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Advanced oxidation phenomena in electrocoagulation process: a myth or a reality?

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ABSTRACT

This review discusses the advanced oxidation process (AOP) phenomena in electrocoagulation (EC) process. AOPs have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical ($^{\cdot}OH$) as the primary oxidant. In principle, as water-containing colloidal particulates, oils, or other contaminants move through the applied electric field, there may be ionisation, electrolysis, hydrolysis, and free-radical formation which may alter the physical and chemical properties of water and contaminants. Further, when the electrochemical reactors operate at a high cell potential and an anodic process occurs in the potential region of water discharge, hydroxyl radicals ($^{\cdot}OH$) are generated. In order to get more probabilities to have free radicals formation in EC, ultrasound during EC may be very useful as discussed by some authors. Further, EC process at pH less than 3 has more chance to produce hydroxyl radicals formation. Finally, this review concludes that there is no proof of the presence of AOP phenomena in EC process and more research is needed here focusing on free radicals formation.

Keywords: Electrocoagulation (EC); Advanced oxidation processes (AOPs); Hydroxyl radical ($^{\cdot}OH$); Electrochemical AOPs (EAOPs); Ultrasound; Electro-oxidation

1. Introduction

The interest in electrochemical methods for wastewater treatment such as electrocoagulation (EC) is permanently growing [1–7]. Electrochemical methods are also considered as promising methods for water and wastewater treatment [8–11]. EC process generates metallic cations by electrodissolution of soluble anodes (e.g. in iron or aluminium) in water [12–16]. The *in situ* formed cations (Fe^{2+} and/or Fe^{3+} or Al^{3+}) destabilise finely dispersed particles by charge neutralisation mechanism and conduct near the anode to form hydroxide forms ($Fe(OH)_{n(s)}$, $n = 2$ or 3, or $Al(OH)_{3(s)}$), which adsorb the dissolved organics by the constitution of large and stable flocs containing less-bound water [3,17–21] following the *sweep* coagulation mechanism. Even if the charge neutralisation mechanism is not practical due to the exactness required and is not sufficient in it, it is an essential key stage since *sweep* coagulation is achieved by over-dosing beyond charge neutralisation and generates the desired voluminous metal floc for its adsorbing properties [21,22].

The flocs can be separated by flotation (transport to the surface by fixation on the $H_{2(g)}$ bubbles—typically of order 20 μm [22]—produced at the cathode), sedimentation, or filtration [6,10,23–32]. Indeed, the greater part of $H_{2(g)}$ bubbles combine additively because hydrogen is a hydrophobic gas [33] and iron is dense to settle out at the recipient bottom [8,26]. It has been demonstrated that $Fe(OH)_{n(s)}$ has alkaline properties and a very high adsorption capacity 100 times more important than chemical $Fe(OH)_{n(s)}$ [24,34].

On the other hand, several EC process mechanisms have been proposed mostly without specifying the solution pH or it was supposed neutral [4,8,10,34–39]. Due to different conditions, such as organic and inorganic solutions, a great confusion exists about iron hydroxides $Fe(OH)_{2(s)}$ and/or $Fe(OH)_{3(s)}$ production in the EC systems. Depending on pH, three mechanisms for EC using iron electrodes have been presented [3].

Further, promising technologies for dyes removal are the advanced oxidation processes (AOPs) involving the *in situ* production of $^{\cdot}OH$ [40]. This species is a strong oxidant with high standard potential ($E^\circ = 2.80$ V/SHE) that reacts with most organics giving mineralisation to CO_2, H_2O and inorganic ions [41–44] (see Table 1). Recently, electrochemical AOPs (EAOPs) based on H_2O_2 electrogeneration have received great attention for the remediation of acidic waters with synthetic dyes [45–52], pesticides [53,54], drugs [55–57] and chemicals [58–60].

This review aims to discuss the AOP phenomena in EC process. AOPs have been broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical ($^{\cdot}OH$) as the primary oxidant. If AOP phenomena occur in EC process, in some experimental conditions which must be determined, its efficiency may be increased.

2. Chemical coagulation

Coagulation is a process for increasing the tendency of small particles in an aqueous suspension to attach to one another and to attach to surfaces such as the grains in a filter bed [61–63]. It is also used to effect the removal of certain soluble materials by adsorption or precipitation. The coagulation process typically includes promoting the interaction of particles to form larger aggregates [61]. It is an essential component of the conventional water treatment systems where the processes of coagulation, sedimentation, filtration, and disinfection are combined to clarify water, remove and inactivate microbial contaminants such as viruses, bacteria and cysts and oocysts of pathogenic protozoa [64–66]. Although the removal of microbial contaminants continues to be an important reason for using coagulation, a newer objective, the removal of natural organic material (NOM) to reduce the formation of disinfection by-products, is growing in importance [67–69].

Aluminium and ferric iron salts have long been used to remove colour caused by NOM [70]. These organic substances are present in all surface waters and in many groundwaters [71]. They can be leached from soil, diffused from wetland sediments and released by plankton and bacteria. NOM adsorbs on natural particles and acts as a particle-stabilising agent in surface water [72,73]. It may be associated with toxic metals and synthetic organic chemicals [74]. NOM includes precursor compounds that form health-related by-products when chlorine and other chemical disinfectants are used for disinfection and oxidation [75]. For these reasons, considerable attention is being directed at the removal of NOM by coagulation in water treatment even when colour removal is not the principle objective [66]. A treatment technique in the USA Environmental Protection Agency's Stage 1 Disinfection By-Products Rule requires NOM removal in the conventional treatment systems by the practice of *enhanced coagulation* [61,67,76–80].

Coagulation has been an important component of high-rate filtration plants in the USA since the 1880s.

Table 1
Redox potentials of different oxidants in water [44]

Oxidant	Acidic	E° (V/SHE)	Basic	E° (V/SHE)
Hydroxyl radical	$^{\cdot}OH/H_2O$	2.80	$^{\cdot}OH/OH^-$	1.89
Ferrate(VI)	$Fe^{VI}O_4{}^{2-}/Fe^{3+}$	2.20	$Fe^{VI}O_4{}^{2-}/Fe(OH)_3$	0.70
Ozone	O_3/O_2	2.08	O_3/O_2	1.24
Hydrogen peroxide	H_2O_2/H_2O	1.78	H_2O_2/OH^-	0.88
Permanganate	$MnO_4{}^-/MnO_2$	1.68	$MnO_4{}^-/MnO_2$	0.59
	$MnO_4{}^-/Mn^{2+}$	1.51		
Hypochlorite	$HClO^-/Cl^-$	1.48	ClO^-/Cl^-	0.84
Chromium(VI)	$Cr_2O_7{}^{2-}/Cr^{3+}$	1.33	$CrO_4{}^{2-}/Cr(OH)_3$	−0.12
Ferrate(IV)	$Fe^{IV}O^{2+}/Fe^{3+}$	$\geqslant 0.87$	Fe^{IV}pyrp/Fe^{III}pyrp[a]	1.00<–<1.40

Note: [a]Pyrp-pyrophosphate; pH 10.0.

Alum [$Al_2(SO_4)_3$] and iron (III) salts have been employed as coagulant chemicals since the beginning, with alum having the most widespread use [81]. In the 1930s, Baylis perfected activated silica as a "coagulant aid." This material, formed on site, is an anionic polymer or a small negatively charged colloid [82]. Synthetic organic polymers were introduced in the 1960s with cationic polymers having the greatest use [83]. Natural starches were employed before the synthetic compounds. Polymers have helped to change pre-treatment and filtration practice, including, the use of multimedia filters and filters with deep, uniform grain-size media, high-rate filtration, direct filtration (rapid mixing, flocculation, and filtration, but no sedimentation), in-line filtration (rapid mixing and filtration only) [67,84], ultra- and nano- filtration membranes and also membranes to protect the more expensive reverse osmosis membranes from biofouling for example [85].

Coagulants are also being used to enhance the performance of membrane microfiltration systems and in pre-treatment that prolongs the bed life of granular activated carbon contactors [85,86]. The development of new chemicals, advances in floc removal process and filter design, and particle removal performance standards and goals have stimulated substantial diversity in the design and operation of the coagulation process and change can be expected to continue into the future [87,88].

2.1. Properties of colloidal systems

Colloids are very small particles that have extremely large surface area [89]. Colloidal particles are larger than atoms and ions but are small enough that they are usually not visible to the naked eye [90]. They range in size from 0.001 to 10 μm resulting in a very small ratio of mass to surface area. The consequence of this smallness in size and mass and largeness in surface area is that in colloidal suspensions: (1) gravitational effects are negligible and (2) surface phenomena predominate [91,92].

Because of their tremendous surface area, colloidal particles have the tendency to adsorb various ions from the surrounding medium that impart to the colloids an electrostatic charge relative to the bulk of surrounding water [82,93]. The developed electrostatic repulsive forces prevent the colloids from coming together and consequently contribute to their dispersion and stability [94].

2.1.1. Electrokinetic properties

The electrokinetic properties of colloids can be attributed to the following three processes [67,91]:

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

Organic substances and bacteria acquire their surface charges as a result of the ionisation of the amino and carboxyl groups as shown below [82]:

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

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

The resulting charge on the surface of such particles is a function of the pH [82]. At high pH values or low hydrogen ion concentrations, the above reactions shift to the right and the colloid is negatively charged. At a low pH, the reactions shift to the left, the carboxyl group is not ionised, and the particle is positively charged due to the ionised amino group. When the pH is at the isoelectric point, the particle is neutral, i.e. neither negatively nor positively charged. Proteinaceous material containing various combinations of both amino and carboxyl groups, are usually negatively charged at pH values above 4 [89].

Oil droplets adsorb negative ions, preferably hydroxides (OH^-), from solution and consequently develop a negative charge [82,93]. Some other neutral particles adsorb selected ions from their surrounding medium such as calcium (Ca^{2+}) or phosphate (PO_4^{3-}) ions rendering them either positively or negatively charged, respectively.

Clays and other colloidal minerals may acquire a charge as a result of a deficit or imperfection in their internal structure [82]. This is known as isomorphic replacement [89]. Clays consist of a lattice formed by cross-linked layers of silica and alumina. In some clays, there are fewer metallic atoms than non-metallic ones within the mineral lattice producing a negative charge [82]. In others, cations of higher valency may be replaced by cations of lower valency during the formation of the mineral lattice that renders the clay particles negatively charged [82]. Examples of such imperfections include (a) the substitution of an aluminium ion (Al^{3+}) by either Mg^{2+} or Fe^{2+} and (b) the replacement of Si^{4+} cation by Al^{3+}. According to Letterman et al. [67], the type and strength of the charge resulting from this imperfection in the clay structure are independent of the surrounding water properties and pH. This is in contrast with the first two processes discussed above wherein both pH and ionic make-up of the surrounding solution play a big role in determining the sign and magnitude of the acquired charge on colloidal particles [89].

