance with observations from Northern Europe and North America during the past 10–20 years. From these facts, physical and chemical fractionation of NOM/DOM may yield valuable information on characteristics and treatability [1].

NOM has a great influence over the fate of inorganic colloids in water. The chemical nature and structure of NOM will be an important factor in determining whether colloids will be stabilised or destabilised by NOM. Fulvic acids (FA, a fraction of HS) are likely to be responsible for coating and imparting a negative charge to colloids. If the adsorbed organic coating produced and increase in absolute surface potential, it will act to stabilise colloids in the water column. On other hand, colloid organic carbon, especially chain-like structures, can aggregate inorganic colloids through the formation of bridges. The importance of each process depends on nature and concentration of OM, as well as on other factors (e.g. origin of NOM, temperature, water treatment process) [1].

3. Coagulation

In conventional turbidity removal processes, coagulation using metal based coagulants (Al, Fe) was considered as a destabilisation process of colloidal particles, involving two primary coagulation mechanisms (Table 1). The presence of NOM affects greatly the chemistry of coagulation. Coagulants remove dissolved NOM by complexation reactions followed by a phase change, i.e. the NOM is removed from solution by forming a solid or adsorbing onto a solid (Table 1). In addition, NOM can coat inorganic particles, altering their coagulation behaviour. The coagulation of waters containing both particles and NOM becomes more complicated, involving several important factors (Table 1). The presence of other charged constituents like calcium and sulphate have also been shown to affect coagulation under certain circumstances. From this, Pernitsky and Edzwald [6] proposed the conceptual view of the coagulation reactions shown in Fig. 1 [1].

3.1. SUVA, *NOM-fractions and treatability*

According to Edzwald and Tobiason [7], SUVA values of 4 and higher indicate that NOM controls the coagulation process, and that good NOM removal can be expected (> 50%). In this case, NOM is dominated by high molecular weight, hydrophobic HA fractions. For SUVA ratios in the range of 2–4, NOM is normally dominated by a mixture of hydrophobic and hydrophilic fractions of different molecular weights, HA and FA, as well as other NOM (algae and algae residues, etc). Here NOM influences coagulation, and fair to good DOC removals can be expected (25–50%). For raw waters with SUVA below 2, NOM is normally dominated by mostly non-humic, low molecular weight and substances with low hydrophobicity. NOM has little influence on coagulation performance, and poor DOC removal can be expected (<25%). The different NOM fractions exhibit different properties in terms of treatability by coagulation. It has been reported that high molecular weight, hydrophobic NOM fractions can be removed efficiently while low molecular weight hydrophilic fractions are not removed. Furthermore, the different fractions exhibit different coagulant demand and show different chlorine and ozone reactivity and by product formation [1].

3.2. *Colloidal charge and zeta potential*

It was reported that the majority of the total colloidal charge exists in the hydrophobic material, with values of

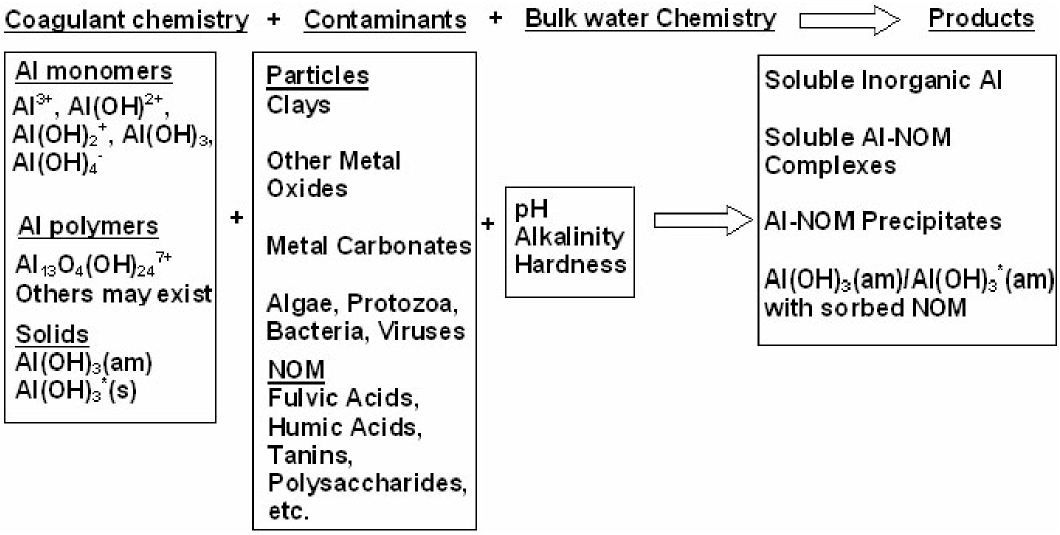


Fig. 1. Conceptual view of coagulation reactions [1,6].

Table 1
Main mechanisms for coagulation, EnC, EC (based on [1,57])

Process	Main mechanisms
Coagulation (coagulant dosing)	Particles presence: 1. Charge neutralisation of the negatively charged colloidal particles by adsorption of positively charged coagulant species. 2. Enmeshment 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 charge neutralisation of the negatively charged colloidal particles by adsorption of positively charged coagulant species. 2. More enmeshment 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.
EnC (increased coagulant dosing and acidified pH)	Particles presence: 1. Most charge neutralisation of the negatively charged colloidal particles by adsorption of positively charged coagulant species. 2. Less enmeshment 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 and electric field)	1. Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralisation. 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 (sweep coagulation). 5. Oxidation of pollutants to less toxic species. 6. Removal by electroflotation or sedimentation and adhesion to bubbles.

5.1±1.3, 3.6±0.7 and 1.0±0.6 meq gDOC^{-1} for the humic, the fulvic and the hydrophilic acid fractions, respectively. Humic and fulvic waters typically exhibit charge densities of 5–15 meq gDOC^{-1}. The charge densities of the hydrophilic fractions are generally very low [1].

Sharp et al. [8] studied seasonal variation in DOC. They calculated charge concentrations and showed that the majority of the charge load comes from the hydrophobic fractions (e.g., 0.0266, 0.0263 and 0.0280 meq L^{-1} for April 2002, January 2004 and August 2004 samples, respectively). The charge density or carboxylic acidity of a fraction is likely to affect the coagulant demand. Higher charges are associated with the larger MW fractions. The charge load of each NOM-fraction shows seasonal variation, and it was concluded that coagulant demand cannot be calculated based solely on bulk parameters such as DOC in a specific raw water. The zeta potential values at a pH of greater than 4 were −13±3.7; -17±0.3, and −25±2.2 mV for the FA fraction, the raw water, and the HA fraction, respectively. In contrast, the zeta potential for the hydrophilic fractions was substantially lower and decreased with pH. Ratnaweera et al. [9] performed jar tests to study the coagulation behaviour of eight natural Norwegian water samples containing NOM. They found that the optimum coagulant dose and the colloidal charge were both proportional to the initial colour, and that DOC and UV-absorbance was well correlated with colour. Zeta potentials at optimum coagulation conditions deviated from zero, indicating that other coagulation mechanisms than charge neutralisation are relevant. From this, they considered it difficult to use zeta potential as the only tool for online dosing control. Sharp et al. [8] performed bench-scale and pilot-scale coagulation experiments on three source waters: two from UK moorland catchments and one from a US snow melt source. From this they presented an overview and a discussion of the links between NOM character and treatability by coagulation. Their work demonstrated the importance of the polarity balance and the charge density of the NOM. NOM composition can vary both temporarily and spatially, with increased DOC concentrations associated with both an increase in hydrophobic content and charge density. The hydrophobic content controls the coagulant demand such that variation in the demand between sources or sampling periods can be accounted for by changes in the hydrophobic content and charge density of the NOM. The raw water hydrophilic content, and specifically the non-acid fraction, provides an indicator of the achievable residual. A clear relationship was revealed between zeta potential and residual DOC. For each source an optimum operational zeta potential exists, in the range between −10 and +3 mV for the investigated raw waters, thus providing a useful guide range for operational control of EnC processes. Henderson et al. [10] investigated surface characteristics and floc properties of three common systems: NOM, algae and clay. They demonstrated that difficulties arise when coagulation is not optimised for the dominant substance/particle. Charge density and specific surface area were important parameters with respect to coagulant demand for charge neutralisation of all three systems. Extra-cellular organic matter (EOM) affected the coagulant demand of algae to such an extent that it could dominate the coagulation process. Algal flocs were much weaker and required five times the flocculation period to reach steady-state floc size compared to NOM and clay flocs. Despite similarities between algae and NOM in terms of organic content and coagulant demand, the fact that algae is a dynamic, biological system creates numerous problems for the coagulation/flocculation processes. Pommerenk and Schafran [11] investigated the removal of sulphate, orthophosphate, fluoride, five organic acids (including HA) and NOM from two sources by adsorption on aluminium hydroxide precipitates. Phosphate was nearly completely removed from solution across a wide range of pH, and was observed to lower the surface charge and shift the isoelectric point of the hydroxide precipitate. Sulfate was removed to a lesser extent than phosphate, lowered the surface charge on the precipitate, but did not shift the isoelectric point. Fluoride was well-removed through adsorption to the precipitate, but did not influence the charge of the aluminium hydroxide. The organic acids displayed varying abilities to be removed through adsorption and different influences on surface charge. The results indicate the importance of the number and location of functional groups and their acid/base properties. The ability to strongly influence surface charge illustrates the impact that adsorption of these anions can have on particle stability [1].

