Desalination and Water Treatment
www.deswater.com

27 (2011) 243–254
March

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doi: 10/5004/dwt.2011.1983

On the controversial effect of sodium sulphate as supporting electrolyte on electrocoagulation process: A review

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Received 2 May 2010; Accepted 2 August 2010

ABSTRACT

One of the important factors for electrocoagulation (EC) process is the conductivity of the solution to be treated. Essential mechanisms in EC are charge neutralisation by metal (Fe/Al) hydroxocations and aggregation by van der Waals forces since flocculation of pollutants with metal is caused by their adsorption on metal hydroxide aggregates. In order to enhance the EC process efficiency in organic wastewater effluents, sodium sulphate (Na_2SO_4) has been used as a supporting electrolyte (SE) to increase the electric current diffusion in the EC cell. However, literature has reported controversial effect of sodium sulphate on EC process. This review tries to understand the sulphate effect on the EC reactions. Na_2SO_4 has been found less efficient than NaCl as SE in EC process for the removal of humic substances, oil-in-water emulsions, and fluoride. However, for unskimmed milk sample and cutting oil emulsion sulphate anions were found to be quite harmful both for electrical consumption and EC efficiency. These results may be related to the facts that in the sulphate media the 70% of the aluminium is in the form of $Al(OH)_{3(am)}$ and in the chloride media this percentage is around 40% and the adsorption of chloride or sulphate ions onto the surface of the $Al(OH)_{3(am)}$ can reduce the adsorption efficiency. Consequently, metal cations must be well distributed in the wastewater before the metal hydroxide formation to decrease the negative effect of SE in EC process.

Keywords: Electrocoagulation (EC); Supporting electrolyte (SE); Sodium sulphate; Coexisting anions; Chemical coagulation (CC)

1. Introduction

Recently, electrocoagulation (EC) is of great interest for water/wastewater treatment [1–4]. EC is an electrochemical treatment process which use soluble and coagulating metal such as iron and aluminium [5–8]. When a direct current (DC) voltage is applied on the electrodes, the anode starts to dissolve electrochemically and produces Al^{3+} or Fe^{2+} ions which are good coagulants [9–11]. When aluminium is used as electrode material, reactions occurring at the surface of the electrodes and in the bulk solution are shown in Eqs. (1)–(6) but reactions (2), (5) and (6) only occur in chloride containing waters.

At the anode:

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (2)$$

at the cathode:

$$3H_2O + 3e^- \rightarrow (3/2)H_2 + 3OH^- \quad (3)$$

in the bulk solution:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (4)$$

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$$Cl_2 + H_2O \rightarrow HOCl + HCl \quad (5)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (6)$$

As seen in the reactions presented above, EC is a process consisting of oxidation, flocculation and flotation [12]. Not only in EC but also in any other electrochemical process, the electrolysis voltage is one of the most important operation variables [5,13]. And it strongly depends on the conductivity of water/wastewater, current density, inter-electrode distance and surface state of the electrodes [14]. Compared with chemical coagulation (CC), EC has in theory, the advantage of removing the smallest colloidal particles: the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion [15,16]. It has also the advantage of producing a relatively low amount of sludge. In addition, it has been reported that the adsorption of the hydroxide on the mineral surface was 100 times more on "in situ" than on pre-precipitated hydroxides when metal hydroxides were used as coagulants [5]. The characteristics of EC are simple equipment and easy operation, brief reactive retention period, decreased or negligible equipment for adding chemical and decreased amount of sludge [17,18].

Although there has been a lot of works on the wastewater treatment by electrochemical methods, there are so far no reports related to the treatment of water containing organic matter (OM) and supporting electrolyte (SE) and also no study that compare the SE types for the EC process [5,19,20]. Although other chemicals such as ferric sulphate [21] and, sodium sulphate [22] have been used as SE, the most widely used SE is the NaCl in electrochemical studies [14,17,23–29]. Is well-known that the availability of the chloride (Cl^-) ions in the water can cause formation of disinfection by-products (DBPs) which are suspected carcinogenic compounds [5], so adding chloride ions to water must be avoided. Hence the question, as mentioned by Yildiz et al. [5], should be answered "Which chemical is the best potential SE for OM removal by EC?"

On the other hand, SE is defined as an electrolyte solution, whose constituents are not electroactive in the range of applied potentials being studied, and whose ionic strength (and, therefore, contribution to the conductivity) is usually much larger than the concentration of an electroactive substance to be dissolved in it [30,31]. For OM removal by electrochemical process such as EC, when the conductivity is low to easily pass the electrical current in the wastewater, adding SE is often more frequent than for inorganic matter removal. This review tries to understand the controversial effect of sodium sulphate (Na_2SO_4) which is reported positive, such as by Yildiz et al. [5] and Yavuz [32], and negative such as by Trompette and Vergnes [33].