2.1.2. Hydration

Water molecules may also be sorbed on the surface of colloids in addition to or in place of other molecules or ions. The extent of this hydration depends on the affinity of particles for water. Colloidal particles that have water-soluble groups on their surface such as hydroxyl, carboxyl, amino and sulphonic exhibit high affinity for hydration and cause a water film to surround the particles. Such colloids are classified as hydrophilic (water-loving) particles. On the other hand, the colloids that do not show affinity for water and do not have bound water films are classified as hydrophobic (water-hating) [89].

2.1.3. Brownian movement

Colloids exhibit a continuous random movement caused by bombardment of the water molecules in the dispersion medium [95]. This action, called *Brownian movement*, imparts kinetic energy to the particles that tend to cause an increase in the frequency of collisions thus promoting coagulation. Elevated temperature increases molecular velocity resulting in more kinetic energy and more intense Brownian movement [88,89].

2.1.4. Tyndall effect

Since colloidal particles have an index of refraction different from that of water, the light passing through the dispersion medium and hitting the particles will be reflected. The turbid appearance due to this interference with the passage of light is termed the *Tyndall effect*. However, it should be noted that this might not always be the case. Hydrophilic colloids may produce just a diffused Tyndall cone or none at all. The reason for this behaviour can be attributed to the bound water layer surrounding colloids. These particles will have an index of refraction not very different from that of the surrounding water. Hence, the dispersed phase and the dispersion medium behave in a similar fashion towards the passage of light [89].

2.2. Destabilisation of colloids

Destabilisation of colloidal particles is accomplished by coagulation through the addition of hydrolysing electrolytes such as metal salts and/or synthetic organic polymers [88,96]. Upon being added to the water, the action of the metal salt is complex [67,89]. It undergoes dissolution, the formation of complex highly charged hydrolysed metal coagulants (hydroxyoxides of metals), interparticle bridging and the enmeshment of particles into flocs [76,97]. Polymers work either on the basis of particle destabilisation or bridging between the particles [98].

The destabilisation process is achieved by the following four mechanisms of coagulation [76,98,99]:

1. Electrical double-layer compression.
2. Adsorption and charge neutralisation.
3. Entrapment of particles in the precipitate (*sweep coagulation*).
4. Adsorption and bridging between particles.

2.2.1. Electrical double-layer compression

When high concentrations of simple electrolytes are introduced into a stabilised colloidal dispersion, the added counter-ions penetrate into the diffused double-layer surrounding the particles rendering it denser and hence, thinner and smaller in volume [95]. The addition of counter-ions with higher charges [82] such as divalent and trivalent ions will result in even steeper electrostatic potential gradients and more rapid decrease in charge with distance from the surface of the particles. The net repulsive energy would become smaller or even would be completely eliminated allowing the particles to approach each other and agglomerate [89].

A mathematical model that describes this coagulation mechanism is explained in detail in [100]. 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 the 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 [88,91].

2.2.2. Adsorption and charge neutralisation

For all practical purposes, the ability of a chemical substance to destabilise and coagulate colloidal particles is the result of a combination of several mechanisms. Long-chained organic amines are often mentioned as being typical coagulants that function by adsorption and electrostatic neutralisation [67,89,91]. The positively charged organic amine molecules ($R–NH_3^+$) are easily and quickly attached to negatively charged colloidal particles. The charge on the particles gets neutralised and the electrostatic repulsion is decreased or eliminated resulting in the destabilisation of the colloids and hence their agglomeration [82]. The organic amines are hydrophobic because of the lack of interaction between the CH_2 groups in their R–chain and the surrounding water. As a result, these positively charged ions are driven out of the water and get adsorbed on the particulate interface. An overdose of $R–NH_3^+$ counter-ions, however, can lead to charge reversal from negative to positive and the restabilisation of the dispersion system.

When coagulants such as metal salts are added to water, they dissociate yielding metallic ions which undergo hydrolysis and form positively charged metallic hydroxyoxide complexes [89]. The commonly used coagulants, trivalent salts of aluminium and iron, produce numerous species because the hydrolysis products themselves tend to polymerise to give polynuclear metallic hydroxides [89]. Examples of aluminium salt polymers are $Al_6(OH)_{15}^{3+}$ and $Al_7(OH)_{17}^{4+}$ and that of iron salt polymers are $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$. When such polyvalent complexes possessing high positive charges get adsorbed on to the surface of the negatively charged colloids, the result is again a neutralisation of the charges, decrease in the repulsion energy and destabilisation of the colloids. In a similar fashion to what occurs with the organic amines, an overdose of metallic salts could reverse the colloidal charge and restabilise the particles.

An important remark which must be mentioned here is that in the electrochemical coagulation, adsorption and charge neutralisation mechanism remain as important as in the conventional coagulation for pollutants removal even if the electric current is applied [21].

2.2.3. Entrapment of particles in precipitate

When the coagulants, alum or ferric chloride ($FeCl_3$) are added in high-enough concentration, they will react with hydroxides (OH^-) to form metal hydroxide precipitates, $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$, respectively. The colloidal particles get entrapped in the precipitates either during the precipitate formation or just after. This type of coagulation by enmeshment of colloids in precipitates is commonly called *sweep coagulation* [67,89].

There are three elements that influence this coagulation mechanism [89]:

(1) *Oversaturation*: The rate of precipitation is a function of oversaturation with the metal hydroxide. To obtain faster precipitation and efficient *sweep coagulation*, high concentrations of $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$ are required.

(2) *Presence of anions*: The rate of precipitation is improved by the presence of various anions in water. The most effective anions in this respect are the sulphate ions.

(3) *Concentration of colloids*: The rate of precipitation is also improved with higher concentration of colloidal particles. The reason for this is that the colloids themselves could act as nuclei for the formation of precipitates. In this case, it can be concluded that lower rather than higher coagulant dosage will be required to coagulate water having higher colloidal particle concentration.

2.2.4. Adsorption and bridging between particles

Polymers destabilise colloidal particles through the formation of bridges that extend between them [89]. The polymers have reactive groups that bind to specific sites on the surface of the colloidal particles. When a group on a polymer molecule attaches to a colloid, the remainder of the long-chain molecule extends away into the water. Once the extended portion of the polymer gets attached to another colloidal particle, the two particles become tied together or bridged by the polymer. If no other particle is available or if there is an overdose of polymer, the free extended portions of the polymer molecule would wrap around the same original particle which could effectively bring about the restabilisation of the colloid. Restabilisation can also occur due to aggressive mixing or extended agitation, which may break the inter-particle bridging and allow the folding back of the freed polymer portions around the same original particle [21,89].

What is also important here to be noticed is that the restabilisation phase also occurs in EC process [21].

2.3. Phenomena of coagulation

Coagulation results from two basic phenomena: (1) perikinetic (or electrokinetic) coagulation in which the zeta potential is reduced by ions or colloids of opposite charge to a level below the van der Waals attractive forces and (2) orthokinetic coagulation (fluid motion) in which the micelles aggregate and form clumps that agglomerate the colloidal particles [62,92,101–103].

The addition of high-valence cations depresses the particle charge and the effective distance of the double layer thereby reducing the zeta potential [101]. As the coagulant dissolves, the cations serve to neutralise the negative charge on the colloids [104]. This occurs before visible floc formation and rapid mixing which "coats" the colloid is effective in this phase [88]. Microflocs are then formed to retain a positive charge in the acid range because of the adsorption of H^+. These microflocs also serve to neutralise and coat the colloidal particle. Flocculation agglomerates the colloids with a hydrous oxide floc [105]. In this phase, surface adsorption is also active. Colloids not initially adsorbed are removed by enmeshment in the floc [62,84].

A desired sequence of operation for effective coagulation was outlined [62]. If necessary, alkalinity should first be added (bicarbonate has the advantage of providing alkalinity without raising the pH). Alum or ferric salts are added next; they coat the colloid with Al^{3+} or Fe^{3+} and positively charged microflocs [105]. Coagulant aids such as activated silica and/or polyelectrolyte for floc build-up and zeta potential control are added last. After addition of alkali and coagulant, a rapid mixing for 1–3 min is recommended followed by flocculation with addition of coagulant aid for 20–30 min [83,84,87,106]. Destabilisation can also be accomplished by the addition of cationic polymers which can bring the system to the isoelectric point without a change in pH. Although polymers are 10–15 times as effective as alum as a coagulant, they are considerably more expensive [106,107].

However, electrical double layer compression and charge neutralisation may be classified as electrokinetic coagulation and *sweep coagulation*, and bridging between particles may be attributed to orthokinetic coagulation [103,108].

3. Free-radical formation in EC process

In our previous work [3], we have studied the EC mechanisms for iron and aluminium electrodes (see Table 2).

Mollah et al. [8] explained that as water-containing colloidal particulates, oils or other contaminants move through the applied electric field, there may be ionisation, electrolysis, hydrolysis and free-radical formation which may alter the physical and chemical properties of water and contaminants [8,109]. As a result, the reactive and excited state causes contaminants to be released from water and destroyed or made less-soluble [110]. Further, when electrochemical reactors operate at a high cell potential and the anodic process (Fig. 1) occurs in the potential region of water discharge, hydroxyl radicals ($^{\cdot}OH$) are generated [111–113]. Apaydin et al. [113] affirmed that ferrous ions act as coagulation materials in the electrochemical treatment and catalytically create hydroxyl radicals to a small extent.

Chou et al. [114] affirmed that increased temperature promoted the generation of hydroxyl radicals in the bulk solution using iron EC which led to higher mass transfer and more frequent collisions of species resulting in an increased reaction rate of the radicals with pollutants. Cho et al. [115] affirmed that electro-oxidation occurs during electrolysis because of the oxidative action of hydroxyl and hypochlorite ions. Hydroxyl ions can successfully remove toxic organic chemicals in wastewater because the hydroxyl radical is more powerful compared with conventional oxidants such as chlorine, chlorine dioxide and potassium permanganate [115].

However, the free radical formation remains to be proved qualitatively and quantitatively in EC process as in the presented case in Fig. 2 [116].

3.1. Ultrasound techniques for free-radical formation in EC process

Sister and Kirshanova [109] studied the ultrasonic techniques in removing surfactants from effluents by EC. Ultrasound was used as an intensifying agent as it has been given much attention lately [117–120] to water treatment and the preparation of drinking water. Ultrasound acting during EC in removing surfactants from effluents was used by Sister and Kirshanova [109] on the following theoretical basis derived from the literature:

(1) Ultrasound saves electrical energy in the EC because the free radicals and outgassing effect in the cavitation raises the electrical conductivity which enables one to maintain constant current at lower voltages.
(2) The erosion in cavitation disrupts the passivating films on the anode and intensifies the electrochemical dissolution of metals. One, therefore, requires less current to obtain the same amount of coagulant (reduced losses) which also saves electricity.
(3) The free radicals formed in cavitation participate in flocculation and there is a release of gas at the electrodes which intensifies those processes.
(4) Ultrasound produces outgassing and flotation effects, and intensifies electroflotation while surface effects and suspension in the acoustic field favour the rapid and more effective coagulation of the pollutants for the same amount of metal ions in the solution [109].