3.3. Coagulation, pH and iso-electric point (IEP)

Qin et al. [12] studied NOM removal by EnC at a water works in Singapore. From jar tests using different coagulation pH and alum dosages the optimum conditions were observed at a pH of 5.2 and a alum dose of 5 mg Al L^{-1}). Under optimal conditions, turbidity and DOC removals of 97 and 45% were obtained, respectively. The DOC removal obtained with conventional coagulation at pH 7.2 was only 35%. It was concluded that control of coagulation pH was critical for NOM removal in treatment of reservoir water. Sharp et al. [8] reported that the IEP (the pH associated with zero charge) of the NOM fractions were 1.5, 1.6, 1.7, 4 and 4.7 for the HA, FA, raw water, hydrophilic acid and the hydrophilic non-adsorbed (HPNIA) fractions, respectively. The addition of coagulants shifted the IEP of the system, indicating interactions between the coagulant and the NOM fractions. The interactions between the individual NOM fractions and coagulant (Me^+) were monitored through changes in IEP of the sample, at various DOCs to coagulant mass ratios (meq DOC: meq Al or Fe). The results show that the hydrophobic fractions produced the largest change in IEP (i.e. a small change in charge ratio imposed a large change in IEP). On this background, Sharp et al. [8] concluded that it is the hydrophobic fractions which appear to be critical in determining the resultant charge properties of the coagulant-NOM system and hence the subsequent coagulant dose requirements. At the coagulation pH of normal operation (pH 5–7), the hydrophilic fractions possess a negligible or slightly positive charge, leading to poor removal and values as low as 16% were reported by Fearing et al. [13]. Jarvis et al. [14] studied how the NOM floc structure was affected by increased organic fraction in the floc. It was observed that when the organic floc fraction went significantly over a mass ratio of 1 mg DOC to 1 mg of Fe (coagulant), the floc size, settling velocity, fractal dimension, and strength were seen to decrease even when the NOM removal during coagulation remained high. These effects were proposed to result from adsorption of NOM on primary particle surfaces (i.e. coagulant precipitates). The operational significance of these results suggests that the correct coagulant dose must be applied to give good floc structure. Sharp et al. [8] stated that a number of UK and US water utilities have been experiencing operational difficulties associated with increased DOC levels during the autumn and winter periods, resulting in increased coagulant demand and increased production of DBPs. During a 3-year study period a seasonal change in NOM composition was observed, with the hydrophobic, FA fraction increasing from 36% in September to 61% in November. A reduction in treatment performance was not simply due to an increased organic carbon concentration (from 4.3 to 14.5 mg DOC L^{-1}), but is also to a change in the charge density of the NOM. Hydrophilic NOM fractions were found to possess a negligible charge density (<0.06 meq $gDOC^{-1}$), they were less amenable to removal by coagulation, and were therefore likely to indicate the DOC residual remaining after treatment. On the other hand, it was the hydrophobic NOM fractions, the FA fraction in particular, that exert the greater dominance on coagulation control. Understanding the seasonal changes in NOM composition and character and their reactivity with the coagulants should lead to a better optimisation of the coagulation process and a more consistent treated water quality [1].

Above we have described the pH effects on the interactions of NOM with surfaces of coagulant flocs; however, pH may also have indirect effects on removal of NOM, especially, on removal of HS. HS are macromolecules which behave like polyelectrolytes; thus their sorption is determined not only by availability of sites, but also by lateral interactions between themselves and the steric arrangements of the macromolecule. When the pH of water decreases HS acquire a coiled configuration (due to lower intermolecular electrostatic repulsion) in solution, thus they may be more effectively adsorbed on surfaces by hydrophobic interactions. With the current trends forecasting an increase in DOC concentrations, an increased understanding of the treatment system and the involved mechanisms is vital, especially as the potential consequences of increasing NOM concentration levels are likely to impact dramatically on the water industry. NOM characterisation, e.g. fractionation, charge measurements, etc. during the coagulation process and comparison across different source waters, seasons and coagulants could be used in a proactive strategy in achieving a more robust and cost-effective water treatment plant operation in general, and during problem periods in specific [1].

4. Enhanced coagulation

4.1. Enhanced coagulation process design and major treatment objectives

Coagulation (followed by filtration) is widely used in water treatment because the process is very effective for controlling a wide range of contaminants. These includes particulate matter that causes turbidity; NOM that causes colour and UV-light absorption; algae; inorganic substances like iron, manganese and arsenic; bacteria, virus and protozoa (e.g. *Cryptosporidium* and *Giardia*) [1].

Jacangelo et al. [15] discussed the increased emphasis by the water industry on the removal of NOM as a result of new regulations. Among NOM removal options, EnC is the most widely used in the water industry. But when coagulation is unable to remove adequate concentrations of NOM, other treatment technologies such as GAC filtration and membrane filtration may need to be used. The capability of a water treatment plant employing coagulation and filtration is of course dependent of the nature, design and operation of the coagulation and filtration steps themselves, but it is also highly influenced by the nature and extent of pre-treatment. Conventional filtration plants, i.e. plants with pre-sedimentation can cope with raw waters with high concentrations of turbidity (>1000–2000 NTU), NOM, and oxidised inorganic matter. Direct filtration plants, in which sedimentation is omitted, can effectively treat "ideal" raw waters with turbidity of 10–20 NTU, and colour up to 40 mg Pt L^{-1}. Dissolved air flotation (DAF) is known to be very effective in removing algae. Algae generally do not settle well, and can clog filter beds. Pre-treatments may include microscreening, pre-ozonation, the addition of other types of oxidants, silica, PAC, etc. Post-treatments may include GAC filtration for taste and odour removal, disinfection, post-corrosion control, etc. In addition, conventional deep bed filters can be replaced by membrane filters, e.g. NF, UF or MF with pre-coagulation, etc) [1]. Conventional filtration, direct filtration and contact (in-line) filtration concepts have all proven effective for controlling NOM as well as protozoa in water, provided optimum or near-optimum coagulation and filtration conditions and management. In the last few years, membrane filters are also used in combination with coagulation, e.g. coagulation followed by ultra filtration. In this application, membrane fouling control is a key operation challenge, and it is very important also in this respect to find the optimum coagulation conditions. Optimum EnC conditions seem the favourable conditions also in this respect [1].

4.2. Optimum coagulation conditions (coagulant type, coagulant dosage and pH)

Deviations from optimum coagulation conditions (i.e. coagulant dose and pH) can seriously affect treatment performance with respect to residual coagulant concentrations, turbidity, particle counts, NOM, and microorganisms. A proper control of coagulant dosage and coagulation pH are the most important operation challenges. Rapid and large variation in raw water quality, with optimal adjustment of the coagulation conditions to the actual raw water quality (e.g. DOC, colour, etc.), represents major operational challenges [1].

Edzwald and Tobiason [7] summarised principles for alum coagulation of NOM as follows: negatively charged NOM creates a coagulant demand for positively charged Al species resulting in a stoichiometric relationship between the alum dosage and the raw water DOC that is pH dependent. They addressed coagulation in a broader view than EnC, termed multiple objectives coagulation. This includes maximisation of particle, turbidity, TOC, and DBP precursor removal, and minimisation of residual coagulant, sludge production and operating costs. Based on full-scale plant data, they also demonstrated a dual coagulation strategy of alum and cationic polymer that reduces sludge production and overall operating costs compared to alum alone. Edzwald [16] presented a review on coagulation in water treatment, emphasising the importance of raw water chemistry, NOM concentration and type, and the chemistry of coagulants. NOM rather than particles in water supplies can control coagulant dosage and selection. The removal of NOM with Al coagulants can involve hydrolysis, complexation, precipitation, and adsorption reactions. O'Melia et al. [17] stated that adsorption of NOM on oxides depends significantly on complex formation reactions between specific sites on oxide surfaces and functional groups on the NOM. Coagulation requirements can and often are set by the TOC concentration in a water source. Frequently there is a stoichiometric relationship between the required coagulant dosage and the TOC of the water to be treated. Other important factors include pH and the concentration of divalent cations [1].