2. Theoretical aspects of electrocoagulation

2.1. Principal of electrocoagulation

EC is a complicated process involving many chemical and physical phenomena that use consumable electrodes (Fe/Al) to supply ions into the water stream [34,35]. Fe/Al is dissolved from the anode generating corresponding metal ions, which immediately hydrolyse to polymeric iron or aluminium hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions and precipitation or by physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electroflotation, sedimentation, and filtration. In CC process, coagulating chemicals are added. By contrast, these coagulating agents are generated in situ in EC process [36,37].

In the EC process, the destabilisation mechanism of the contaminants, particulate suspension, and breaking of emulsions may be summarised as follows: (1) compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode. (2) Charge neutralisation of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. (3) Floc formation: the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that are still remaining in the aqueous medium [7,36].

Water is also electrolysed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and float the flocculated pollutants to the surface through natural buoyancy. In addition, the following physiochemical reactions may also take place in the EC cell [7,36]: (1) cathodic reduction of impurities present in wastewater; (2) discharge and coagulation of colloidal particles; (3) electrophoretic migration of the ions in solution; (4) electroflotation of the coagulated particles by O_2 and H_2 bubbles produced at the electrodes; (5) reduction of metal ions at the cathode; and (6) other electrochemical and chemical processes.

2.2. Electrode passivation and activation

Electrode passivation, specifically of aluminium electrodes, has been widely observed and recognised as detrimental to reactor performance [18,35,38]. This formation of an inhibiting layer, usually an oxide on the electrode surface, will prevent metal dissolution and electron transfer, thereby limiting coagulant addition to the solution. Over time, the thickness of this layer increases, reducing the efficacy of the EC process. The use of new materials, different electrode types and arrangements, and more sophisticated reactor operational strategies (such as periodic polarity reversal of the electrodes) have certainly let to significant reductions of impact passivation [39]. In addition, addition of anions will also slow down the electrode passivation. The positive effect was as follows: $Cl^- > Br^- > I^- > F^- > ClO_4^- > OH^-$ and SO_4^{2-}. Specially, addition of a certain amount of Cl^- into the aqueous solution will inhibit the electrode passivation process largely by removing the passivating oxide layer form on electrode surface due to its catalytic action [40,41]. It is also necessary to rinse regularly the surface of the electrode plates. Generally, iron is used in wastewater treatment and aluminium is used in water treatment because there are a definite amount of metal ions required to remove a given amount of pollutants and iron is relatively cheaper. However, attention must be paid to the fact that Al is actually toxic [6]. The aluminium plates are also finding application in wastewater treatment either alone or in combination with iron plates due to the high coagulation efficiency of Al^{3+}. When there are a significant amount of Ca^{2+} or Mg^{2+} ions in water, the cathode material is recommended to be stainless steel [36,40].

2.3. Comparison between electrocoagulation and chemical coagulation

CC and EC have the same phenomenon in which the charged particles in colloidal suspension are neutralised by mutual collision with metallic hydroxide ions and are agglomerated, followed by sedimentation or flotation. The difference between EC and CC is mainly in the way of which aluminium or iron ions are delivered [42–44]. EC is a process consisting of creating metallic hydroxide flocs within the water by electrodissolution of the soluble anodes, usually made of iron or aluminium. In CC, hydrolysing metal salts, based on aluminium or iron, e.g., aluminium and ferric sulphates and chlorides, are very widely used as coagulants in water treatment. Table 1 presents some advantages for EC, compared to CC, and some disadvantages of EC [36,45].

3. Effects of conductivity and pH on electrocoagulation

3.1. Effect of conductivity on electrocoagulation

When the electrolytic conductivity is low, the current efficiency will decrease. And, high-applied bias potential is needed which will lead to the passivation of electrode and increase treatment cost [40]. Generally, NaCl was added in order to increase the electrolytic conductivity [46]. Active chloride will also produce in the Cl^- electrolysis, which will contribute to the water disinfection and

Table 1
Advantages and disadvantages for EC compared to CC [36]