Table 2
EC mechanisms using Fe (pH 2, 7 and 12) and Al (pH 7) electrodes [3]

Fe mechanisms
Mechanism 1 (pH 2)
Anode:
$2Fe_{(s)} - 4e^- \rightarrow 2Fe^{2+}_{(aq)} \quad (E^\circ = +0.447\ V)$ (3)
$2H_2O_{(l)} - 4e^- \rightarrow O_{2(g)} + 4H^+_{(aq)} \quad (E^\circ = -1.229\ V)$ (4)
Solution:
$2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} \rightarrow 2Fe(OH)_{2(s)}$ (5)
Cathode:
$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} (E^\circ = 0.000\ V)$ (6)
Total:
$2Fe_{(s)} + 6H_2O_{(l)} \rightarrow O_{2(g)} + 4H_{2(g)} + 2Fe(OH)_{2(s)}$ (7)
Mechanism 2 (pH 7)
Anode:
$2Fe_{(s)} - 4e^- \rightarrow 2Fe^{2+}_{(aq)} (E^\circ = +0.447\ V)$ (3)
$Fe^{2+}_{(aq)} - e^- \rightarrow Fe^{3+}_{(aq)} (E^\circ = -0.771\ V)$ (8)
$Fe_{(s)} - 3e^- \rightarrow Fe^{3+}_{(aq)} (E^\circ = +0.037\ V)$ (9)
Solution:
$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$ (5)
$2Fe^{3+}_{(aq)} + 6OH^-_{(aq)} \rightarrow 2Fe(OH)_{3(s)}$ (10)
Cathode:
$8H_2O_{(l)} + 8e^- \rightarrow 4H_{2(g)} + 8OH^-_{(aq)} (E^\circ = -0.828\ V)$ (11)
Total:
$3Fe_{(s)} + 8H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + 2Fe(OH)_{3(s)} + 4H_{2(g)}$ (12)
Mechanism 3 (pH 12)
Anode:
$2Fe_{(s)} - 6e^- \rightarrow 2Fe^{3+}_{(aq)} (E^\circ = +0.037\ V)$ (9)
Solution:
$2Fe^{3+}_{(aq)} + 6OH^-_{(aq)} \rightarrow 2Fe(OH)_{3(s)}$ (10)
Cathode:
$6H_2O_{(l)} + 6e^- \rightarrow 3H_{2(g)} + 6OH^-_{(aq)} (E^\circ = -0.828\ V)$ (11)
Total:
$2Fe_{(s)} + 6H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 3H_{2(g)}$ (13)

Al mechanism (pH = 7)
Anode:
$Al_{(s)} - 3e^- \rightarrow Al^{3+}_{(aq)} (E^\circ = +1.66\ V)$ (14)
$2H_2O_{(l)} - 4e^- \rightarrow O_{2(g)} + 4H^+_{(aq)} (E^\circ = -1.229\ V)$ (4)
Solution:
$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)}$ (14)
$Al(OH)^-_{4(aq)} \rightarrow OH^-_{(aq)} + Al(OH)_{3(s)}$ (15)
Cathode:
$4H_2O_{(l)} + 4e^- \rightarrow 2H_{2(g)} + 4OH^-_{(aq)} (E^\circ = -0.828\ V)$ (11)
$Al_{(s)} + 4OH^-_{(aq)} - 3e^- \rightarrow Al(OH)^-_{4(aq)}$ (16)
Total:
$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 5H_{2(g)} + 2Al(OH)_{3(s)} + O_{2(g)}$ (17)

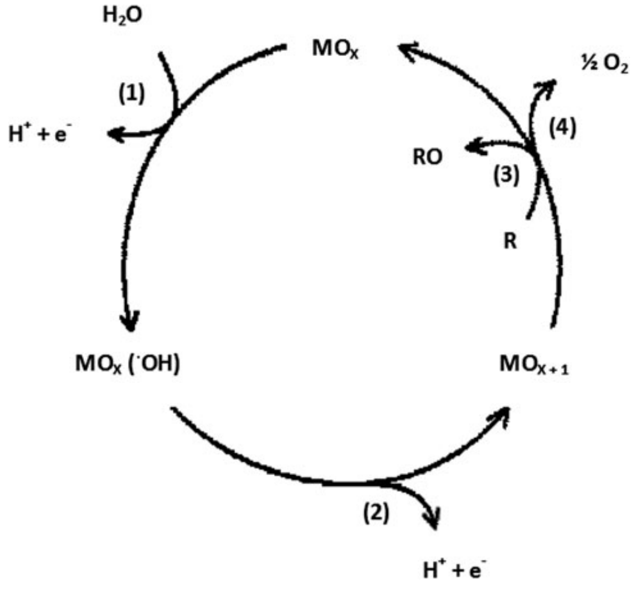

Fig. 1. Schematic representation of the electrochemical oxidation of organics on oxide anodes (MO_x) forming the higher oxide (MO_{x+1}). (1) H_2O discharge; (2) higher oxide formation; (3) organic oxidation; and (4) O_2 evolution [111].

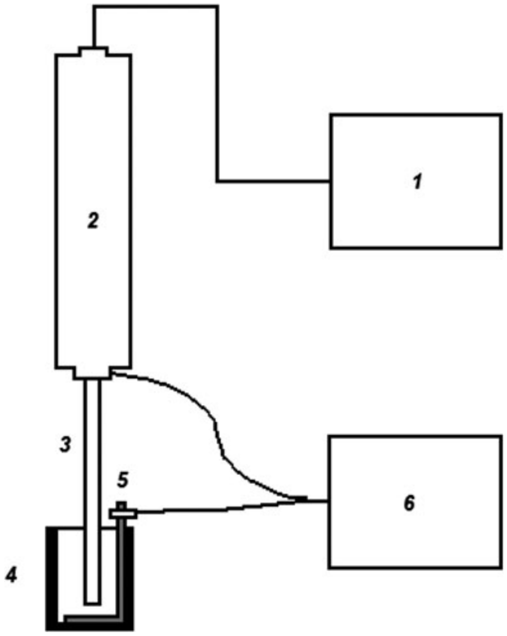

Fig. 3. Laboratory apparatus scheme: (1) ultrasonic source; (2) magnetostriction converter; (3) waveguide radiator; (4) thermostatic cell; (5) Al electrode; (6) direct current (DC) source [109].

Furthermore, Sister and Kirshanova [109] performed a series of experiments with a laboratory system (Fig. 3) to determine the scope for ultrasonic intensification of EC elimination of surfactants from effluents. Ultrasound mixes and disrupts macromolecules or agglomerates, and also provides a high degree of removal of organic and inorganic pollutants, toxic substances and pathogenic microflora, and the use of certain methods is recommended for operation at 20–25 kHz and ultrasonic power density $5–30 \times 10^{-1}$ W/cm^2 [109]. They selected the following parameters: current density 50–250 A/m^2, treatment time 5–40 min, ultrasonic power density $5–30 \times 10^{-1}$ W/cm^2. The frequency in all experiments was 22 ± 1 kHz. The surfactants concentrations (mixture of sintanol and sulphanol in a 1:1 ratio) in the model were 100–500 mg/L, which corresponds to the surfactants contents in industrial effluents where surfactants are used as wetting agents, emulsifiers and stabilisers, i.e. substances entering the effluents in concentrations comparable with those of other pollutants. They found that the best current density is 100–150 A/m^2, time of joint ultrasonic and EC treatment 8–12 min with ultrasonic power density 1–2 W/cm^2. Fig. 4 shows results obtained on treating an actual effluent from wet cleaning. The current density and the specific ultrasonic loading were respectively 150 A/m^2 and 2 W/cm^2 [109].

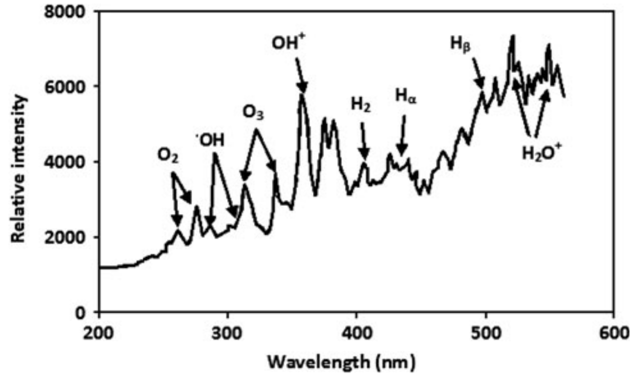

Fig. 2. Identification of radical species formed with oxygen atomisation under corona discharge [116].

However, Kovatcheva and Parlapanski [23] reported that the sound used may cause a few negative effects directly related to the purification process such as the following:

- Destruction of a part of the obtained colloidal hydroxides by the action of the acoustic waves. This means a diminution of the solid phase that takes part in the adsorption process and a diminution of the removed contaminants, respectively.
- Destruction of a part of the formed adsorption layer on the surface of the colloidal particles and

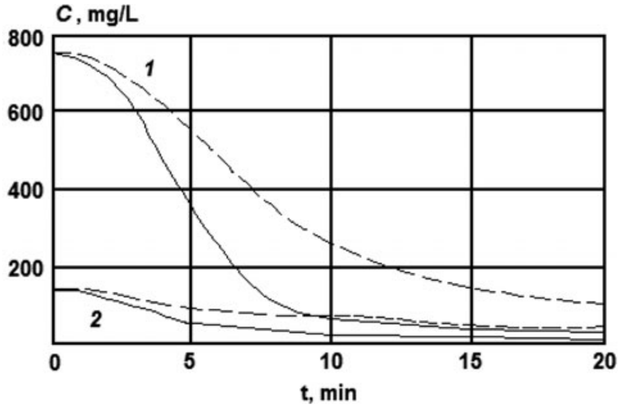

Fig. 4. Effects of ultrasound on surfactants concentration during EC treatment of effluents: solid line with ultrasound; dashed line without ultrasound; (1) nonionic surfactant; (2) anion-active surfactant [109].

possible return of the adsorbed ions to the liquid phase.
- Disorganisation of the migration processes in the medium by the ultra-sonic waves [23].

Consequently, as seen above, the free radicals formation in EC process with and without ultrasound techniques needs further research to be proved and then optimised.