Eikebrokk [18–20] demonstrated in contact filtration pilot experiments with aluminium and iron-based coagulants that compliance with the total residual coagulant concentration standard of 0.1 mg Me L^{-1} was the determining factor with respect to identifying minimum coagulant dosage requirements when treating low turbidity surface waters with NOM concentrations measured as colour and TOC in the range of 15–50 mg Pt L^{-1} and 2–6 mg TOC L^{-1}, respectively. Compliance with the turbidity (<0.2 NTU) and colour (<5 mg Pt L^{-1}) could be obtained with lower coagulant doses. He distinguished between absolute and practical minimum doses; the difference being that for the absolute minimum dose level the maximum residual metal concentration of 0.15 mg Me L^{-1} can be obtained only within a very narrow pH-window. When using the 25% higher practical minimum dosage, the pH window for optimum process performance and compliance with the water quality standards can be obtained within a wider range of pH. The great importance of controlling the coagulation pH within strict limits was clearly demonstrated. The width of the optimum "pH-window" increased with increasing coagulant dose level, indicating the relationship between coagulant dosage and ease of operation from the operator's point of view. As an illustrating example, raw water with a specific UV-absorption (SUVA) of 4.8 and a TOC of 5 mg L^{-1} would require a minimum dose of 3.5 mg Al L^{-1} and 7.25 mg Fe L^{-1} to cope with the residual metal standard of 0.1 mg Me L^{-1}. The correspondent reductions in colour and TOC would be in the range of 90 and 50–60%, respectively. The specific coagulant dose requirements presented above agree well with data presented by Pernitsky and Edzwald [6] who tested coagulation requirements for raw waters with different NOM, turbidity and alkalinity levels. For all waters examined, they found that 0.5–0.8 mg Al per mg of TOC in the raw water was required, which is in accordance with stoichiometric estimates presented by Edzwald [16].

Mesdaghinia et al. [21] studied EnC effectiveness in removal of DBPs. From jar test experiments on Iranian river water they concluded that NOM removal was a function of coagulant type, coagulant dose, and pH of coagulation. Ferric chloride was consistently more effective than alum in removing NOM. Coagulation pH appeared to be a determining factor for maximum NOM removal, and the removal of DBP precursors was significantly enhanced at pH 5.5 in comparison with the initial pH of the water. Pre-adjustment of pH with sulphuric acid reduced the required coagulant dosage and thus the production of sludge. Jiang and Graham [22] studied the consequences of EnC, i.e. the use of excess coagulant and lowering the coagulation pH in order to improve NOM removal, including increased sludge production and increased treatment costs, and the need for chemical storage and feed facilities to be changed. They stated that the use of various types of pre-polymerised coagulants that have been developed in recent years can improve NOM and trihalomethane formation potential (THMFP) removals at relatively lower dosages, and thereby reduce the operational and economic consequences of EnC. Matilainen et al. [23] compared the efficiency of aluminium and ferric sulphate coagulants for NOM removal during coagulation/flotation of drinking water in Finland. Approximately 95% of high molar mass organic substances (HPSEC) were removed with both coagulants. The greatest difference between the coagulants occurred in the removal of organic compounds having molar masses of 1000–4000 g mol^{-1}, which were removed 25% more efficiently with the iron-based than the aluminium-based coagulant. Low molar mass material was poorly removed regardless of the coagulant (10%). In terms of overall NOM removal, iron was 10% more efficient than aluminium. However, turbidity removal during coagulation/flotation was more efficient with aluminium, especially during the winter period. Turbidity was effectively removed during filtration [1].

Fearing et al. [13] reported that over 70% removal of hydrophobic and hydrophilic acid fractions, while only 16% of the hydrophilic non-acid fraction was obtained using conventional coagulation treatment during elevated NOM loadings at a treatment facility. From jar tests on isolated NOM fractions, it was concluded that increased removal of the hydrophilic fractions could be obtained when conditions were optimised. From this, an optimised two-stage coagulation process was proposed to increase the removal of recalcitrant fractions of NOM. Wang et al. [24] studied the effectiveness of enhanced alum coagulation for removal of NOM at various alum dosages and pH conditions for three source waters in Taiwan. Jar tests were performed with alum dosages ranging from 60–120 mg L^{-1} of alum, and pH values from 5.0 to 8.0. DOC removals of up to 50% were achieved, depending on raw water DOC and alkalinity levels. Freese et al. [25] performed laboratory and pilot scale tests to compare the effectiveness of EnC with ozonation and granular activated carbon adsorption in treating various types of raw water in South Africa. Reductions of up to 50% in THMFP and 50-70% in organic carbon and colour were obtained using EnC, which compared favourably with ozonation and GAC filtration. The latter process was especially effective in the removal of micro pollutants, generally being in excess of 70%. Inorganic coagulants were found to be more effective than polymeric coagulants for OM removal, and the addition of inorganic acids to depress pH allowed for increased organics removal at lower coagulant doses [1].

4.3. Removal of protozoa during EnC

States et al. [26] studied the influence of EnC and decreased coagulation pH levels on the removal of *Cryptosporidium* oocysts, TOC, turbidity and particle counts. A series of pilot-plant trials were performed with commonly used coagulants (ferric chloride, alum, and polyaluminium chloride) at various pH levels to treat river water spiked with large numbers of *Cryptosporidium* oocysts. The results show that TOC removal is significantly enhanced by coagulation at lower pH levels and that all three coagulants are effective in removing *Cryptosporidium* oocysts (mean removal = 4.3 log units). However, turbidity and particle counts appeared to be unreliable indicators of oocyst removal. The investigation suggested that lowering coagulation pH does not interfere with removal of *Cryptosporidium*. Dai and Hozalski [27] performed experiments in bench-scale 0.25 m deep rapid filters with 0.55 mm glass beads to study how the removal of *Cryptosporidium* oocysts by filtration was effected by NOM and biofilms. They found that the oocyst removal efficiency was decreased as a result of presence of NOM and biofilm-coatings in the filter bed, indicating that water treatment facilities employing biologically active filters have a greater potential for oocyst breakthrough and proper coagulation is critical for effective removal of oocysts in the filters. Oocysts pre-equilibrated with NOM were more hydrophobic and significantly more negative than those obtained for untreated oocysts. Fortunately, the use of alum for coagulation was able to neutralise the surface charge of the NOM-coated oocysts and provide high removal efficiency. Xagoraraki and Harrington [28] evaluated the removal of viable *Cryptosporidium parvum* oocysts and changes in zeta potential during alum coagulation and sedimentation. The removal of oocysts and their zeta potential were evaluated at three raw water DOC concentration levels and a wide range of alum doses and coagulation pH values. The study showed that the NOM content of the raw water, i.e. the initial DOC concentration affected the removal and zeta potential of the oocysts. Charge neutralisation was not considered a relevant removal mechanism for oocysts under the conditions used in this study. Sweep coagulation appeared to be the primary removal mechanism at the lowest DOC concentration tested. For the highest DOC concentration used in this study, optimal coagulation for oocyst removal coincided with optimal coagulation conditions for NOM removal, suggesting that NOM plays a key role in the interaction between oocysts and the aluminium hydroxide precipitate [1].

Logsdon [29] stated that deviations from optimum or near-optimum coagulation and improper management of filtration rate increases can severely deteriorate filtration performance for removal of protozoa. Likewise, improper backwash water recycling can disrupt coagulation. Continuous monitoring of coagulation and filtration is an aid to effective management of the treatment process. Production of filtered water having a turbidity of 0.1 NTU or lower should be the goal if effective control of cysts and oocysts is to be attained. However, no concentration of cysts could be associated with a specific value of filtered water turbidity. Hamilton et al. [30] concluded that if oocysts are present in a work's raw water, there is strong evidence to suggest that minimising treated water turbidity/particle count will reduce *Cryptosporidium* risk. However, neither particle counters nor turbidimeters are able to detect *Cryptosporidium* oocyst or reliably predict their occurrence in treated waters. Particle counters have demonstrated some benefits in three areas, namely: higher sensitivity to changes in water quality at low turbidities (<0.1 NTU), higher sensitivity changes associated with larger particle sizes (e.g. filter breakthrough events), and the ability to monitor changes in particle size distribution [1].