Advantages for EC compared to CC
1. In the CC process, the hydrolysis of the metal salts will lead to a pH decrease and it is always needed to modulate the effluent pH. The CC is highly sensitive to pH change and effective coagulation is achieved at pH 6–7. While in the EC, the pH neutralisation effect made it effective in a much wide pH range (4–9).
2. Flocs formed by EC are similar to chemical floc. But, EC floc tends to be much larger, contains less bound water, is acid resistant, and is more stable. In the CC process, it is always followed by sedimentation and filtration. While in the EC process, it can be followed by sedimentation or flotation. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected, and removed.
3. Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low-sludge producing technique.
4. Use of chemicals is avoided in EC process. Thus, it need not neutralise excess chemicals, and secondary pollution caused by chemical substances that are added can be avoided.
5. The EC process has the advantage of treating the water with low temperature and low turbidity. In this case, the CC has difficulty in achieving a satisfying result.
6. EC requires simple equipment and is easy to be operated.
Disadvantages of EC
1. The “sacrificial electrodes” are dissolved into wastewater as a result of oxidation, and need to be regularly replaced.
2. The passivation of the electrodes over time has limited its implementation.
3. The use of electricity may be expensive in many places.
4. High conductivity of the wastewater suspension is required.

DBPs formation [47]. And, the addition of Cl^- will also decrease the negative effect of CO_3^{2-} and SO_4^{2-}. The presence of CO_3^{2-} and SO_4^{2-} will lead to the deposition of Ca^{2+} and Mg^{2+} and formation of solide layer, which will decrease the current efficiency rapidly. It is therefore recommended that among the anions present, there should be 20% Cl^- to ensure a normal operation of EC in water treatment. However, NO_3^- widely present in the water solution nearly has no effect on the EC process [36].

3.2. Effect of pH on electrocoagulation

The pH of solution plays an important role in CC and EC processes [48]. Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerisation reaction of electrochemically dissolved Al^{3+}. The formation of Al^{3+} single-core coordination compounds can be described as follows:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad (7)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (8)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad (9)$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad (10)$$

With the extension of hydrolysis of Al^{3+}, multicore coordination compounds and $Al(OH)_{3(am)}$ precipitate can be formed:

$$Al^{3+} \rightarrow Al(OH)_n^{3-n} \rightarrow Al_2(OH)_2^{4+} \rightarrow Al_{13} \text{ complex} \rightarrow Al(OH)_{3(am)} \quad (11)$$

In the pH range of 4–9, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_3$, and $Al_{13}(OH)_{32}^{7+}$ are formed. The surface of these compounds has large amounts of positive charge, which can lead to adsorption/charge neutralisation and net catching reaction [49,50]. At pH > 10, $Al(OH)_4^-$ is dominant, and the coagulation effect rapidly decreases. At low pH, Al^{3+} is dominant, which has relatively no coagulation effect [36,51–53].

However, when an Al cathode is also utilised, it can be chemically attacked by OH^- generated during H_2 evolution at high pH values as follows [53]:

$$Al + 3H_2O + OH^- \rightarrow Al(OH)_4^- + (3/2)H_{2(g)} \quad (12)$$

and treated wastewater contains higher amount of aluminium ions than those expected from reaction (1). Note that a Fe or steel anode is not attacked by OH^- in alkaline medium, thus avoiding the formation of an excess of $Fe(OH)_4^-$ species.

In the CC process, pH is needed to be adjusted because the pH of solution will decrease with the addition of coagulants. In the EC, the evolution of H_2 at the cathode will increase the OH^- concentration. Thus, pH in the aqueous solution will increase when the pH of original water is in the range of 4–9. However, when the pH of the original water is higher than 9, the pH of the treated water will decrease [36].

4. Controversial effect of sodium sulphate (Na_2SO_4) on electrocoagulation process

4.1. Positive effect of sodium sulphate (Na_2SO_4) on electrocoagulation process

Yildiz et al. [5] investigated the effects of SE type and concentration on the batch removal of water with high concentration of natural organic matter (NOM) by the EC method using plate electrodes. The addition of SE has a twofold effect which can be summarised as follows: firstly increasing the ionic strength of the water causing compression of the electrical double layer (EDL) and secondly raising the electrical conductivity of the water causing more current passing through the circuit under the same applied potential. The concentration of 5 mm SE was optimum up to 100 mg/l of NOM, while concentration of 10 mm is more favourable for higher concentrations than 100 mg/l of NOM. To determine the most favourable SE type, NaCl, Na_2SO_4 and $NaNO_3$ were used as SE in the test runs. Under the conditions of initial pH of the solution equal to 5.0 and initial concentration of 100 mg/l NOM, charge loadings were within the range of 2.10–3.74 F/m^3 for Na_2SO_4 and NaCl, respectively. Additionally at the same initial conditions for a treatment period of 9 min specific energy consumptions and removal efficiencies were ranged between the 4.75 and 9.70 kWh/m^3, and between 97 and 99% for Na_2SO_4 and NaCl, respectively. Taking in consideration that the availability of the chloride (Cl^-) ions in the water can cause formation of DBPs, Yildiz et al. [5] concluded that the most favourable SE type is Na_2SO_4 for this treatment technique. These authors obtained similar results in less different conditions [45].