An interesting research has been done by Sánchez-Carretero et al. [121] where the use of an ultrasound processor is proposed to enhance the efficiency of the electrosynthesis of ferrates with boron-doped diamond (BDD) anodes [121]. BDD anode has an extreme oxygen overvoltage (>3 V) before O_2 forms and enables effective production of hydroxyl radicals ($^{\cdot}OH$) directly from the electrolysed water [122]. The chemical dissolution of the iron powder used as raw material, due to the extreme pH on the nearness of the anode surface, improves the results significantly. The application of ultrasound during electrolyses, besides having a positive effect on the dissolution of the raw material, also favours the mass transport of iron species to the electrode surface, and thus, its use enhances the efficiency of the process. The hydroxyl ion concentration and the current density also have a clear influence on the results: high current density favours iron dissolution and hydroxyl radical generation, whereas high hydroxyl ions concentration contributes to the stability of produced ferrate [121].

3.2. A combined EC–electrooxidation treatment for industrial wastewater

The advantages of EC and electro-oxidation processes considered separately have pushed researchers [123–127] to combine these electrochemical processes for industrial wastewater treatment. EC is a relatively quick process (30 min) and very effective in removing colloidal and suspended particles, as seen in changes in coliforms, turbidity and colour, in the general absorbance by UV–vis spectroscopy. However, it is relatively ineffective in eliminating stable persistent organic compounds; in their work [124], only half of the chemical oxygen demand (COD) was eliminated from wastewater and an oxidation peak in the cyclic voltammetry scan remained. Electro-oxidation is very effective in breaking down organic compounds through oxidation as reflected in the elimination of COD, 5-day biochemical oxygen demand (BOD_5), and oxidative peak in cyclic voltammetry, but requires so much time (21 h) that it has very limited practicality, especially when colloidal and suspended particles are present. Electro-oxidative mineralisation of electrocoagulated wastewater, in which most of the colloids and charged species have been removed, takes less than 2 h. In the coupled technique, EC quickly coagulates and removes the colloidal and suspended particles, as well as many charged species, then electro-oxidation oxidises the remaining organics. The coupled process eliminates COD, BOD_5, colour, turbidity and coliforms in a practical amount of time (2 h) [124].

In EC process, once the iron has been dissolved, it acts as coagulant. Iron ions hydrolyse and mononuclear complexes are formed depending on pH (Table 2) [3]. The presence of iron ions and iron complexes destabilise the colloidal particles breaking the emulsion [128]. This process leads to flocculation which generates bigger particles. The flocs settle and form sludge at the bottom of the reactor [124].

Reports indicate that wastewaters containing several carboxylic acids (formic, oxalic and maleic) were oxidised using BDD electrodes. In all cases, the only product generated was carbon dioxide with no other intermediates detected by HPLC [124].

Previous research [124] indicates that the oxidation of organics with concomitant oxygen evolution assumes that both organic oxidation and oxygen evolution take place on a BDD anode surface via intermediation of hydroxyl radicals generated from the reaction with water shown in Eqs. (18) and (19):

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD}(^{\cdot}\mathrm{OH}) + \mathrm{H}^+ + \mathrm{e}^- \quad (18)$$

$$\mathrm{BDD}(^{\cdot}\mathrm{OH}) + \mathrm{R} \rightarrow \mathrm{BDD} + m\mathrm{CO_2} + n\mathrm{H_2O} \quad (19)$$

Reaction (19) is in competition with the side reaction of hydroxyl radical conversion to O_2 without any participation of the anode surface as indicated in Eq. (20) [124]:

$$\mathrm{BDD}(^{\cdot}\mathrm{OH}) \rightarrow \mathrm{BDD} + (1/2)\mathrm{O}_2 + \mathrm{H}^+ + \mathrm{e}^- \qquad (20)$$

$^{\cdot}$OH is a non-selective, very powerful oxidant agent that reacts with organics yielding dehydrogenated or hydroxylated derivatives until their mineralisation (conversion into CO_2 and inorganic ions) is achieved [129].

4. Electrochemical advanced oxidation processes

The most common EAOP is electro-Fenton in which H_2O_2 is formed by the two-electron reduction of O_2 at a carbonaceous cathode such as graphite, carbon felt, reticulated vitreous carbon and gas diffusion electrodes [40,41,130–136]:

$$\mathrm{O}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2\mathrm{O}_2 \qquad (E^\circ = 0.69\ \mathrm{V/NHE}) \qquad (21)$$

The low oxidation ability of H_2O_2 is enhanced by adding Fe^{2+} ion as a catalyst to the acidic solution to yield Fe^{3+} ion and $^{\cdot}$OH from Fenton's Reaction [137–139]:

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + {}^{\cdot}\mathrm{OH} + \mathrm{OH}^- \qquad (22)$$

The optimum pH of Reaction (22) is 3–4 [140], 3 [141], 2.8 [40], or 2 [138]. An advantage of the electro-Fenton process is the regeneration of Fe^{2+} by continuous Fe^{3+} reduction at the cathode from Reaction (23) with $E^\circ = 0.77\,\mathrm{V/SHE}$ [136,142], thus enhancing the destruction rate of organic pollutants [40]:

$$\mathrm{Fe}^{3+} + \mathrm{e}^- \rightarrow \mathrm{Fe}^{2+} \qquad (23)$$

when a one-compartment cell is employed in electro-Fenton, the anode can also form heterogeneous $^{\cdot}$OH that destroys the organic matter (OM) [40]. This process is more effective using a BDD anode, since its high O_2 overpotential favours the large production of hydroxyl radical on its surface (BDD($^{\cdot}$OH)) during water discharge [143–146]:

$$\mathrm{BDD} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{BDD}(^{\cdot}\mathrm{OH}) + \mathrm{H}^+ + \mathrm{e}^- \qquad (18)$$

The coupling of Fenton's Reaction (22) and advanced oxidation via Reaction (18) improves the electro-Fenton process [40].

In photoelectro-Fenton (PEF), the solution treated by electro-Fenton is irradiated with a UVA lamp of $\lambda_{\max} = 360\,\mathrm{nm}$ [40,47,50,53,55–58,147]. A variant of this EAOP is the solar photo-electroFenton process that uses sunlight ($\lambda > 300\,\mathrm{nm}$) as renewable and inexpensive energy source [57,59,148]. The UVA light enhances the mineralisation process by the faster Fe^{2+} regeneration and $^{\cdot}$OH production from $Fe(OH)^{2+}$ photoreduction, which is the predominant Fe^{3+} species at pH near 3 [40,137]:

$$\mathrm{Fe(OH)}^{2+} + h\nu \rightarrow \mathrm{Fe}^{2+} + {}^{\cdot}\mathrm{OH} \qquad (24)$$

Furthermore, aqueous free radicals are very reactive powerful oxidants, and short lived; thus, they easily recombine to form water [110]. One of the most reactive aqueous radical species is the hydroxyl radical ($^{\cdot}$OH). This radical has an electron affinity value of 136 kcal and is able to oxidise all organic compounds. The $^{\cdot}$OH is the primary oxidant involved in the organic oxidation reaction because (a) oxidation extent is limited only by the quantity of electric energy, and (b) the oxidation yields derived are greater than the one gram equivalent weight per Faraday relationship [110].

On the other hand, Ramseier et al. [149] treated drinking water with ozone, chlorine, chlorine dioxide, monochloramine, ferrate(VI) and permanganate to investigate the kinetics of membrane damage in native drinking water bacterial cells. Only ozonation resulted in a decrease in the total cell concentrations for the investigated reaction times. Rate constants for the membrane damage reaction varied over seven orders of magnitude in the following order: ozone > chlorine > chlorine dioxide ≈ ferrate > permanganate > chloramine. The rate constants were compared with literature data and were, in general, smaller than previously measured rate constants. This confirmed that membrane integrity is a conservative and therefore safe parameter for disinfection control. Interestingly, the cell membranes of high nucleic acid content bacteria were damaged much faster than those of low nucleic acid content bacteria during treatment with chlorine dioxide and permanganate [149].

5. Radical hydroxyl formation in EC process at pH 2.8

As seen above, the optimum pH of Reaction (22) is between 2 and 4. This means that, to get great probability for $^{\cdot}$OH production (i.e. electro-Fenton reaction) during EC process, we must be in *Mechanism 1* for EC process (see Table 2). However, Reaction (22) needs H_2O_2 presence which may be produced following Reaction (21). Further, Reaction (21) needs O_2 presence which may be produced by Reaction (4) (see *Mechanism 1* in Table 2). Let us consider *Mechanism 1* with Reactions (21) and (22):

Anode:

$$2Fe_{(s)} - 4e^- \rightarrow 2Fe^{2+}_{(aq)} \tag{3}$$

$$2H_2O_{(l)} - 4e^- \rightarrow O_{2(g)} + 4H^+_{(aq)} \tag{4}$$

Solution:

$$2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} \rightarrow 2Fe(OH)_{2(s)} \tag{5}$$

$$Fe^{2+}_{(aq)} + H_2O_{2(g)} \rightarrow Fe^{3+}_{(aq)} + {}^{\cdot}OH + OH^-_{(aq)} \tag{22}$$

Cathode:

$$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \tag{6}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{21}$$

Total:

$$2Fe_{(s)} + 5H_2O_{(l)} \rightarrow 2Fe(OH)_{2(s)} + {}^{\cdot}OH + (5/2)H_{2(g)} \tag{25}$$

This modified *Mechanism 1* takes into consideration, the hydroxyl radical formation probability during EC process.

On the other hand, as with all processes, there are some disadvantages to AOPs [150,151] (see Table 3). These include the unspecific nature of the hydroxyl radical in its reactivity and the possible production of by-products with unknown toxicity. In terms of NOM removal, it could be possible that the AOPs produce species which are more hydrophilic in nature than the original NOM and are therefore, more difficult to remove [150]. On this subject, a good review is presented by Pignatello et al. [152].

6. Peroxi-EC mechanism

An interesting approach by Önder et al. [153] and Roa-Morales et al. [154] that simultaneously takes place is when peroxide (H_2O_2) is added into wastewater while electrolysis is taking place. In acidic media (bulk solution), the reduction half-reaction for the hydrogen peroxide is [155]:

$$H_2O_2 + 2e^- + 2H^+ \leftrightarrow 2H_2O \tag{26}$$

As indicated by Bard [156], the hydrogen peroxide will form the hydroxyl radical at the cathode:

$$H_2O_2 + e^- + H^+ \leftrightarrow H_2O + {}^{\cdot}OH \tag{27}$$

The aqueous media is agitated with the injection of air. Some of the Al^{3+} ions produced in the anode can be reduced at the cathode. Then, the aluminium will react in the solution as [154]:

$$3H_2O2 + 3H^+ + Al^0 \leftrightarrow 3\,{}^{\cdot}OH + Al^{3+} + 3H_2O \tag{28}$$

A chain reaction then occurs between the hydroxyl radical and an organic compound R:

$$RH + {}^{\cdot}OH \leftrightarrow R^{\cdot} + H_2O \tag{29}$$

$$R^{\cdot} + O_2 \leftrightarrow ROO^{\cdot} \tag{30}$$

$$ROO^{\cdot} + RH \leftrightarrow ROOH + R^{\cdot} \tag{31}$$

Therefore, the main advantage of adding H_2O_2 is to produce this hydroxyl radical which will react with the organic pollutants present in the wastewater [154].