Logsdon [29] reviewed five pilot plant investigations, treating raw waters with turbidity generally below 10 NTU: Logsdon et al. [31] investigated *Giardia* removal (seeded cysts) in direct filtration pilot trials with a dual media anthracite and sand filter, a filtration rate of 10 m h^{-1}, and a coagulant dose of 10 mg L^{-1} alum (i.e. approx. 0.9 mg Al L^{-1}). Operational variations tested included sub-optimal and very inadequate coagulation, filtration rate increases, and turbidity breakthrough with high head loss [1]. Logsdon [29] concluded from the review that at optimum coagulation conditions when filtered water turbidity was 0.1 NTU or lower, removal of cysts and oocysts was more effective than when turbidity was above 0.1 NTU. Sub-optimal coagulation resulted in filtered water turbidity in the range of 0.1–1 NTU. Higher concentrations of cysts and increased filtered water turbidity were observed during filter ripening. Filtration rate increases ranging from 50 to 150% in 10 s did not cause filtered water turbidity to increase when flocs were strengthened with a non-ionic polymer. When alum was used with no polymer, a filtration rate increase from 10 m h^{-1} to 27 m h^{-1} for a period of 2 min caused turbidity to increase from 0.3 to 1.0 NTU, and the *Giardia* cysts concentration increased 25-fold. When the filtration rate was decreased to 10 m h^{-1}, both turbidity and *Giardia* cyst concentration returned to levels observed before the rate increase. The results also showed that turbidity breakthrough at the end of a filter run can be accompanied by a massive discharge of micro organisms. Recycling of filter backwash water by returning it to the influent raw water will normally increase the concentration of suspended solids and microorganisms in the influent water, and it may upset the coagulation chemistry. Emelko [32] used bench-scale glass filter columns to investigate dual- and tri-media filter removals of both viable and formalin-inactivated *Cryptosporidium parvum* oocysts. She found that formalin-inactivated *C. parvum* oocysts were good surrogates for viable oocysts in filtration studies conducted during stable operation, ripening and coagulation failure, and that dual and tri-media filters performed equally well. *C. parvum* removal was high (4.6–5.8-log) during stable operation, but was moderately lower (4.0–5.7-log) during filter ripening. During the coagulant failure conditions, the *C. parvum* removal was severely compromised relative to both filter ripening and stable operation. Removals of non-coagulated oocysts ranged from 0.5–2.5-log [1].

4.4. Operational challenges and bottlenecks

4.4.1. Coagulant dosage and coagulation pH

Proper coagulation is essential for good clarification and filtration performance and for the control of pathogens and DBPs. Improper coagulation can cause high residual coagulant residuals in treated water and post-treatment precipitation of particles causing turbidity, deposition and coatings of pipes in the distribution system. Minimising of solids residuals from coagulation has also become a more important part of utility operations due to increased disposal costs and landfilling restrictions. These issues have put additional pressure on utilities to optimise coagulation to meet the multiple treatment objectives: 1) to maximise the removal of particles, turbidity and microorganisms/pathogens by downstream solid-liquid separation, 2) to maximise TOC and DBP removals, 3) to minimise residual coagulant concentrations, 4) to minimise solid residuals (sludge) production, and 5) to minimise operating costs [1]. Budd et al. [33] stated that optimisation of coagulation is central to the drinking water industry's ability to meet goals for particulate (turbidity) and NOM removal. They stressed the importance of adopting a holistic view of treatment objectives when considering possible changes to the coagulation process, and highlight the necessity of evaluating coagulation as a multiple-input process that can be fine-tuned through adjustment of two fundamental parameters – pH and coagulant dose. Changes that might be undertaken include trying a different coagulant dose and pH, using alternative coagulants, and adding coagulants in a different sequence. Their recommendations were based on coagulation evaluations performed at a number of US water treatment facilities over the past 15 years [1].

Coagulant dosage and coagulation pH are traditionally determined according to results from jar-tests or operator's experience, which often lead to coagulant overdosing or insufficient dosing, reduced water treatment performance and increased treatment costs. From extensive pilot experiments, Eikebrokk [18,19] showed how residual metal (Al, Fe) determined the coagulant dosage requirement in order to meet the relevant Norwegian drinking water quality standards for treatment plants applying coagulation (i.e. residual Al or Fe <0.15 mg L^{-1}; turbidity <0.2 NTU, colour <5 mg Pt L^{-1}, and TOC <3 mg L^{-1}). The example of pilot investigation results using ferric coagulation-contact filtration illustrates that although TOC removal efficiency in excess of 60% was obtained with a coagulant dosage of 5 mg Fe L^{-1}, a dosage of 6.5 mg L^{-1} was required to comply with the residual Fe standard of 0.15 mg L^{-1}. With 5 mg L^{-1} of Fe, a residual Fe concentration in excess of 0.4 mg L^{-1} was detected. With the 5 mg Fe L^{-1} dosage, the optimum pH-range is very narrow (4.9–5.2). With 6.5 mg Fe L^{-1} however, more than 60% TOC removal was achieved within a wide range of pH (3-6). However, even 6.5 mg Fe L^{-1} was close to the minimum dosage required in order to comply with the 0.15 mg residual Fe L^{-1} standard within a reasonably wide pH range (5.0–5.5). Emelko [32] investigated the removal by alum coagulation of viable as well as formalin-inactivated *Cryptosporidium parvum* oocyst in bench-scale dual- and tri-media filters. Her results indicated that formalin-inactivated oocysts were suitable surrogates for viable oocysts. She also found that poor coagulation conditions severely compromised removal of viable and inactivated oocyst by dual- and tri-media filters compared to stable operating conditions and filter ripening, emphasising the importance of optimised coagulation for the successful removal of oocysts during filtration. During filter ripening, the *C. parvum* removals were moderately lower (approximately 0.5–1-log) than during stable operation, while during coagulation failure conditions the *C. parvum* removal capacity of both dual- and tri-media filers was severely decreased (by more than 3-log) relative to both ripening and stable (optimised) conditions. Tri-media filters offered only marginally higher oocyst removals than dual-media filters. Although a sub-optimal coagulant dose may result in excessive residual metal concentrations, reduced removal of pathogens like *Giardia* and *Cryptosporidium*, and non-compliance with the water quality standards, coagulant overdosing should be avoided. In conventional filtration applying presedimentation the negative effects of overdosing are normally limited to increased costs, excessive sludge production, etc. However, restabilisation may occur, resulting in poor treatment performance [1].

4.4.2. Effect of pH adjustment on overall performance of the plant

EnC involves adjustment of pH, alkalinity and increase coagulant doses. This can result in number of secondary impacts on water treatment as seen in Table 2. If pH is lowered to improve coagulation and organic removal, it is typically necessary to raise pH in the final effluent from the plant to provide less corrosive finished water. The pH may be adjusted at one or more points in the treatment, including rapid mixing, pre-filtration and post-filtration. In case of EnC it is recommended to readjust the pH after the filtration process as compare to pre-filtration. This is due to the fact that some OM may be adsorbed onto the floc that may carry over from the clarification process, and any pre-filtration pH adjustment may then result in "release" of that OM, which could pass though the filters and contribute to subsequent DPB formation [1].

4.4.3. Metal coagulant residuals

As discussed above, total residual metal coagulant concentrations often determine the coagulant dosage needed in order to comply with the water quality standards. Srinivasan et al. [34] analysed data from the Buffalo Pond WTP in Saskatchewan (Canada) in order to examine seasonal variations and factors influencing residual aluminium concentrations. Analysis of eight-year data showed that the DOC present in the raw water played a major role in controlling efficacy of alum coagulation. They found that when alum/DOC ratio was less than 7, insufficient alum addition led to incomplete coagulation resulting in colloidal material mostly consisting of organic aluminium in particulate form. Hence particulate aluminium increased in treated water. But this

Table 2
Secondary impacts on water treatment of EnC [1]

Secondary impacts	Explication
Increases solids	The higher coagulant dosages directly result in increased sludge volumes.
Poorer dewatering characteristics	The increased metal (Al^{3+}, Fe^{2+}/Fe^{3+}) concentrations typically result in poorer dewatering characteristics. As a result, a change to EnC may result in lower ultimate, dewatered solid concentrations.
Increased concrete/metal corrosion.	The lower pH of the coagulated water for TOC removal will be significantly more aggressive on concrete and metals as compared to a more neutral coagulation pH used for turbidity removal.

increase in residual aluminium did not increase the turbidity of treated water. This indicated that an adequate alum dose in response to DOC is important in minimising residual aluminium in treated water. The plant data also showed that when freshly regenerated GAC contactors were used, peaks of dissolved aluminium occurred as a result of alkaline metal (calcium and magnesium) oxides present in the regenerated GAC that shifted the pH of filtered water to alkaline range with consequent formation of soluble aluminium species like $Al(OH)_4^-$. Srinivasan and Viraraghavan [35] conducted aluminium speciation experiments in a pilot scale water treatment plant using different alum doses. In addition, they conducted jar tests at various alum/DOC ratios. They concluded that an alum/DOC ratio of at least 7.3 should be maintained in order to meet the operating guidelines of 100 μg L^{-1} of total aluminium proposed by Health Canada given that finished water soluble aluminium levels may be in the range of 35-40 μg L^{-1}. For lower alum/DOC ratios (1.37 and 5.3) most of the total aluminium in filtered water was in the form of particulate aluminium, and soluble organic aluminium increased compared to the level in raw water. Jekel [36] investigated the interactions of HA and aluminium coagulants and reported that at low coagulant dosages, i.e. less than 10 mmol of Al^{3+} $gDOC^{-1}$ in raw water (i.e. 0.27 mg Al $mgDOC^{-1}$), high residual aluminium levels were found and low amounts of DOC were removed. He concluded that the minimum dosage of aluminium should be in the order of 20–40 mmol Al^{3+} per gram of DOC (i.e. 0.54–0.108 mg Al $mgDOC^{-1}$) to overcome the complexing and coagulation problem and to achieve low aluminium residuals [1].