On the other hand, EC can be successfully applied to the treatment of oil-in-water (O/W) emulsions. Cañizares et al. [54] studied the efficiency of the EC process, when aluminium electrodes are used. The pH was found to be the most significant parameter, and good removal efficiencies were only obtained for pH in the range 5–9. The electrical charge passed was observed to be directly related to the aluminium supplied to the waste. For a given oil concentration it is required that a minimum electrical charge is passed to break-up the emulsion. Further increases in the electrical charge lead to increase in the chemical oxygen demand (COD) removal. The influence of the oil concentration is related to that of the electrical charge passed: for a given dose

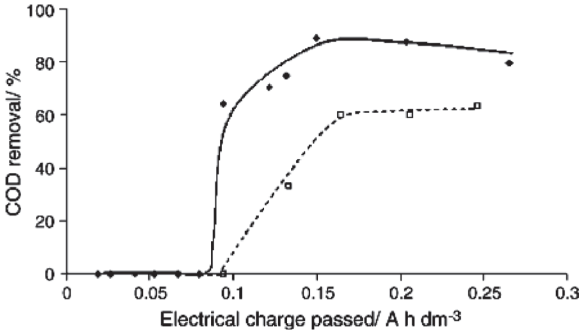

Fig. 1. Influence of the supporting electrolyte in the continuous EC experiments. Temperature, 25 °C; oil concentration, 3000 mg l^{-3}; initial pH, 8.5; supporting media, (■) 3000 mg NaCl L^{-3}, (□) 3000 mg Na_2SO_4 L^{-3} [54].

Table 2
Percentage of soluble aluminium generated in the EC process as a function of the supporting electrolyte and the electrical charge passed [54]

Electrical charge passed (Ah/l)	Soluble aluminium(%)	
	NaCl	Na_2SO_4
0.09	54.6	32.7
0.13	55.3	32.8
0.15	55.6	32.8
0.20	56.0	32.9

Temperature, 25 °C; initial pH, 8,5; supporting media, 3000 mg NaCl/l and 3000 mg Na_2SO_4/l.

of aluminium, the higher the oil content the lower the COD-removal efficiency. Likewise, to produce the break-up of the emulsion it is required a minimum dose of aluminium (electrical charge passed), lower doses do not attain the rupture of the emulsion. The type of electrolyte (NaCl and Na_2SO_4) and its concentration were also found to influence the process efficiency. Better efficiencies were obtained in the treatment of chloride-containing wastes and for low concentration of electrolyte [54]. Indeed, Fig. 1 shows the changes of COD removal with the electrical charge passed for both electrolytes studied. It can be seen that in sulphate medium the electrical charge passed necessary to achieve the break-up of the emulsion is larger than in chloride medium. Likewise, for the same electrical charge passed, better removals of COD are obtained in chloride medium. Moreover, it can be observed that in case of sulphate-containing emulsions, there is no optimum dosage of aluminium, as the COD removal achieves a constant value with the electrical charge passed. Both observations (the effect of the concentration of chlorides and the effect of the type of the electrolyte) can be explained in terms of the formation of aluminium species, which is largely influenced by the presence of these ions. Thus, it is reported that sulphate media promotes the formation of precipitates over the formation of polymeric hydroxo-ions. This can be clearly observed in Table 2, which summarises the percentages of soluble aluminium in both media for different current charges. These percentages do not seem to depend importantly on the total concentration of aluminium, although a slight increase is observed with the charge passed. However, the influence of the media is clear: in the sulphate media the 70% of the aluminium is in the form of amorphous aluminium hydroxide precipitate and in the chloride media this percentage is around 40%. According to the literature [55–58], the remaining aluminium should be mainly in the form of polymeric hydroxocations. This means that the active sites that promotes the coalescence are higher in the chloride media (the aluminium is more efficiently used) as the aluminium hydroxide which is not on the surface of the particles is not effective from the treatment point of view, and due to its smaller size (and thus, to their more efficient aluminium content) the polymeric ions are expected to yield better efficiencies [54]. Other point that explains the Cañizares et al. [54] experiments is the adsorption of chloride or sulphate ions onto the surface of the aluminium hydroxide precipitates. This adsorption can reduce the net positive charges of the surfaces of the particles or increase the negatively charged sites. The effect is more important with the sulphate ion due to its higher charge. Consequently, this can also explain the different results obtained [54].