The results presented by Roa-Morales et al. [154] agree with those presented by Ksibi [157] who indicated that hydrogen peroxide can be used as a chemical oxidation treatment for domestic wastewater. The addition of $1.5\,\mathrm{mL\,L^{-1}}$ reduces the COD from 322 to $49\,\mathrm{mg\,L^{-1}}$ [35].

7. Role of hydroxyl radical during electrolytic degradation of contaminants

Electrolytic degradation of contaminants can occur either by direct oxidation or by indirect oxidation [158,159]. Indirect oxidation of contaminants occurs by an oxidant produced *in situ* at any of the electrode surfaces during electrolysis of water, whereas the direct electrochemical oxidation is a result of electron transfer between the electrode surface and the substrate (contaminant). The scheme for these possible pathways is presented in Fig. 5 [158].

The hydroxyl radical is frequently considered as one of the possible reasons contributing to contaminant loss in many of the studies aimed at indirect electrochemical oxidation of contaminant [160–165]. These researchers have hypothesised that hydroxyl radical can be produced by chemical oxidation of water and/or by direct oxidation of hydroxyl ions [158].

Table 3
Comparison of AOPs against the conventional treatment of NOM [150]

Treatment	Benefits	Drawbacks
Coagulation	Low cost, proven technology	High chemical dose, longer reaction time, NOM only transferred to the sludge and $Fe(OH)_3$
Fenton's reagent	Lower chemical dose, enhanced removals, reduced residuals	NOM mainly transferred to the sludge and $Fe(OH)_3$
Photo-Fenton's reagent	Lower chemical dose, enhanced removals, reduced residuals, reduced reaction times	NOM mainly transferred to the sludge and $Fe(OH)_3$
TiO_2/UV	No chemicals added, no residuals, enhanced removals, lower reaction times	Higher cost due to UV light, NOM is destroyed rather than transferred

$$2H_2O \rightarrow 2\,{}^{\cdot}OH + 2H^+ + 2e^- \qquad (32)$$

$$OH^- \rightarrow {}^{\cdot}OH + e^- \qquad (33)$$

Amadelli et al. [166] observed the degradation of trans-3,4-dihydroxycinnamic acid at PbO_2 electrodes during electrolysis. By observing variations of the electrode potentials for repeated chronopotentiometric measurements, they concluded that the hydroxyl radical was responsible for the loss of the contaminant [158]. Panniza and Cerisola [144] tested the effect on anode material on the electrochemical degradation of 2-naphthol and, using cyclic voltammetry, attributed the degradation to hydroxyl radicals produced at the anode. Different mechanisms of contaminant loss during electrolytic oxidation with naphthalene as a model compound are tested [160]. Among many side reactions tested in lab-scale, 500 ml batch reactors, with naphthalene as a model contaminant, direct anodic oxidation of naphthalene was also tested at pH 4 and pH 7. Naphthalene disappearance was attributed to the oxidation either directly at the anode or through the involvement of hydroxyl radicals formed *in situ* [158].

Despite numerous studies on the direct electrochemical degradation of chemicals, the role of hydroxyl radical during electrolytic degradation is still not well understood. Researchers have typically assigned the cause of contaminant degradation to the indirect oxidation by hydroxyl radical formed *in situ* based on the intermediates [167] formed during *in situ* tests [see Reaction (34)]. Generically, the discovery of hydroxylated products (e.g. hydroxylated aromatics) is often cited as evidence that the hydroxyl radical is present during a process. In fact, this kind of circumstantial evidence is quite weak as any number of potential oxidation processes can generate hydroxylated products in aqueous solution [158].

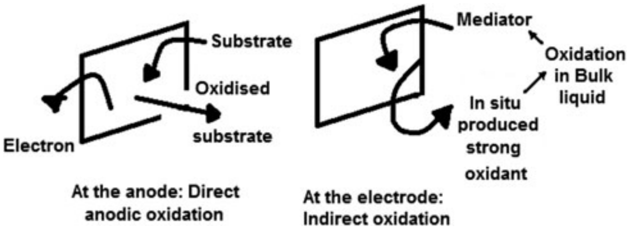

Fig. 5. Hypothetical model showing direct and indirect electrochemical oxidations [158].

$$\begin{aligned}{}^{\cdot}OH + OM &\rightarrow \text{intermediates}\\ &\rightarrow \text{harmless species } (CO_2,\ H_2O,\ \text{etc.})\end{aligned} \qquad (34)$$

Li and Goel [158] investigated the role of hydroxyl radical in electrochemical oxidation of organic contaminants with naphthalene as a model compound. The strategy employed was a competitive kinetic for hydroxyl radical between naphthalene and other hydroxyl scavengers, if the hydroxyl radical is produced *in situ* at the anode by the electrolysis of water. Methanol, d3-methanol, acetone and d6-acetone were used as competitors for hydroxyl radical and their molar concentrations were calculated based on their reaction constants with hydroxyl radical. The hydroxyl radical was not responsible for naphthalene loss in these experiments. The first-order-reaction rate constants in the batch experiments containing only naphthalene, 2 mM of each of acetone and d6-acetone were 0.93, 0.94 and $1.18 \times 10^{-1}\,h^{-1}$, respectively. Higher concentrations (4 mM) acetone and d6-acetone did not affect naphthalene degradation. Rate constants using methanol and d6-methanol as competitors for hydroxyl radical in batch degradations test were 1.28 and $0.99 \times 10^{-1}\,h^{-1}$, respectively. Based on the naphthalene degradation trends and reaction rate constants, it was concluded that under the given set of conditions, hydroxyl radical was not responsible for naphthalene degradation during electrolytic degradation tests. Li and Goel [158] concluded that the role of hydroxyl radical should be considered very carefully in modelling such indirect electrolytic oxidation processes.

8. Ozone assisted EC

It is well established that ozone can react in aqueous solution with various organic and inorganic compounds either by a direct ozone attack and/or indirect free radical reaction involving the hydroxyl radical ($^{\cdot}OH$, $O_2^{\cdot-}$ and $HO_2^{\cdot}$ [168]) induced by the ozone decomposition in water. These useful benefits of ozonation as an AOP have suggested several researchers such as Nielson and Smith [168], Song et al. [169], Hernández-Ortega et al. [170] and Asaithambi et al. [171] to add ozone to EC reactor as an electrochemical process. For example, Asaithambi et al. [171] investigated the hybrid technique of ozone assisted EC for the removal of colour and COD in the industrial effluent treatment. The synergistic effect of the combined process was tested with conventional processes of EC and ozonation. The results showed that the hybrid technique was more effective than EC and ozonation alone. The percentage COD removal increased from 45 to 92% with increase in current density from 100 to 500 A/m^2. The maximum removal of COD efficiency was found to be 83% at current density of 300 A/m^2, initial COD concentration 2,500 mg/L, initial pH 6 and ozone gas mixture flow rate 15 L/min requiring an energy consumption of 5.1 kWh/m^3. The complete colour removal was observed within 2 h of process time in all experimental conditions.

On the other hand, He et al. [172] studied the use of a combination of EC and ozonation for the decolorisation of the azo dye, C.I. Reactive Yellow 84 (RY84). They showed that a synergistic effect was achieved by combining EC with ozone for the decolorisation of RY84. Under the experimental conditions, the decolorisation rate increased with an increase in current density. However, the decolorisation rate decreased with an increase in initial dye concentration and salt concentration. The interelectrode distance did not substantially affect the decolorisation rate. Other operating parameters such as initial pH, ozone flow rate and temperature had both positive and negative effects. Over 97% of the colour decay was achieved within 10 min reaction time under reasonable experimental conditions. When the decolorisation of RY84 was complete, the efficiency of removal of total organic carbon was more than 85%.

9. Future tendencies of EC process

Electrochemical processes, particularly EC, remain promising technologies for water and wastewater treatment [172–174]. To increase the EC efficiency, there is a new tendency of using EC process simultaneously with electro-oxidation in the same device [175]. This tendency was recently lead by some researchers such as Mahvi et al. [175] and Cotillas et al. [176]. Indeed, Cotillas et al. [176] described a novel integrated electrochemical process for urban wastewater regeneration. The electrochemical cell consists of BDD or dimensionally stable anode (DSA) as anode, stainless steel as cathode and perforated aluminium plate which behaves as a bipolar electrode between anode and cathode. Thus, in this cell, it is possible to carry out, at the same time, two different electrochemical processes: electrodisinfection and EC. The treatment of urban wastewater with different anodes and different operating conditions is studied. First of all, in order to check the process performance, these authors carried out experiments with synthetic wastewaters showing that it is possible to achieve 100% of turbidity removal by the electrodissolution of the bipolar electrode. Next, they studied the effect of the current density and the anode material during the electrodisinfection–EC process of actual effluents. Their results show that it is possible to remove *Escherichia coli* (*E. coli*) and turbidity simultaneously of an actual effluent from a wastewater treatment plant. The use of BDD anodes allows removing *E. coli* completely at an applied electric charge of 7.7 Ah/m^3 when working with a current density of 6.65 A/m^2. On the other hand, with DSA anodes, the current density necessary to achieve the total removal of *E. coli* is higher (11.12 A/m^2) than that required with BDD anodes [176].

However, the main question which may be addressed here is about the dominating mechanism in this highly efficient cell, i.e. AOP phenomena (mainly hydroxyl radicals' formation) presence vs. EC phenomena (adsorption/charge neutralisation and *sweep* coagulation) presence, even if Mahvi et al. [175] and Cotillas et al. [176] have not discussed the hydroxyl radicals formation in their set-ups. What is sure here is the fact that the simultaneous combination of electro-oxidation and EC in the same device would be promising new process for large applications in wastewater treatment industry.

10. Conclusions

This review tried to discuss the presence of the AOP phenomena in EC process. After a large research in the related literature, there is no proof, at least until now, of the presence of AOP phenomena in EC process. However,

(1) To get more probabilities to have free radicals formation in EC, ultrasound acting during EC may be very useful as discussed by some researchers.
(2) We have proposed the modified *Mechanism 1* which takes into consideration, the hydroxyl radical formation probability during EC process at pH 2.8.

Finally, this review concludes that there is no proof of the presence of AOP phenomena in the EC process and more research is needed here focusing on free radicals formation.

References

[1] D. Ghernaout, M.W. Naceur, A. Aouabed, On the dependence of chlorine by-products generated species formation of the electrode material and applied charge during electrochemical water treatment, Desalination 270 (2011) 9–22.