4.4.4. Importance of mixing

Rapid mixing after coagulation is an important design parameter. The coagulant must be uniformly mixed with the raw water. In case mixing is poor local under- and overdosing occurs, resulting in poor performance of the process. The parameter expressing mixing intensity is called the velocity gradient or G-value (s^{-1}). A recommended G-value for rapid mixing is minimally 1500 s^{-1}. Mixing intensity and time has significant effect on the mechanisms (e.g. sweep coagulation, sedimentation) involved in the following process of coagulation. Between the hydrolysis of the coagulant in water and the development of large flocs, short-lived water soluble aluminium and iron(III) hydroxide complexes, metal hydroxide sols are formed, which also carry a positive charge. These latter two metal hydroxide types (which also exist for a brief period - a few seconds - only) are the ones capable of destabilising the dispersion and adsorbed NOM on they surfaces. The bond between the suspended solids to be removed and the metal hydroxide sols and water soluble metal hydroxide complexes must be established within this short period. Rapid mixing of the coagulant will ensure rapid hydrolysis of the coagulant, contact between the sols and the suspended solids and will retard the development of large flocs which are inactive in destabilising the dispersion and removing of NOM [1].

4.4.5. Microorganisms and turbidity in treated water

In general, EnC is an effective multi-purpose treatment process with respect to NOM, turbidity/particles, and microorganisms including protozoa. Process optimisation efforts should also identify possible conflicting optimum operating conditions for the different target substances. Vrijenhoek et al. [37] have shown that by adjusting pH and alum dose it is possible to obtain synergetic effects and efficiently remove both NOM and turbidity (<0.1 NTU). The pH should be kept relatively low to allow adsorption of NOM on surfaces of alum hydroxides, while alum dose should be high (20–60 mg L^{-1}) to allow sweep coagulation for turbidity removal. There are numerous investigations showing that protozoan parasites like *Giardia* and *Cryptosporidium* can be efficiently removed from water by EnC processes, without compromising the removal of NOM and turbidity/particles. However, in most cases success or not is a matter of treatment process optimisation [1].

5. Coagulation and EnC modelling

A mathematical model is a systematic attempt to translate conceptual understanding of the real-world system into mathematical terms. Thus, a model is a valuable tool for testing our understanding of how a system works. From a practical point of view, models can be used for design of water treatment units, because with their help parameters of the treatment train (e.g. filter area and depth) can be calculated more accurately. Models can also be used to improve operation of water treatment processes. By simulating different scenarios models enable operators to adjust operational parameters like coagulant doses, filter loading rates, backwashing conditions and frequency, etc. to optimal levels. Models can also be applied to improve automation and process control systems because they allow predictions and use of computers to simulate different patterns of control actions to find the most appropriate one. Up-to-date, however, this kind of automation is more frequently used for operation of wastewater treatment plants. Roughly models can be divided in **mechanistic** and **empirical** (even though all models contain certain elements of both). Mechanistic models strive to understand and mathematically describe the mechanisms behind the processes occurring in a given system. Empirical models are simpler and often obtained by fitting mathematical equations to a set of experimental data ("black box" approach) [1].

5.1. Modelling of DOC removal

The removal of NOM by coagulation is impacted by a number of factors, e.g. NOM character and concentration, turbidity and alkalinity, other organic as well as inorganic constituents of the raw water. High levels of variation can occur in a range of water quality parameters such as turbidity, alkalinity, colour, NOM, algae and microorganisms. Mathematical models that relate the character and concentration of DOM in the raw water to inorganic coagulant dosing that maximise the removal of DOC have been developed. The models can also be used to predict the required coagulant dosage when treating raw waters of different quality. Van Leeuwen et al. [38] used models to predict alum coagulant dosage that were subsequently applied to treat two Australian raw waters in jar tests and in pilot plant trials. DOC removals of 50–60% were obtained with application of the model predicted alum doses for maximising DOC removal when coagulation was performed at pH 6. Much higher coagulant doses at similar pH resulted in comparatively minor additional DOC removal. THMFP was found to be proportional to the residual DOC and appeared to be linearly related. Formation of individual trihalomethanes (THMs) was consistent in each water source but different between the two sources. Harrington et al. [39] developed an interactive, user-friendly computer program to simulate inorganic water quality changes, THM formation, disinfectant decay and removal of NOM in water treatment processes. Furthermore, they discussed the selection, development and verification of empirical models to include in the program. Tseng and Edwards [40] presented a Langmuir model for prediction of full-scale removal of TOC during enhanced coagulation. Case studies of 27 full-scale utilities showed accurate prediction of TOC removal by coagulation at a range of utilities using alum, ferric, or poly aluminium chloride coagulants. Edwards [41] predicted the concentration of DOC remaining after EnC with a standard error of about 10% or 0.4 mg L^{-1}. Model inputs were coagulant dosage, coagulation pH, raw water UV_{254}-abs, and raw water DOC. When calibrated to a specific site, the standard predictive error could be improved to 4% or 0.27 mg DOC L^{-1}. Performance differences between equimolar dosages of alum and ferric coagulants were attributed to: equal or better removal of DOC using ferric at very high coagulant dosages; equal or better removal of DOC using alum at lower coagulant doses, or differing acidity of coagulants, producing a performance advantage for the more acidic coagulant [1].

5.2. Mechanisms for DOC removal used in the models

In order to develop mechanistic models, an understating of the mechanisms involved in DOC removal is important. The three mechanisms most commonly referred to as important for DOC removal during chemical coagulation are charge neutralisation, entrapment, and adsorption. Charge neutralisation is the mechanism used to explain the removal of NOM in operational regions where aluminium hydroxide precipitation is minimal. Cationic aluminium species interact with anionic NOM to form insoluble charge-neutral products. A linear increase in the required cation concentration (e.g. Al, Fe) with anion concentration is expected. In operational regions where aluminium hydroxide precipitates are formed, NOM can be removed by entrapment (sweep coagulation) in the hydroxide or adsorption to hydroxide surfaces. The concentration of coagulant has to be high to cause rapid precipitation of $Al(OH)_3$. Colloids, including colloidal NOM can act as nuclei for precipitate formation, and can become entrapped during floc aggregation. These mechanisms apply mainly for removal of colloidal NOM, typically higher molecular weight HA. These acids generally have low charge densities and therefore require low coagulant doses to induce destabilisation. However, the more soluble fractions of NOM (FA) have higher anionic charge densities that facilitate their dissolution. The sweep coagulation which operates most effectively on colloidal NOM is unlikely to be effective for these soluble FA. Charge neutralisation may remove soluble FA, but high doses of coagulant will be required to neutralise the high anionic charge, and the high coagulant dose required by soluble FA is likely to correspond to overdosing of HA colloids resulting in restabilisation of the colloids [1].

A fourth mechanism that is occasionally alluded to is the chemical interaction of soluble NOM with soluble coagulant metal ions such as aluminium. The metal cation and the chemically bound (complexed) NOM remains in solution until either the binding capacity of NOM has been satisfied, or the solubility of the metal-NOM complex is exceeded. The complex does not need to be charge-neutral to precipitate [1].

Most of the models developed for EnC (e.g. by Edwards [41]) take into account only adsorption mechanisms. At acidic pH (used for EnC) aluminium species are positively charged, therefore negatively charged OM is effectively adsorbed by electrostatic interactions. Other assumptions included in the model are as follows: part of the DOC consists of non-sorbable fractions that are not removed by coagulation, the adsorption capacity of flocs is a function of pH, the characteristics of DOC do not change with pH, and adsorption can be described with a Langmuir isotherm [1].