4.2. *Negative effect of sodium sulphate (Na_2SO_4) on electrocoagulation process*

Trompette and Vergnes [33] investigated the influence of some SEs on aluminium electrode oxidation and pH variation during EC of an unskimmed milk sample and a cutting oil emulsion. Among the electrolytes studied, sulphate anions were found to be quite harmful both for electrical consumption and EC efficiency. At the opposite, chloride and ammonium ions were particularly beneficial respectively for aluminium corrosion and pH regulation, whereas sodium cations were observed to have a neutral role. The results indicate that EC can be realised at low anodic potential even in the presence of sulphate ions when the $[Cl^-]/[SO_4^{2-}]$ ratio is around or greater than 1/10. The detrimental effect of sulphates on EC efficiency can be thwarted by the use of the ammonium salt thanks to its related buffer effect [33]. Indeed, in the presence of sodium and ammonium electrolytes at 0.02 M, the same researchers [59] studied the EC efficiency of latex and milk samples with the use of aluminium electrodes. The comparative results have highlighted the clear advantage of ammonium salts to obtain better and faster phase separation within the same experimental conditions. The origin of this behaviour has been ascribed to the buffer effect of the ammonium/ammonia couple and the expected role of dissolved ammonia gas on the cohesiveness of generated aggregates [59].

To investigate the effects of the type and concentration of coexisting anions on defluoridation in EC process, Hu et al. [37] conducted batch experiments with bipolar aluminium electrodes and potentiodynamic polarisation tests with monopolar systems. Their results demonstrate that the type of the dominant anion directs the EC defluoridation reaction. The defluoridation efficiency was almost 100% and most of the fluoride removal reaction occurred on the surface of the anode in the solution without the coexisting anions, due to the electro-condensation effect (Fig. 2). In the solutions with coexisting anions, most of the defluoridation took place in bulk solution. The residual fluoride concentration is a function of the total mass of Al(III) liberation from anodes and the types of the functions in the solutions with and without coexisting anions are different. The existence of sulphate ions inhibits the localised corrosion of aluminium electrodes, leading to lower defluoridation efficiency because of lower current efficiency. The presence of chloride or nitrate ions prevented the inhibition of sulphate ions, and the chloride ions were more efficient. Different corrosion types occurred in different anion-containing solutions and the form of corrosion affected the kinetic over-potential. The bypass flow causes the decrease of current efficiency and the proportion of the bypass flow of current increased due to a rise of the kinetic over potential and the conductivity of the solution [37].

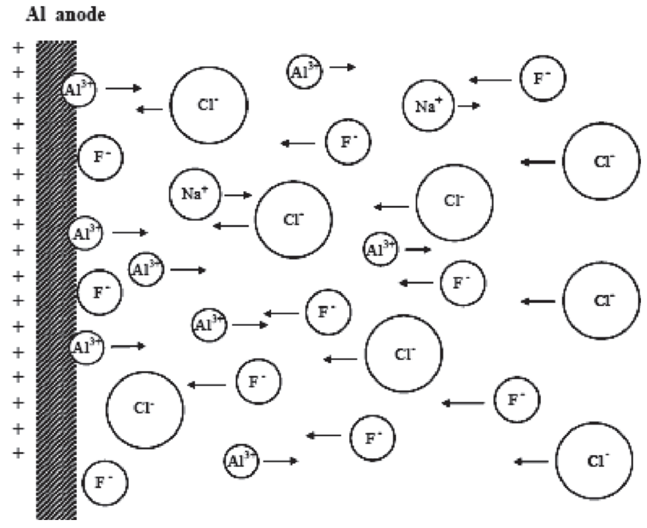

Fig. 2. Diagram of the electro-condensation effect. Anions would be attracted to the anode due to the electric force, and the concentration of anions near the anode would be higher than in bulk solution [37].

The following section discusses paradoxes with SE and gives some examples of references who have tried with more success to explain the SE effect.

5. Paradoxes with supporting electrolyte

The use of a SE raises a number of questions, such as [60]:

1. Which species is carrying the current?
2. If the reactant is carrying the current in the diffusion layer, how does the SE have an effect?
3. If the SE is motionless in the diffusion layer, is it also motionless in the bulk of the solution-even if convection can occur in the bulk whereas migration occurs everywhere?

The SE, consisting of anions and cations that are contained in the waste to be treated, or added for sufficient conductivity of the medium, can have appreciable effects on (i) the rate of metal dissolution, (ii) the ohmic drop—and thus on the cell voltage and energy consumption, and (iii) surface phenomena occurring between polluting species and the metal hydroxides [22,61,62]. A fourth item to be added could be the electrochemical stability of the electrolyte ions. Whereas the effect of usual parameters e.g., cell voltage, current density, stirring rate or flow velocity, pH, electrolyte concentration, electrode specific area or residence time in the cell, has been investigated for the treatment of various wastes, the effect of the electrolyte nature has been scarcely examined. Nevertheless, because the electrolytic charge in a wastewater to be treated by electrochemical techniques can either originate from its production, or be caused by salt addition for sufficient conductivity, it is important to know, at least qualitatively the effect of both cations and anions of the overall electrochemical operation [61].