[2] D. Ghernaout, B. Ghernaout, M.W. Naceur, Embodying the chemical water treatment in the green chemistry—A review, Desalination 271 (2011) 1–10.

[3] (a) D. Ghernaout, B. Ghernaout, A. Boucherit, M.W. Naceur, A. Khelifa, A. Kellil, Study on mechanism of electrocoagulation with iron electrodes in idealised conditions and electrocoagulation of humic acids solution in batch using aluminium electrodes, Desalin. Water Treat. 8 (2009) 91–99; (b) S. Vasudevan, J. Lakshmi, G. Sozhan, Studies on the removal of arsenate from water through electrocoagulation using direct and alternating current, Desalin. Water Treat. 48 (2012) 163–173.

[4] M.M. Naim, A.A. Moneer, G.F. El Said, Defluoridation of commercial and analar sodium fluoride solutions without using additives by batch electrocoagulation-flotation technique, Desalin. Water Treat. 44 (2012) 110–117.

[5] M. Kobya, E. Demirbas, O. Sahin, Effect of operational parameters on the removal of phenol from aqueous solutions by electrocoagulation using Fe and Al electrodes, Desalin. Water Treat. 46 (2012) 366–374.

[6] N. Drouiche, H. Lounici, M. Drouiche, N. Mameri, N. Ghaffour, Removal of fluoride from photovoltaic wastewater by electrocoagulation and products characteristics, Desalin. Water Treat. 7 (2009) 236–241.

[7] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, HF wastewater remediation by electrocoagulation process, Desalin. Water Treat. 51 (2013) 1596–1602.

[8] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, J. Hazard. Mater. B84 (2001) 29–41.

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

[10] Y. Xu, J.-Q. Jiang, K. Quill, J. Simon, K. Shettle, Electrocoagulation: A new approach for the removal of boron containing wastes, Desalin. Water Treat. 2 (2009) 131–138.

[11] (a) J. Jeong, C. Kim, J. Yoon, The effect of electrode material on the generation of oxidants and microbial inactivation in the electrochemical disinfection processes, Water Res. 43 (2009) 895–901; (b) D. Haaken, T. Dittmar, V. Schmalz, E. Worch, Influence of operating conditions and wastewater-specific parameters on the electrochemical bulk disinfection of biologically treated sewage at boron-doped diamond (BDD) electrodes, Desalin. Water Treat. 46 (2012) 160–167.

[12] K. Nielson, D.W. Smith, Ozone-enhanced electroflocculation in municipal wastewater treatment, J. Environ. Eng. Sci. 4 (2005) 65–76.

[13] (a) D. Ghernaout, B. Ghernaout, A. Boucherit, Effect of pH on electrocoagulation of bentonite suspensions in batch using iron electrodes, J. Disp. Sci. Technol. 29 (2008) 1272–1275; (b) D.S. Filho, G.B. Bota, R.B. Borri, F.J.C. Teran, Eletrocoagulation/flotation followed by fluidized bed anaerobic reactor applied to tannery effluent treatment, Desalin. Water Treat. 37 (2012) 359–363.

[14] A. Saiba, S. Kourdali, B. Ghernaout, D. Ghernaout, In *Desalination*, from 1987 to 2009, the birth of a new seawater pretreatment process: Electrocoagulation—an overview, Desalin. Water Treat. 16 (2010) 201–217.

[15] D. Ghernaout, B. Ghernaout, From chemical disinfection to electrodisinfection: The obligatory itinerary? Desalin. Water Treat. 16 (2010) 156–175.

[16] (a) D. Belhout, D. Ghernaout, S. Djezzar-Douakh, A. Kellil, Electrocoagulation of a raw water of Ghrib Dam (Algeria) in batch using aluminium and iron electrodes, Desalin. Water Treat. 16 (2010) 1–9; (b) H. Wang, J.-Q. Jiang, R. Xu, F. Li, Treatment of landscape water (LSW) by electrocoagulation process, Desalin. Water Treat. 37 (2012) 62–68.

[17] G. Sharma, H.K. Shon, S. Phuntsho, Electrocoagulation and crossflow microfiltration hybrid system: Fouling investigation, Desalin. Water Treat. 43 (2012) 253–259.

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

[19] D. Ghernaout, A. Mariche, B. Ghernaout, A. Kellil, Electromagnetic treatment-doubled electrocoagulation of humic acid in continuous mode using response surface method for its optimisation and application on two surface waters, Desalin. Water Treat. 22 (2010) 311–329.

[20] D. Ghernaout, B. Ghernaout, A. Saiba, A. Boucherit, A. Kellil, Removal of humic acids by continuous electromagnetic treatment followed by electrocoagulation in batch using aluminium electrodes, Desalination 239 (2009) 295–308.

[21] (a) J.K. Edzwald, Dissolved air flotation and me, Water Res. 44 (2010) 2077–2106; (b) D. Ghernaout, B. Ghernaout, A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation, Desalin. Water Treat. 2 (2009) 203–222.

[22] (a) D. Ryan, A. Gadd, J. Kavanagh, M. Zhou, G. Barton, A comparison of coagulant dosing options for the remediation of molasses process water, Sep. Purif. Technol. 58 (2008) 347–352; (b) B. Bazrafkan, Q. Wei, R. Fabris, C.W.K. Chow, J. van Leeuwen, D. Wang, M. Drikas, Assessment of a new combined fractionation technique for characterization of the natural organic matter in the coagulation process, Desalin. Water Treat. 48 (2012) 252–260.

[23] V.K. Kovatcheva, M.D. Parlapanski, Sono-electrocoagulation of iron hydroxides, Colloids Surf. A 149 (1999) 603–608.

[24] A. Gürses, M. Yalçin, C. Doğar, Electrocoagulation of some reactive dyes: A statistical investigation of some electrochemical variables, Waste Manage. 22 (2002) 491–499.

[25] M. Ahmadi, H. Amiri, S.S. Martinez, Treatment of phenol–formaldehyde resin manufacturing wastewater by the electrocoagulation process, Desalin. Water Treat. 39 (2012) 176–181.

[26] X. Chen, G. Chen, P.L. Yue, Investigation on the electrolysis voltage of electrocoagulation, Chem. Eng. Sci. 57 (2002) 2449–2455.

[27] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminium electrodes, Ind. Eng. Chem. Res. 42 (2003) 3391–3396.

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

[29] P.K. Holt, G.W. Barton, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A 211 (2002) 233–248.

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

[31] N. Bektaş, H. Akbulut, H. Inan, A. Dimoglo, Removal of phosphate from aqueous solutions by electrocoagulation, J. Hazard. Mater. B106 (2004) 101–105.

[32] S.-H. Shin, Y.-H. Kim, S.-K. Jung, K.-H. Suh, S.-G. Kang, S.-K. Jeong, H.-G. Kim, Combined performance of electrocoagulation and magnetic separation processes for treatment of dye wastewater, Korean J. Chem. Eng. 4 (2004) 806–810.

[33] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, Removal of fluoride from semiconductor wastewater by electrocoagulation–flotation, Water Res. 39 (2005) 895–901.

[34] V. Kovacheva-Ninova, Electrochemical treatment of mine wastewaters containing heavy metal ions, Annu. Min. Miner. Process. (Part II), Sofia (Bulgaria) 46 (2003) 215–220.

[35] J.G. Ibáñez, M.M. Singh, Z. Szafran, Laboratory experiments on electrochemical remediation of the environment. Part 4: Color removal of simulated wastewater by electrocoagulation-electroflotation, J. Chem. Educ. 8 (1998) 1040–1041.

[36] A.S. Koparal, U.B. Öğütveren, Removal of nitrate from water by electroreduction and electrocoagulation, J. Hazard. Mater. B89 (2002) 83–94.

[37] N. Daneshvar, H. Ashassi-Sorkhabi, M.B. Kasiri, Decolorization of dye solution containing Acid Red 14 by EC with a comparative investigation of different electrode connections, J. Hazard. Mater. B112 (2004) 55–62.

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

[39] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile wastewater, Sep. Purif. Technol. 37 (2004) 117–125.

[40] E.J. Ruiz, C. Arias, E. Brillas, A. Hernández-Ramírez, J.M. Peralta-Hernández, Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photoelectro-Fenton processes with a boron-doped diamond anode, Chemosphere 82 (2011) 495–501.

[41] (a) E. Brillas, I. Sirés, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev. 109 (2009) 6570–6631; (b) T. Methatham, M.-C. Lu, C. Ratanatamskul, Removal of 2,4-dichlorophenol as herbicide's by-product by Fenton's reagent combined with an electrochemical system, Desalin. Water Treat. 32 (2011) 42–48.

[42] C.A. Martínez-Huitle, E. Brillas, Electrochemical alternatives for drinking water disinfection, Angew. Chem. Int. Ed. 47 (2008) 1998–2005.

[43] C.A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. A general review, Appl. Catal. B-Environ. 87 (2009) 105–145.

[44] (a) V.K. Sharma, Oxidation of inorganic contaminants by ferrates (VI, V, and IV)-kinetics and mechanisms: A review, J. Environ. Manag. 92 (2011) 1051–1073; (b) V.K. Sharma, Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism, Coord. Chem. Rev. 257 (2013) 495–510; (c) V.K. Sharma, M. Sohn, G.A.K. Anquandah, N. Nesnas, Kinetics of the oxidation of sucralose and related carbohydrates by ferrate(VI), Chemosphere 87 (2012) 644–648; (d) V.K. Sharma, G.W. Luther, F.J. Millero, Mechanisms of oxidation of organosulfur compounds by ferrate (VI), Chemosphere 82 (2011) 1083–1089; (e) Z. Luo, M. Strouse, J.-Q. Jiang, V.K. Sharma, Methodologies for the analytical determination of ferrate(VI): A review, J. Environ. Sci. Health—Part A Toxic/Hazard. Subst. Environ. Eng. 46 (2011) 453–460; (f) V.K. Sharma, Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: A review, J. Environ. Sci. Health—Part A Toxic/Hazard. Subst. Environ. Eng. 45 (2010) 645–667.

[45] E. Guivarch, S. Trevin, C. Lahitte, M.A. Oturan, Degradation of azo dyes in water by electro-Fenton process, Environ. Chem. Lett. 1 (2003) 38–44.

[46] A. Kraft, M. Stadelmann, M. Blaschke, Anodic oxidation with doped diamond electrodes: A new advanced oxidation process, J. Hazard. Mater. B103 (2003) 247–261.

[47] J.M. Peralta-Hernández, Y. Meas-Vong, F.J. Rodríguez, T.W. Chapman, M.I. Maldonado, L.A. Godínez, *In situ* electrochemical and photo-electrochemical generation of the Fenton reagent: A potentially important new water treatment technology, Water Res. 40 (2006) 1754–1762.