5.3. Predicting DOC removal

A model for predicting the DOC concentration remaining after EnC was developed by Edwards [41]. This model takes into account only adsorption mechanisms, described by a Langmuir isotherm. The model uses only parameters that are routinely measured, and it can readily be applied at water treatment plants. The fraction of non-sorbable DOC that is not removed by coagulation is calculated by:

$$\text{Fraction non-sorbable DOC} = K_1\,(\text{SUVA})_{\text{raw water}} + K_2 \quad (1)$$

where K_1 and K_2 are empirical fitting constants. The sorbable DOC can then be calculated by:

$$\text{Sorbable DOC} = (1 - \text{fraction non-sorbable DOC}\}\ \text{DOC}_{\text{initial}} \quad (2)$$

The model is based on the Langmuir equation:

$$x/M = (a\,b\,[C]_{\text{eq}})/(1 + b\,[C]_{\text{eq}}) \quad (3)$$

where x is DOC removed (mg DOC L^{-1}), M is coagulant added and metal hydroxide formed (mmole L^{-1}), C_{eq} is sorbable DOC in solution at equilibrium, and a and b are sorption constants. The constant a can be determined by:

$$a = x_3\,\text{pH}^3 + x_2\,\text{pH}^2 + x_1\,\text{pH} \quad (4)$$

where x_1, x_2 and x_3 are fitting constants. Combining these equations gives:

$$[(1 - \text{SUVA}\,K_1 - K_2)\,\text{DOC}_{\text{initial}} - [C]_{\text{eq}}]/M = [(x_3\,\text{pH}^3 + x_2\,\text{pH}^2 + x_1\,\text{pH})\,b\,[C]_{\text{eq}}]/(1 + b\,[C]_{\text{eq}}) \quad (5)$$

This equation can be solved in an Excel sheet if the six empirical constants (K_1, K_2, x_1, x_2, x_3, b) are known. The DOC concentration remaining after coagulation is then:

$$\text{DOC (mg L}^{-1}) = C_{\text{eq}}\,(\text{mg L}^{-1}) + \text{non-sorbable DOC (mg L}^{-1}) \quad (6)$$

Edwards [41] also determined the values for the empirical constants, still keeping the standard error below 10%. Several other empirical models predicting DOC or TOC removal by coagulation can be found in the literature. However, according to Tseng and Edwards [40] the accuracy of these models is lower than the Langmuir adsorption model described above [1].

6. Electrocoagulation

Coagulation and flocculation are traditional methods for the treatment of polluted water. In these processes, coagulating agents (e.g. alum or ferric chloride) and other additives (e.g. polyelectrolytes) are dosed to produce larger aggregates, which can be separated physically. This is a multi-stage process that requires considerable land area and a continual supply of chemicals. A more cost-effective method to clean a wide range of polluted water, on-site, and with minimal additives, is required for sustainable water management. EC treatment of water may fit this description [42].

EC involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions and hydrogen gas occurring at the cathode. EC has been proposed since before the turn of the century with Vik et al. [43] describing a treatment plant in London built in 1889 (for the treatment of sewage by mixing with seawater and electrolysing). In 1909 in the US, there was a patent for wastewater treatment by electrolysis with sacrificial aluminium and iron anodes [43]. Matteson et al. [44] describe a device of the 1940s, the "electronic coagulator", which electrochemically dissolved aluminium (from the anode) into solution, reacting this with the hydroxyl ion (from the cathode) to form aluminium hydroxide. The hydroxide flocculates and coagulates the suspended solids purifying the water. A similar process was used in Britain in 1956 [42] for which iron electrodes were used to treat river water [42].

Presently EC is marketed by a small number of companies around the world. A variety of designs have been employed with no dominant design. Often the EC units are used simply as a replacement for chemical dosing systems and do not take advantage of the electrolytic gases produced in the EC process [42]. It is clear that EC has the capability to remove a large range of pollutants under a variety of conditions ranging from: suspended solids; heavy metals; petroleum products; colour from dye-containing solution; aquatic humus; and defluoridation of water [42].

6.1. Possible mechanisms

The pH, pollutant type and concentration, the bubble size and position, floc stability and agglomerate size all influence the operation of the electrocoagulation unit. The overall mechanism is a combination of mechanisms functioning synergistically. The dominant mechanism may vary throughout the dynamic process as the reaction progresses. The dominant mechanism will almost certainly shift with changes in operating parameters and pollutant types [42]. A current is passed through a metal electrode, oxidising the metal (M) to its cation (M^{n+}) [Eq. (7)]. Simultaneously, water is reduced to hydrogen gas and the hydroxyl ion (OH^-) [Eq. (8)]. EC thus introduces metal cations *in situ* electrochemically, using sacrificial anodes (usually aluminium or iron) [42].

$$M \rightarrow M^{n+} + ne^- \quad (7)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (8)$$

The cation hydrolyses in water forming a hydroxide with the dominant species determined by solution pH. Eqs. (9)–(12) illustrate this in the case of aluminium [42].

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+ \quad (9)$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (10)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3^0 + H^+ \quad (11)$$

$$Al(OH)_3^0 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad (12)$$

Highly charged cations destabilise any colloidal particles by the formation of polyvalent polyhydroxide complexes. These complexes have high adsorption properties, forming aggregates with pollutants. Evolution of hydrogen gas aids in mixing and hence flocculation. Once the floc is generated, the electrolytic gas creates a flotation effect removing the pollutants to the floc - foam layer at the liquid surface [42,45].

6.2. Chemical issues

The control, operation and chemical interactions of the system affect performance and reliability. Section 6.1 of the literature review discussed the possible pollutant removal mechanisms and their interactions. Adding to complexity, the chemical interactions of the pollutants (type and concentration) with the electrode material, electrode passivation and operational region should also be considered. Literature has not revealed a systematic approach to these issues, and this is reflected in the variety of reactor designs and methods used for passivation control [42].

6.2.1. Electrode material

The electrode material impacts markedly on the performance of the EC reactor. The anode material determines the cation introduced into solution. Several researchers have studied the choice of electrode material with a variety of theories as to the preference of a particular material. The most common electrodes were aluminium or iron plates [42]. Do and Chen [42] compare the performance of iron and aluminium electrodes for removing colour from dye-containing solutions. Their conclusion was that the optimal EC conditions varied with the choice of iron or aluminium electrodes, which in turn is determined by: initial pollutant concentration, pollutant type, and stirring rate [42]. One group (Baklan and Kolesnikova [42]) investigated the relationship between "size" of the cation introduced and removal efficiency of organic waste. The size of the cation produced (10–30 µm for Fe^{3+} compared to 0.05–1 µm for Al^{3+}) was suggested to contribute to the higher efficiency of iron electrodes. Their conclusion is based on a single experiment, however, using chemical absorption of oxygen as their only measure [42]. Hulser et al. [42] observe that EC is strongly enhanced at aluminium surfaces in comparison to steel. This is attributed to a higher efficiency due to the *in situ* formation of dispersed aluminium-hydroxide complexes through hydrolysis of the aluminate ion, which does not occur with steel electrodes [42].

6.2.2. Passivation

One of the greatest operational issues with EC is electrode passivation. The passivation of electrodes is concern for the longevity of the process. Passivation of aluminium electrodes has been widely observed in the literature. It was observed that during EC with iron electrodes, deposits of calcium carbonate and magnesium hydroxide were formed at the cathode and an oxide layer was formed at the anode. Nikolaev et al. [42] investigated various methods of preventing and/or controlling electrode passivation including: changing polarity of the electrode; hydromechanical cleaning; introducing inhibiting agents; and mechanical cleaning of the electrodes. According to these researchers, the most efficient and reliable method of electrode maintenance was to periodically mechanically clean the electrodes which for large-scale, continuous processes is a nontrivial issue [42].

6.2.3. Solution pH

Solution pH determines the speciation of metal ions. The pH influences the state of other species in solution and the solubility of products formed. Thus, solution pH influences the overall efficiency and effectiveness of EC. The pH of the solution can easily be altered. An optimal pH seems to exist for a given pollutant, with optimal pH values ranging from 6.5 to 7.5 [42].

6.3. Some EC results in NOM removal

Moreno-Casillas et al. [46] concluded that EC can be considered as an accelerated corrosion process that may be explained by a Pourbaix diagram. An EC mechanism for chemical oxygen demand (COD) removal was developed whose model fits the data from KASELCO and of the experiments realised. The mechanism is congruent with the iron Pourbaix diagram, and with previous characterisation of EC by-products. The mechanism explains the causes of the great variability in COD removal efficiency. Summarizing, COD removal efficiency and its variability will depend on: the formation of floc, which for Fe electrodes usually occurs at values of pH higher than 7.5; the reactivity of organic compounds with Fe(II) and/or Fe(III); the solubility of the compounds formed; the final pH (especially for acidic compounds the final pH is an important factor for COD removal); the pH increment, and consequently on the acidity of the wastewater rather than on the initial pH; and the electrode material [46].

The EC of aqueous suspensions of ultrafine kaolin particles was measured in a single stirred cell apparatus and in a continuously flowing system consisting of three cells in series. The electrodes were fabricated of steel mesh through which the suspension freely circulated, and were set at a distance of 0.08 m in the cylindrical containers. The coagulation rate can be described by a second order rate equation that incorporates the electrophoretic migration of particles toward the anode, and the subsequent release of discharged particles into the bulk. The constants in this rate equation were derived from basic electrophoretic and coagulation phenomena, and depend on the zeta potential of the particles, the applied voltage, the initial particle concentration and the electrode geometry. It was possible with the derived equations to describe the experimental reduction in concentration with time for the voltage and concentration ranges tested [44].