With Al electrodes, sodium chloride, sulphate and nitrate salts have been used for the treatment of various wastewaters through removal of fluoride [37], humic substances [5], or cadmium traces [63]. The moderate consistence of the results reported is probably due to different operating conditions, and more particularly different electrical modes. The three above salts were also tested with iron electrodes for the case of humic substance-containing waste [5]. Generally speaking, chloride ion is known to be corrosive, whereas sulphate and nitrate species are far less aggressive [64]. The effect of cations e.g., sodium, potassium or ammonium, has been very little investigated, except by Trompette et al. [33,59]—as seen above - who evidenced the positive effect of ammonium in the destabilisation of milk or latex with Al electrodes [61].

In their recent investigation, Izquierdo et al. [61] studied the influence of the electrolyte nature, by considering chloride, sulphate and nitrate anions with sodium, potassium or ammonium cations on the treatment of dilute suspensions of soluble cutting oils, and using Al or Fe electrodes. Aluminium electrodes can be dissolved with a high current efficiency in all cases, whereas dissolution of iron is little efficient with nitrate salts and potassium sulphate. In addition, the cell voltage required with Fe electrodes to allow the same current density can be 2 V higher than with Al plates. The specific energy required for the electrochemical process with a 3 mm gap cell was estimated to range from 0.75 kWh/m^3 with Al electrodes in sodium chloride media to ~5 kWh/m^3 with Fe electrodes immersed in sulphate solutions [61].

Kobya et al. [65] investigated the decolorisation of the levafix orange textile dye in aqueous solution by EC using aluminium anode. The effect of conductivity was investigated between 250–4000 μS/cm by using NaCl as the SE. The decolorisation efficiency and cell voltage decrease steadily as conductivity increases. The decrease in the decolorisation efficiency may be attributed to a change in the ionic strength due to changing conductivity of the aqueous medium. Ionic strength affects the kinetics and equilibria of reactions like (3) and (4) between charged species occurring during EC [18].

Önder et al. [66] investigated the feasibility of the removal of surfactants from model solution and the polluted water sample by EC utilising Fe^{2+} ions from a soluble anode as an alternative method. As a result of the studies the removal of surfactant (linear alkylbenzene sulfonate, LAS) having a concentration of 10 mg/l has been achieved with an efficiency of 100%. Experiments were conducted to examine the effects of some parameters such as SE concentration. Yet, sodium sulphate (Na_2SO_4) has been used as a SE to observe the effects of. Although it has a negligible effect on the removal efficiency, energy consumption has lowered dramatically as shown in Fig. 3. This must be due to the presence of an electrolyte (i.e., iron hydroxide aggregates) having opposite charge already, effectively reducing the repulsive potential between the colloids making it possible leading to aggregation. Energy consumption was much higher in the case of absence of Na_2SO_4 because of high resistance in the solution due to poor conductivity [66].

Table 3, from technical definitions for electrolyte (weak and strong), SE, and catalyst [30,67] lets us to conclude that the SE is the electrocatalyst even if Cl$^-$ may be converted to Cl_2 when NaCl is used as SE.

On the other hand, even in CC process some studies have been performed on effects of coexisting anions – not as SEs as in EC - such as SO_4^{2-} on CC efficiency, anions naturally present in water or added in some

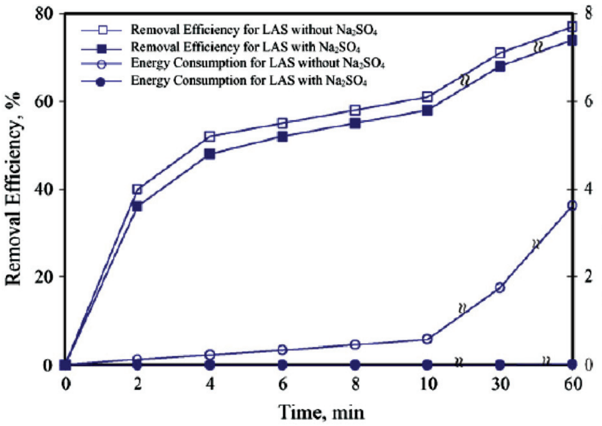

Fig. 3. Effect of supporting electrolyte on linear alkylbenzene sulfonate (LAS) removal efficiency and energy consumption (initial concentration: 10 mg/l; applied current density: 2.75 A/m^2) [66].