[48] J.M. Peralta-Hernández, Y. Meas-Vong, F.J. Rodríguez, T.W. Chapman, M.I. Maldonado, L.A. Godínez, Comparison of hydrogen peroxide-based processes for treating dye-containing wastewater: Decolorization and destruction of Orange II azo dye in dilute solution, Dyes Pigm. 76 (2008) 656–662.

[49] I. Sirés, N. Oturan, E. Guivarch, M.A. Oturan, Efficient removal of triphenylmethane dyes from aqueous medium by in-situ electrogenerated Fenton's reagent at carbon-felt cathode, Chemosphere 72 (2008) 592–600.

[50] A. Wang, J. Qu, H. Liu, J. Ru, Mineralization of an azo dye Acid Red 14 by photoelectro-Fenton process using an activated carbon fiber cathode, Appl. Catal. B-Environ. 84 (2008) 393–399.

[51] A. Özcan, Y. Şahin, A.S. Koparal, M.A. Oturan, Carbon sponge as a new cathode material for the electro-Fenton process. Comparison with carbon felt cathode and application to degradation of synthetic dye Basic Blue 3 in aqueous medium, J. Electroanal. Chem. 616 (2008) 71–78.

[52] A. Özcan, M.A. Oturan, N. Oturan, Y.S. Ahina, Removal of Acid Orange 7 from water by electrochemically generated Fenton's reagent, J. Hazard. Mater. 163 (2009) 1213–1220.

[53] E. Brillas, M.A. Baños, J.A. Garrido, Mineralization of herbicide 3,6-dichloro-2 methoxybenzoic acid in aqueous medium by anodic oxidation, electro-Fenton and photoelectro-Fenton, Electrochim. Acta 48 (2003) 1697–1705.

[54] M. Diagne, N. Oturan, M.A. Oturan, Removal of methyl parathion from water by electrochemically generated Fenton's reagent, Chemosphere 66 (2007) 841–848.

[55] E. Guinea, C. Arias, P.L. Cabot, J.A. Garrido, R.M. Rodríguez, F. Centellas, E. Brillas, Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide, Water Res. 42 (2008) 499–511.

[56] M. Skoumal, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, E. Brillas, Mineralization of the biocide chloroxylenol by electrochemical advanced oxidation processes, Chemosphere 71 (2008) 1718–1729.

[57] M. Skoumal, R.M. Rodríguez, P.L. Cabot, F. Centellas, J.A. Garrido, C. Arias, E. Brillas, Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton degradation of the drug ibuprofen in acid aqueous medium using platinum and boron-doped diamond anodes, Electrochim. Acta 54 (2009) 2077–2085.

[58] E. Brillas, M.A. Baños, S. Campos, C. Arias, P.L. Cabot, J.A. Garrido, R.M. Rodríguez, Catalytic effect of Fe^{2+}, Cu^{2+} and UVA light on the electrochemical degradation of nitrobenzene using an oxygen-diffusion cathode, New J. Chem. 28 (2004) 314–322.

[59] C. Flox, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, E. Brillas, Solar photoelectro-Fenton degradation of cresols using a flow reactor with a boron-doped diamond anode, Appl. Catal. B-Environ. 75 (2007) 17–28.

[60] M.A. Oturan, M. Pimentel, N. Oturan, I. Sirés, Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during electrochemical Fenton treatment, Electrochim. Acta 54 (2008) 173–182.

[61] P.J. Delphos, G.M. Wesner, Mixing, coagulation, and flocculation, in: E.E. Baruth (Tech. Ed.), Water Treatment Plant Design, fourth ed., American Water Works Association, American Society of Civil Engineers, McGraw-Hill, New York, NY, 2005 (Chapter 6), pp. 6.1–6.25.

[62] W.W. Eckenfelder Jr., Industrial Water Pollution Control, third ed., McGraw-Hill, New York, NY, 2000.

[63] G. Tchobanoglous, F.L. Burton, H.D. Stensel, Wastewater Engineering, Treatment and Reuse, fourth ed., Metcalf & Eddy, McGraw-Hill, New York, NY, 2003.

[64] J.F. Richardson, J.H. Harker, J.R. Backhurst, Particulate solids, in: J.F. Richardson, J.H. Harker, J.R. Backhurst (Eds.), Coulson and Richardson's Chemical Engineering, Particle Technology and Separation Processes, vol. 2, fifth ed., Butterworth-Heinemann, Oxford, 2002, (chapter 1), pp. 1–94

[65] A. Rushton, A.S. Ward, R.G. Holdich, Solid-Liquid Filtration and Separation Technology, VCH Verlagsgesellschaft mbH, Weinheim, 1996.

[66] P.H. Jones, M.A. Tompeck, Water treatment, in: J.R. Pfafflin, E.N. Ziegler (Eds.), Encyclopedia of Environmental Science and Engineering, fifth ed., CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006, pp. 1311–1328.

[67] R.D. Letterman, A. Amirtharajah, C.R. O'Melia, Coagulation and flocculation, in: R.D. Letterman (Tech. Ed.), Water Quality and Treatment, a Handbook of Community Water Supplies, fifth ed., American Water Works Association, McGraw-Hill, New York, NY, 1999 (Chapter 6), pp. 6.1–6.66.

[68] R. Beckett, J. Ranville, Natural organic matter, in: G. Newcombe, D. Dixon (Eds.), Interface Science in Drinking Water Treatment, Theory and Applications, vol. 10, in: A. Hubbard (Series Ed.) Interface Science and Technology, Academic Press, Elsevier, Amsterdam, 2006 (Chapter 17), pp. 299–315.

[69] (a) V.K. Sharma, Kinetics and mechanism of formation and destruction of *N*-nitrosodimethylamine in water—a review, Sep. Purif. Technol. 88 (2012) 1–10; (b) E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, Impact of fractional character on the coagulation of NOM, Colloids Surf. A 286 (2006) 104–111.

[70] J.E. Van Benschoten, J.K. Edzwald, Chemical aspects of coagulation using aluminium salts-I. Hydrolytic reactions of alum and polyaluminum chloride, Water Res. 24 (1990) 1519–1526.

[71] J.E. Van Benschoten, J.K. Edzwald, Chemical aspects of coagulation using aluminium salts-II. Coagulation of fulvic acid using alum and polyaluminum chloride, Water Res. 24 (1990) 1527–1535.

[72] A.I. Schäfer, Natural Organics Removal Using Membranes, Principles, Performance and Cost, Technomic, Lancaster, PA, 2001.

[73] W. Lick, Sediment and Contaminant Transport in Surface Waters, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2009.

[74] J.G. Farmer, M.C. Graham, Freshwaters, in: R.M. Harrison (Ed.), Understanding our Environment, an Introduction to Environmental Chemistry and Pollution, third ed., Royal Society of Chemistry, Cambridge, 1999 (Chapter 3), pp. 71–138.

[75] J.A. Salvato Jr., Environmental health, in: J.R. Pfafflin, E.N. Ziegler (Eds.), Encyclopedia of Environmental Science and Engineering, fifth ed., CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006, pp. 334–360.

[76] B.A. Dempsey, Coagulant characteristics and reactions, in: G. Newcombe, D. Dixon (Eds.), Interface Science in Drinking Water Treatment, Theory and Applications, vol. 10, in: A. Hubbard (Series Ed.), Interface Science and Technology, Academic Press, Elsevier, Amsterdam, 2006 (Chapter 2), pp. 5–25.

[77] H.L. Shorney, Disinfection by-product precursor removal by enhanced softening and coagulation, PhD thesis, University of Kansas, 1998.

[78] Y.F. Xie, Disinfection by-Products in Drinking Water: Formation, Analysis, and Control, Lewis, Taylor & Francis e-Library, Boca Raton, FL, 2005.

[79] S. Hong, S. Kim, C. Bae, Efficiency of enhanced coagulation for removal of NOM and for adsorbability of NOM on GAC, Desalin. Water Treat. 2 (2009) 89–94.

[80] A. Aryal, A. Sathasivan, W. Zhan, Effect of suspended solids in secondary wastewater effluent on DOC removal by enhanced coagulation, Desalin. Water Treat. 32 (2011) 27–32.

[81] P. Baham, J.R. Pfafflin, Effects of chemicals, in: J.R. Pfafflin, E.N. Ziegler (Eds.), Encyclopedia of Environmental Science and Engineering, fifth ed., CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006, pp. 271–281.

[82] G. Lagaly, From clay mineral crystals to colloidal clay mineral dispersions, in: H. Stechemesser, B. Dobiáš (Eds.), Coagulation and Flocculation, second ed., Taylor & Francis Group, Boca Raton, FL, 2005 (Chapter 8), pp. 519–600.

[83] B.A. Bolto, Coagulation and flocculation with organic polyelectrolytes, in: G. Newcombe, D. Dixon (Eds.), Interface Science in Drinking Water Treatment, Theory and Applications, vol. 10, in: A. Hubbard (Series Ed.) Interface Science and Technology, Academic Press, Elsevier, Amsterdam, 2006 (Chapter 5), pp. 63–88.

[84] A. Anzalone, J.K. Bewtra, H.I. Ali, Physical and chemical treatment of wastewaters, in: J.R. Pfafflin, E.N. Ziegler (Eds.), Encyclopedia of Environmental Science and Engineering, fifth ed., CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006, pp. 972–989.

[85] (a) J.K. Edzwald, J. Haarhoff, Seawater pretreatment for reverse osmosis: Chemistry, contaminants, and coagulation, Water Res. 45 (2011) 5428–5440; (b) S.G.S. Rodriguez, M.D. Kennedy, J.C. Schippers, G. Amy, Organic foulants in estuarine and bay sources for seawater reverse osmosis—comparing pre-treatment processes with respect to foulant reductions, Desalin. Water Treat. 9 (2009) 155–164; (c) K.O. Nowack, F.S. Cannon, Ferric chloride plus GAC for removing TOC, in: Proceedings of the AWWA Water Quality Technology Conference, November 17–21, Boston, MA, 1996.

[86] M.R. Wiesner, M.M. Clark, J. Mallevialle, Membrane filtration of coagulated suspensions, J. Environ. Eng., ASCE 115 (1989) 20–40.

[87] J.F. Atkinson, R.K. Chakraborti, J.E. Van Benschoten, Effects of floc size and shape in particle aggregation, in: I.G. Droppo, G.G. Leppard, S.N. Liss, T.G. Milligan (Eds.), Flocculation in Natural and Engineered Environmental Systems, CRC Press, Boca Raton, FL, 2005 (Chapter 5), pp. 95–120.

[88] J. Gregory, Floc formation and floc structure, in: G. Newcombe, D. Dixon (Eds.), Interface Science in Drinking Water Treatment, Theory and Applications, vol. 10, in: A. Hubbard (Series Ed.) Interface Science and Technology, Academic Press, Elsevier, Amsterdam, 2006 (Chapter 3), pp. 25–43.