An EC parameter was defined, $\Phi = [\tau_{m,0.5}\ (u/x)]^{-1}$, where $\tau_{m,0.5}$ is the time required to reduce a specific concentration of uncharged particles by one-half, u is the electrophoretic velocity and x is a geometric parameter. With the EC parameter as an independent variable, the half-time for the EC of a series of concentrations of charged particles was measured, and compared to a theoretical derivation of the relationship between halftime and Φ. Experimental results validated this relationship, and showed that it is a useful parameter in assessing the overall efficiency of an EC process. The EC in a series of stirred cell reactors, with electrodes in parallel, was measured, and the results compared to a theoretically derived expression that incorporates the cell residence time, the number of cells, and the EC parameter. Reasonable agreement was found between the experimental results and the theoretically predicted fraction coagulated [44].

Iron EC proved to be an excellent pre-treatment for virus removal by microfiltration (MF). The log reduction value (LRV) for MS2 virus suspended in simulated natural water was 4.5 (99.997% removal) when generating 10 mg L^{-1} Fe by EC. As expected, virus removal improved with increasing iron concentration. Without EC pre-treatment, the LRV for MF was only 0.5 (32% removal). At low iron dosages and lower pH values (6.3 and 7.3), virus removal by EC–MF was predominantly due to adsorption of the negatively charged viruses onto the positively charged iron flocs and the subsequent removal of the flocs by MF. However, virus removal at high Fe(III) dosages was attributed to enmeshment prior to removal by MF. These results suggest that other clarification technologies capable of removing flocs (e.g. media filtration) would also be effective for virus removal, as was MF in this study. In a comparison of the processes, EC significantly outperformed chemical coagulation with ferric chloride as a pre-treatment for MF. For example, at pH 7.3 and an iron dose of 10 mg L^{-1}, the LRVs for MS2 virus removal were 4.5 and 2.0 for EC and coagulation, respectively. The dramatic improvement in virus removal by EC compared with coagulation held true for all iron dosages (2–10 mg L^{-1}) and pHs tested (6.3, 7.3, and 8.3). It was proposed and subsequently verified by modelling and additional experiments that locally higher iron and virus concentrations within the EC unit improved virus removal. These bench-scale results, which demonstrate the significant advantage of iron EC compared with coagulation for virus removal, should be verified at the pilot scale. Furthermore, the results here suggest that EC might also be superior to coagulation for natural OM removal during membrane pre-treatment [47].

7. EnC as a link between coagulation and EC

7.1. Comparison between coagulation and EC

EC has been widely studied in water and wastewater treatment to remove heavy metals, organics, bacteria, hardness, turbidity, and other contaminants. In the EC process, the electrodes are consumed as the coagulant is generated and precipitated; no liquid chemical is added; alkalinity is not consumed; and pH adjustment is not needed. Additionally, compared with coagulation, the EC process reportedly requires less coagulant and produces less sludge. According to one estimate, the space required for EC is less than coagulation because EC does not require chemical storage, dilution, and rapid mixing. Because EC systems typically use solid iron or aluminium anodes rather than corrosive iron or aluminium salt solutions, EC units can be more easily incorporated into ''packaged'' plants and transportable water treatment plants for use in remote areas or in emergency water supply treatment, which was one of the driving forces to undertake this research [47].

For Yildiz et al. [48], the difference between EC and coagulation is mainly in the way of metal 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. 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 [48]. Awad and Abuzaid [49] investigated the anodic oxidation of phenol using porous graphite. The experiments were designed so that the effect of residence time at different currents on phenol oxidation would be elucidated. Phenol removal efficiency was a function of the applied current and the residence time and was around 50% at a current of 2.0 A and a residence time of 35 min. Phenol removal efficiency was found to increase with the increase in current and residence time. An empirical model was developed to predict the effect of flow rate or residence time and current on the phenol removal efficiency. Percentage of phenol completely oxidised, measured by the amount of CO_2 produced, increased with current and residence time and reached 48% at a current of 2 A and a residence time of 23.3 min. It was found that the phenol removal rate increases with the decrease in residence time. Maximum current (CO_2) efficiencies were achieved at currents of 1.0 and 1.25 A at residence times of 35 and 23.3 min, respectively. Residence time was identified as an important parameter in affecting removal efficiency and complete detoxification of phenol [49].

7.2. Why EnC and EC

From this review study, it is clear that EnC was proposed essentially in order to remove dissolved species (DBPs precursors) as precipitated solids from water. Indeed, the shape of the HS [40–50% of NOM is of humic origin, and the rest of non-humic origin (Fig. 2)] can also play an important role in organo-metal interaction. Various chemical parameters such as pH, conductivity, etc., can influence the orientation of NOM in the water. Indeed, pH has a larger effect on the orientation of HS: at higher pH (i.e., alkaline condition), the acidic functional groups such as carboxylic (-COOH) and phenolic (Ar-OH) deprotonates (or ionises), producing many negatively charged sites, then repel each other and keep the molecule in a stretched shape. However, under acidic conditions, or with increasing concentration of electrolytes (which causes reduction in intermolecular repulsion force), these negative charges are neutralised and the geometry from the stretched shaped changes to coiled shaped (Fig. 3), which may cause the precipitation of the humic molecule. Fig. 3 presents a schematic representation of the effect of pH, electrolyte (NaCl) concentration (M), and NOM concentration on FA and HA conformation, based on viscosity measurements (for HA, measurements were only possible for pH > 6.5. At low pH, the HS precipitates. However, the FA is still soluble and remains an elongated fiber, even at a pH of 2 to 3. From the coagulation point of view, few removal of NOM may be obtained by just lowering the pH alone which may cause the HS to precipitate. However, more prevalent FAs will have lesser of an effect [50]. Indeed, the effectiveness of the removal of NOM varies with the nature of the NOM (its molecular weight, charge density, polarity) and with properties of the raw water. Moreover, there are some compounds, such as phenols, which cannot be removed at all in a coagulation step. In such cases, when conventional treatment is unsatisfactory, other processes are needed [51,52] like EnC.

On the other hand, EC which was started in other context for essentially industrial wastewater purification is proposed to water treatment for its high electrical charge neutralisation efficiency. EnC acts essentially by increased coagulant dosing (more than coagulation) and EC by electrical field.

Further, the EC technologies are essentially electrolytic processes that involve the destabilisation of suspended, emulsified or dissolved pollutants in an aqueous medium, by the application of an electric current. In EC (a process similar to chemical coagulation), there is a reduction of the net surface charge to a point where the colloidal particles can approach closely enough for Van der Waal's forces to hold them together and allow aggregation to take place. The surface charge reduction is a consequence of the decrease of the repulsive potential of the electrical double layer by the presence of an electrolyte having an opposite charge. This mechanism corresponds to the destabilisation of colloidal particles [53].

Nevertheless, the application of EnC to maximise removal of organics may not necessarily result in attainment of stringent levels of THMs in drinking water, where chlorine is used as disinfectant. This is due to the concentration of residual DOM that is recalcitrant to removal by coagulation [38]. This problem does not occur when EC process is used, since disinfection is assured by EC itself. Indeed, in our precedent work [54], laboratory experiments were carried out to investigate EC as electro-disinfection of artificial wastewater contaminated by no pathogenic *Escherichia coli* (*E. coli*) species in batch culture and two surface waters using three different electrodes. Aluminium electrodes were found most efficient in *E. coli* cells destruction comparatively with stainless steel and ordinary steel. Only 30 min are required for EC to achieve total *E. coli* cells removal. EC has shown the same efficiency toward algae and coliforms in two kinds of surface waters. The main mechanisms of EC are charge neutralisation of microorganisms by electrical field and metallic cations followed by their flotation or sedimentation [54]. Further, the laboratory tests show that the EC process using aluminium electrodes is highly efficient (96%) for HA removal. The *in situ* formed cations ($AlOH^{2+}$ and AlO^+) neutralise humic macromolecules and contribute to the formation of hydroxides ($Al(OH)_{3(s)}$) which adsorb OM at an optimal pH 7 [55]. The recent technical

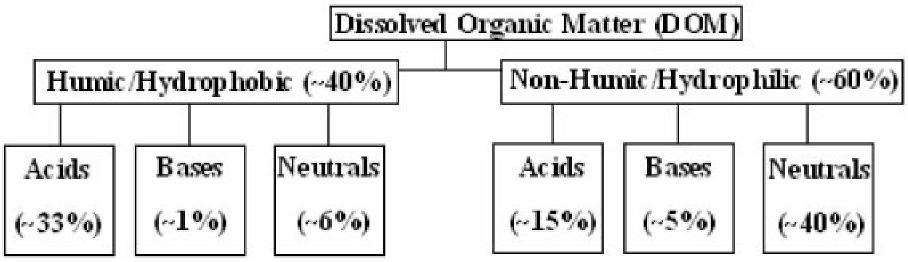
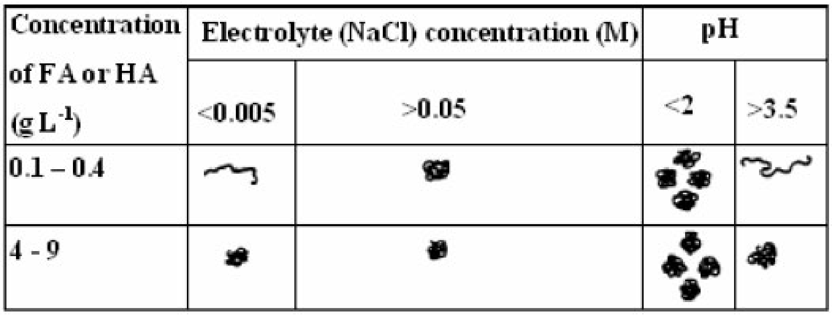


Fig. 2. Classification of NOM [50].