Table 3
SE is the electrocatalyst [30,67]

Electrolyte
A substance whose aqueous solutions conduct electricity.
Weak electrolyte
A substance that conducts electricity poorly in a dilute aqueous solution.

Strong electrolyte
A substance that conducts electricity well in a dilute aqueous solution.

Catalyst
A substance that speeds up a chemical reaction without being consumed itself in the reaction.
A substance that increases the rate at which a reaction occurs.

SE
As an electrolyte solution, whose constituents are not electroactive in the range of applied potentials being studied, and whose ionic strength (and, therefore, contribution to the conductivity) is usually much larger than the concentration of an electroactive substance to be dissolved in it. Consequently, SE is the electrocatalyst even if Cl$^-$ may be converted to Cl_2 when NaCl is used as SE.

experiments to water. The following section will give some examples from literature.

6. Coexisting anions in coagulation process

Coagulation is a key and basic unit process in water purification [68]. Enhanced coagulation is recommended by US EPA as an optimal way to control DBPs at the first stage in performing D/DBP rule for its high efficiency in removing NOM [69]. The removal efficiency and mechanism of NOM in coagulation had been extensively investigated [70–72]. Furthermore, some inorganic compounds, such as phosphate, fluoride, soluble silica, were found that could bind with Al(III) or Fe(III) salt in coagulation process [73–75]. Plankey et al. [73] investigated the kinetic of aluminium fluoride complexation in acid water and reported different formation pathways of AlF^{2+}. Cheng et al. [74] studied the effects of phosphate on removal of humic substances by aluminium sulphate and found that most of phosphate was removed in the presence of humic acid. These results implied that bromide would also be reduced through similar mechanism in CC. However, in actual environment, except humic acid, large amount of anions, e.g., HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, $H_2PO_4^-$ and F^- coexist with bromide in raw water. Some of these anions were reported that had influence or could be removed in coagulation process [37,76].

Ge and Zhu [68] investigated effects of coexisting anions on removal of bromide by aluminium coagulation. It was observed that bromide was removed of 62.1–87.0% in raw water, while the removal efficiency of bromide was achieved 82.8–99.2% in deionised water through the combination of Br^- with Al(III) in various pathways. The coexisting anions in raw water significantly affected the removal of bromide. Removal efficiency decreased by 11.5, 21.2, 14.6, 8.0 and 40.8% with the addition of HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and $H_2PO_4^-$, respectively, for their affinities with Al(III) or accelerating the formation of $Al(OH)_{3(am)}$. These results demonstrated that bromo-DBPs in drinking water could be controlled though removing bromide by enhanced coagulation.

From Ge and Zhu [68] results', it is obvious that SO_4^{2-} as coexisting anion has a negative effect on the removal of bromide by CC as SO_4^{2-} decreased (21.2%) the bromide removal. On the other hand, Gao and Yue [77] studied the effect of SO_4^{2-}/Al^{3+} ratio and OH^-/Al^{3+} value on the characterization of coagulant poly-aluminium-chloride-sulphate (PACS) and its coagulation performance in water treatment.

Coexisting anions effects may be related the EDL theory. Fig. 4 presents charged double layer around a negatively charged colloid particle and variation of electrostatic potential with distance from particle surface [78]. Indeed, anions are the main constituents of the diffuse layer (Fig. 4). In terms of coagulation mechanisms, there is EDL compression when Al/Fe salt as coagulant is added to water [5]. Indeed, the destabilisation process is achieved by the following four mechanisms of coagulation [79–81]:

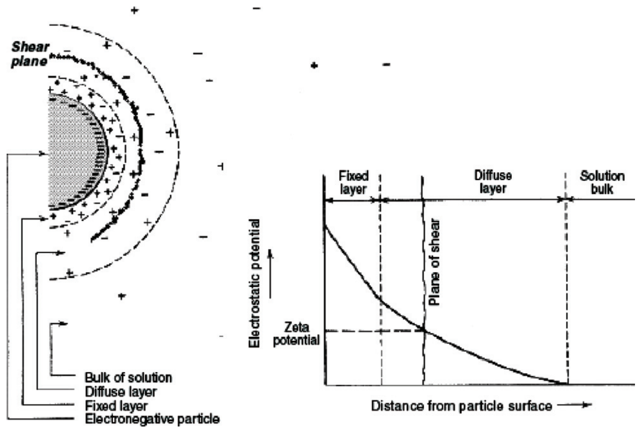

Fig. 4. Charged double layer around a negatively charged colloid particle (left) and variation of electrostatic potential with distance from particle surface (right) [78].

1. EDL compression.
2. Adsorption/charge neutralisation.
3. Entrapment of particles in precipitate (*sweep coagulation*).
4. Adsorption and bridging between particles.

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 [82]. 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 [83]. The net repulsive energy would become smaller or even would be completely eliminated, allowing the particles to approach each other and agglomerate [84]. A mathematical model that describes this coagulation mechanism is explained in detail in [85]. The prediction of this model is in agreement with what is known as the *Schulze–Hardly rule*. This rule states that the coagulation of colloidal particles is achieved by ions of added electrolytes, which carry opposite charge to that of the colloids, and that the destabilisation capability of the ions rises sharply with ion charge [86]. Table 4 illustrates the relative effectiveness of various electrolytes in the coagulation of negatively and positively charged colloids. For example, the relative power of Al^{3+}, Mg^{2+}, and Na^{+} for the coagulation of negative colloids is shown to vary in the ratio of 1000:30:1. A similar ratio is observed for the relative capability of PO_4^{3-}, SO_4^{2-}, and Cl^{-} for the coagulation of positively charged colloids [87].

7. Design considerations

On the other hand, rapid mixing in coagulation process is to rapidly disperse coagulant into raw water, followed by flocculation, sedimentation, and filtration [88–95]. This process has a strong influence on the overall treatment efficiency [96]. Considering that the hydrolysis products, $Me_l(OH)_m^{n+}$ (Me: metal ions; OH: hydroxide ion; l, m, n: constants), of the coagulants such as alum or Fe(III) are produced within a very short time of 10^{-4} to 1 s and moreover, aluminium hydroxide starts to precipitate in about 7 s, it is important to make the metallic coagulants rapidly disperse into the whole fluid bulk [97]. However, it is practically impossible to disperse them within 1 s and thus it is recommended in many publications for operation and design to disperse as rapidly as possible [98,99]. In addition, since the mechanical mixing devices cannot disperse coagulants within such a short time, most of the operators increase the amount of coagulant determined in the laboratory by about 30–40%. It leads to getting the required efficiency of coagulation just by increasing collision opportunities between coagulant ions and colloids [93,100–104], but it may also lead to an overdosing of the metal Me (which admissible concentration is lowered to 0.1 mg/l in drinking water) [105].

Consequently, as seen above, rapid mixing in CC and EC processes must be well optimised to be done in about 7 s (i.e., before metal hydroxide formation) to decrease the negative effects of coexisting anions and SE in CC and EC processes, respectively. In other words, charge neutralisation must have the opportunity to act before *sweep coagulation*. This idea is introduced by the enhanced coagulation concept which was proposed for the dissolved NOM removal from surface waters [7,69,71,105]. As concluded by Timmes et al. [106], for seawater pretreatment prior to desalination operations, future EC reactor design should be based on the concept of EC as a dosing platform rather than a treatment process. This means that EC reactor must be practically designed like CC reactor (rapid mixing) and followed by flocculation reactor (slow mixing).

8. Conclusions

From this review, the main conclusions are:

1. When the conductivity of the water/wastewater (such as oily or organic wastewater) to be electrochemically treated is low causing technical and economical problems, the adjunction of a SE must be considered to increase the ionic strength of the solution and, therefore, its conductivity. As the voltage between the two electrodes decreases, the Joule effect drops and the process efficiency is enhanced. Sodium sulphate is often chosen among others (such as NaCl) as a SE because of its low aggressivity towards the electrodes.
2. Literature examples demonstrate that Na_2SO_4 is less efficient than NaCl as SE in EC process for the removal of humic substances, O/W emulsions, and fluoride. However, for unskimmed milk sample and cutting oil emulsion sulphate anions were found to be quite harmful both for electrical consumption and EC efficiency. These results may be related to the pollutant type and the metal species liberated from the anode. Indeed, in the sulphate media the 70% of the aluminium is in the form of amorphous aluminium hydroxide precipitate and in the chloride media this percentage is around 40%.
3. SE may be considered as the electrocatalyst even if Cl^{-} may be converted to Cl_2 when NaCl is used as SE, and SE is for electrochemical process like air is for sound transmission.
4. The answer to Yildiz et al.'s [5] question: *"Which chemical is the best potential SE for OM removal by EC?"* may be H_2O (H^+, OH^-) instead of NaCl (Na^+, Cl^-), Na_2SO_4 (Na^+, SO_4^{2-}), etc., meaning that the organic effluent must be diluted/dispersed as far as possible in water's molecules dipoles by using highly intense rapid mixing which would be an other subject (avoiding, thus, DBPs formation risk and SO_4^{2-} efficiency problems if NaCl and Na_2SO_4 are added to the wastewater, respectively).
5. Future EC reactor design should be based on the concept of EC as a dosing platform rather than a treatment process. This means that EC reactor must be practically designed like CC reactor (rapid mixing) and followed by flocculation reactor (slow mixing).

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