Concentration of FA or HA ($g L^{-1}$)	Electrolyte (NaCl) concentration (M)		pH	
	<0.005	>0.05	<2	>3.5
0.1 – 0.4				
4 - 9				

Fig. 3. Physical orientation of HSs due to pH and ionic strength [50].

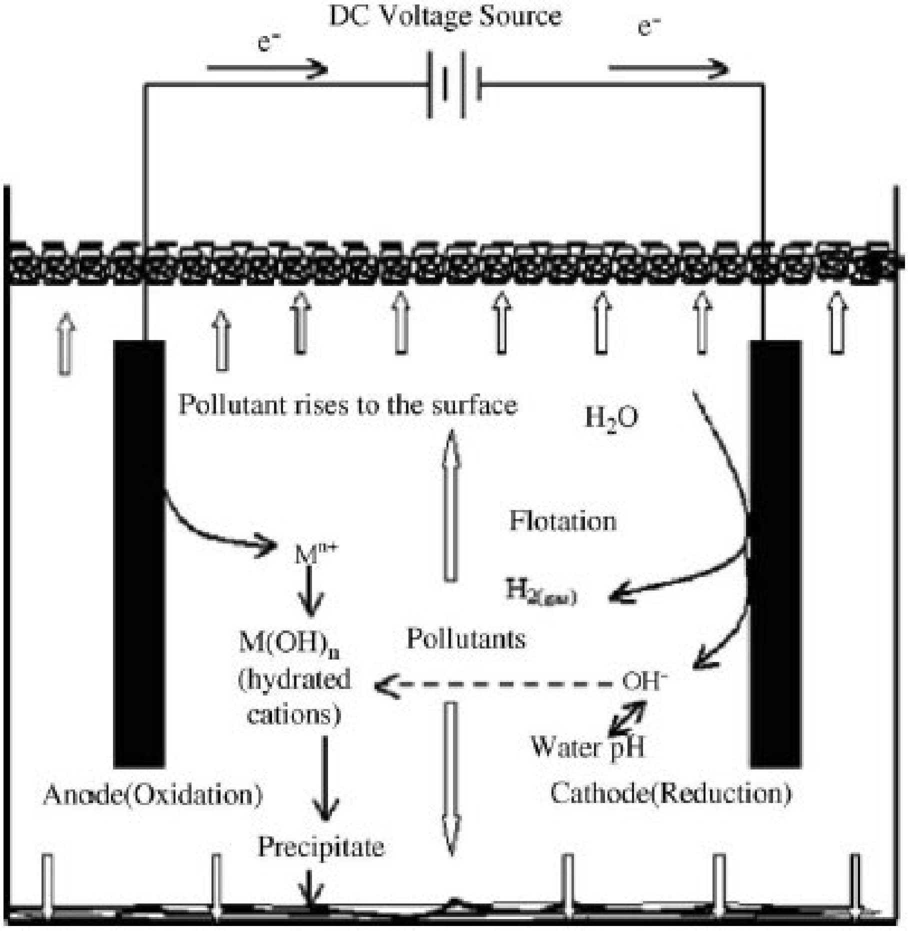


Fig. 4. Schematic diagram of a bench-scale two-electrode EC cell [57].

Table 3
Advantages of EC as compared to the conventional coagulation process [61,63]

Advantages of EC
1. Simplicity of the required equipment, versatility, safety and easy automation of the process (does not require the addition of any chemicals).
2. Ambient operability, large volume handling ability, non-toxicity (non-consumption of chemicals and no eventual secondary pollutants to discard at acceptable physical and chemical condition).
3. It also requires comparatively less treatment time and very effective removal efficiency with simplified operation.
4. Process results in high-energy efficiency, selectivity and cost effectiveness, as well as a decreased amount of precipitate or sludge (less quantity of reagents - *in situ* coagulant generation) which sediments rapidly.
5. Low current requirement allows such processes to be run by green energy sources such as solar power, wind mills and fuel cells.
6. Produced metal ions attract all the negatively charged particles, especially the bacteria, causing their coagulation and sedimentation.
7. Removing small colloidal particles (they have a larger probability of being coagulated because of the electric field that sets them in motion).
8. Addition of excessive amount of coagulants can be avoided, due to their in situ generation by electro-oxidation of a sacrificial anode.
9. Gases simultaneously formed by hydrolysis result in very fine bubbles that associate with the coagulated contaminants and buoy them up for removal by flotation.
10. No alkalinity consumption, no change in bulk pH, the direct handling of corrosive chemicals is nearly eliminated.

improvements combined with a growing need for small-scale decentralised water treatment facilities have led to a reevaluation of EC. Current density is identified as the key operational parameter influencing which pollutant removal mechanism dominates. The conclusion is drawn that EC has a future as a decentralised water treatment technology [56].

Fig. 4 presents a schematic diagram of a bench-scale two-electrode EC cell [57] showing that EC process is mainly characterised by two main electrochemical reactions: oxidation (anode) and reduction (cathode), and two separation processes: precipitation and flotation.

Table 1 presents a comparison between coagulation, EnC and EC. EnC may have two forms: the first one is by increasing coagulant dosing relatively to coagulation; the second is as for the first by increasing coagulant dosing with acidifying pH to achieve more DOM removal. In other words, coagulation acts by coagulant dosing, EnC by increased coagulant dosing or by increased coagulant dosing with acidifying pH, and EC by coagulant electrochemical dosing and electrical field (i.e., electrochemical reactions). When particles are present alone in water, their removal by coagulation is easier than NOM (since the structure of aquatic OM is extremely complicated [58]). Further, when particles and NOM are simultaneously present (i.e., raw surface water), their removal becomes difficult due to implicated diverse chemical reactions (Table 1). Some advantages of EC as compared to the conventional coagulation process are summarised in Table 3. However, some disadvantages must be taken in consideration such as: the “sacrificial electrodes” are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced; an impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit; high conductivity of the wastewater suspension is required; and gelatinous hydroxide may tend to solubilise in some cases [59].

8. Conclusions

The following observations and conclusions arose from this review:

- In water treatment every contaminant, every molecule, and every ion must be removed first by chemical coagulation which had been proved efficient at a certain level especially concerning solid colloids (mineral, organic and biological), but not sufficiently efficient about dissolved organic molecules.
- Since DBPs problems apparition, it was obvious that coagulation, EnC, or EC have to deal principally with dissolved NOM electrical charge. EnC and EC approaches are proved more efficient.
- NOM removal by EnC depends on a variety of factors including pH, alkalinity, coagulant type and dosage, and the type and concentration of NOM. On the other hand, EC depends on pH, nature of the anodes, the anions in solution, voltages, residence time in the electrode regions etc. and many of these overlap with the EnC factors.
- For EnC, deviations from optimum coagulation conditions (i.e. coagulant dose and pH) can seriously

affect treatment performance with respect to residual coagulant concentrations (less than 1.0 mg L^{-1} for Al [60] and 0.3 mg L^{-1} for Fe [61]), turbidity, particle counts, NOM, and microorganisms; hence, a proper control of coagulant dosage and coagulation pH are the most important operation challenges.

- It is necessary to characterise NOM to evaluate optimum dosages according to coagulants used [62].
- The EC method for purifying raw water is a promising method that can be used for treating surface raw water, and renders it safe for human consumption. The method proves to be efficient in reducing bacterial load, water turbidity, and chemical contaminants such as sulphates, nitrates and phosphates [63].
- Finally, EnC is really a link between coagulation and EC which starts to be the future water treatment technology.

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