[89] N.K. Shammas, Coagulation and flocculation, in: L.K. Wang, Y.-T. Hung, N.K. Shammas (Eds.), Handbook of Environmental Engineering, Physicochemical Treatment Processes, vol. 3, The Humana Press, Totowa, NJ, 2005 (Chapter 4), pp. 103–139.

[90] F. Woodard, Industrial Waste Treatment Handbook, Butterworth–Heinemann, Boston, MA, 2001.

[91] C.N. Sawyer, P.L. McCarty, G.E. Parkin, Chemistry for Environmental Engineering, fourth ed., McGraw-Hill, New York, NY, 1994.

[92] (a) J.K. Edzwald, J.E. Tobiason, Enhanced coagulation: USA requirements and a broader view, Water Sci. Technol. 40 (1999) 63–70; (b) R.M. Pashley, M.E. Karaman, Applied Colloid and Surface Chemistry, John Wiley & Sons, New York, NY, 2004.

[93] T.D. Reynolds, Unit Operations and Processes in Environmental Engineering, Brooks/Cole Engineering Division, Monterey, CA, 1982.

[94] R.F.V. Romo, M.M. Pitts, Application of electrotechnology for removal and prevention of reverse osmosis biofouling, Environ. Progress 18 (1999) 107–112.

[95] J.H. Masliyah, S. Bhattacharjee, Electrokinetic and Colloid Transport Phenomena, John Wiley & Sons, Hoboken, NJ, 2006.

[96] H.S. Weinberg, V.J. Pereira, Z. Ye, Drugs in drinking water treatment options, in: D.S. Aga (Ed.), Fate of Pharmaceuticals in the Environment and in Water Treatment Systems, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2008 (Chapter 10), pp. 217–228.

[97] P. Jarvis, B. Jefferson, J. Gregory, S.A. Parsons, A review of floc strength and breakage, Water Res. 39 (2005) 3121–3137.

[98] K.J. Wilkinson, A. Reinhardt, Contrasting roles of natural organic matter on colloidal stabilization and flocculation in freshwaters, in: I.G. Droppo, G.G. Leppard, S.N. Liss, T.G. Milligan (Eds.), Flocculation in Natural and Engineered Environmental Systems, CRC Press, Boca Raton, FL, 2005 (Chapter 7), pp. 143–170.

[99] M.G. Kılıç, Ç. Hoşten, A comparative study of electrocoagulation and coagulation of aqueous suspensions of kaolinite powders, J. Hazard. Mater. 176 (2010) 735–740.

[100] E.J.W. Verwey, J.Th.G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, New York, NY, 1948.

[101] C.R. O'Melia, Fundamentals of particle stability, in: G. Newcombe, D. Dixon (Eds.), Interface Science in Drinking Water Treatment, Theory and Applications, vol. 10, in: A. Hubbard (Series Ed.), Interface Science and Technology, Academic Press, Elsevier, Amsterdam, 2006 (Chapter 18), pp. 317–362.

[102] D.J. Shaw, Introduction to Colloid and Surface Chemistry, fourth ed., Butterworth-Heinemann, Oxford, 1992.

[103] D.N. Thomas, S.J. Judd, N. Fawcett, Flocculation modelling: A review, Water Res. 33 (1999) 1579–1592.

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

[105] W.P. Cheng, Y.P. Kao, R.F. Yu, A novel method for on-line evaluation of floc size in coagulation process, Water Res. 42 (2008) 2691–2697.

[106] S.N. Liss, T.G. Milligan, I.G. Droppo, G.G. Leppard, Methods for analyzing floc properties, in: I.G. Droppo, G.G. Leppard, S.N. Liss, T.G. Milligan (Eds.), Flocculation in Natural and Engineered Environmental Systems, CRC Press, Boca Raton, FL, 2005 (Chapter 1), pp. 1–21.

[107] T. Beveridge, Large-scale centrifugation, In: I.D. Wilson, E.R. Adlard, M. Cooke, C.F. Poole (Eds), Encyclopedia of Separation Science, Academic Press, Chester, 2000.

[108] D. Ghernaout, B. Ghernaout, Sweep flocculation as a second form of charge neutralisation—a review, Desalin. Water Treat. 44 (2012) 15–28.

[109] V.G. Sister, E.V. Kirshankova, Ultrasonic techniques in removing surfactants from effluents by electrocoagulation, Chem. Pet. Eng. 41 (2005) 553–556.

[110] J.P. Chen, S.-Y. Chang, Y.-T. Hung, Electrolysis, in: L.K. Wang, Y.-T. Hung, N.K. Shammas (Eds.), Handbook of Environmental Engineering, Physicochemical Treatment Processes, vol. 3, The Humana Press, Totowa, NJ, 2005 (Chapter 10), pp. 359–378.

[111] O. Simond, V. Schaller, Ch. Comninellis, Theoretical model for the anodic oxidation of organics on metal electrodes, Electrochim. Acta 42 (1997) 2009–2012.

[112] O. Simond, Ch. Comninellis, Anodic oxidation of organics on Ti/IrO$_2$ anodes using Nafion® as electrolyte, Electrochim. Acta 42 (1997) 2013–2018.

[113] Ö. Apaydin, U. Kurt, M.T. Gönüllü, An investigation on the treatment of tannery wastewater by electrocoagulation, Global NEST J. 11 (2009) 546–555.

[114] W.-L. Chou, C.-T. Wang, K.-Y. Huang, Investigation of process parameters for the removal of polyvinyl alcohol from aqueous solution by iron electrocoagulation, Desalination 251 (2010) 12–19.

[115] J.H. Cho, J.E. Lee, C.S. Ra, Effects of electric voltage and sodium chloride level on electrolysis of swine wastewater, J. Hazard. Mater. 180 (2010) 535–541.

[116] C. Tsouris, V.M. Shah, K.D. Blankenship, D.W. DePaoli, J. Dong, M.Z.-C. Hu, S.Z. Yiacoumi, W.-T. Shin, T.-Y. Ying, K.-L. Yang, Phase equilibria modification by electric fields, Final report, US Department of Energy, Project number: 55119, Grant number: DE-FG07-96ER55119, 2000.

[117] (a) T. Blume, I. Martínez, U. Neis, Wastewater disinfection using ultrasound and UV light, in: U. Neis (Ed.), Ultrasound in Environmental Engineering II, TU Hamburg-Harburg Reports on Sanitary Engineering, vol. 35, 2002, pp. 117–128; (b) G.Y. Chai, B. Cao, G.Y. Zhao, A.R. Greenberg, W.B. Krantz, Effects of concentration polarization, temperature and pressure on ultrasound detection of inorganic fouling and cleaning in a spiral-wound membrane module, Desalin. Water Treat. 50 (2012) 411–422.

[118] (a) V. Naddeo, V. Belgiorno, R.M. A. Napoli, Behaviour of natural organic matter during ultrasonic irradiation, Desalination 210 (2007) 175–182; (b) M.-W. Wan, L.C.C. Biel, M.-C. Lu, R. de Leon, S. Arco, Ultrasound-assisted oxidative desulfurization (UAOD) using phosphotungstic acid: Effect of process parameters on sulfur removal, Desalin. Water Treat. 47 (2012) 96–104.

[119] (a) M. Landi, V. Naddeo, V. Belgiorno, Influence of ultrasound on phenol removal by adsorption on granular activated carbon, Desalin. Water Treat. 23 (2010) 181–186; (b) M.A. Oturan, E. Brillas, Electrochemical advanced oxidation processes (EAOPs) for environmental applications, Portugaliae Electrochim. Acta 25 (2007) 1–18.

[120] J. Madhavan, F. Grieser, M. Ashokkumar, Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments, J. Hazard. Mater. 178 (2010) 202–208.

[121] A. Sánchez-Carretero, M.A. Rodrigo, P. Cañizares, C. Sáez, Electrochemical synthesis of ferrate in presence of ultrasound using boron doped diamond anodes, Electrochem. Commun. 12 (2010) 644–646.

[122] D. Voglar, D. Lestan, Electrochemical separation and reuse of EDTA after extraction of Cu contaminated soil, J. Hazard. Mater. 180 (2010) 152–157.

[123] C. Durante, M. Cuscov, A.A. Isse, G. Sandonà, A. Gennaro, Advanced oxidation processes coupled with electrocoagulation for the exhaustive abatement of Cr-EDTA, Water Res. 45 (2011) 2122–2130.

[124] I. Linares-Hernández, C. Barrera-Díaz, B. Bilyeu, P. Juárez-GarcíaRojas, E. Campos-Medina, A combined electrocoagulation–electrooxidation treatment for industrial wastewater, J. Hazard. Mater. 175 (2010) 688–694.

[125] M. Panizza, G. Cerisola, Applicability of electrochemical methods to carwash wastewaters for reuse. Part 2: Electrocoagulation and anodic oxidation integrated process, J. Electroanal. Chem. 638 (2010) 236–240.

[126] J.R. Parga, G. González, H. Moreno, J.L. Valenzuela, Thermodynamic studies of the strontium adsorption on iron species generated by electrocoagulation, Desalin. Water Treat. 37 (2012) 244–252.

[127] X. Zhao, B. Zhang, H. Liu, J. Qu, Removal of arsenite by simultaneous electro-oxidation and electro-coagulation process, J. Hazard. Mater. 184 (2010) 472–476.

[128] G. Chen, Y.T. Hung, Electrochemical wastewater treatment processes, in: L.K. Wang, Y.-T. Hung, N.K. Shammas (Eds.), Handbook of Environmental Engineering, Advanced Physicochemical Treatment Technologies, vol. 5, The Humana Press, Totowa, NJ, 2007 (Chapter 2), pp. 57–106.

[129] B. Boye, M.M. Dieng, E. Brillas, Anodic oxidation, electro-Fenton and photoelectro-Fenton treatments of 2,4,5-trichlorophenoxyacetic acid, J. Electroanal. Chem. 557 (2003) 135–146.

[130] Z. Qiang, J.H. Chang, C.P. Huang, Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions, Water Res. 36 (2002) 85–94.

[131] F. Al Momani, C. Sans, S. Esplugas, A comparative study of the advanced oxidation of 2,4-dichlorophenol, J. Hazard. Mater. B107 (2004) 123–129.

[132] J.M. Friedrich, C. Ponce-de-León, G.W. Reade, F.C. Walsh, Reticulated vitreous carbon as an electrode material, J. Electroanal. Chem. 561 (2004) 203–217.

[133] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allah, Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination 194 (2006) 166–175.

[134] Q. Wang, A.T. Lemley, Oxidation of diazinon by anodic Fenton treatment, Water Res. 36 (2002) 3237–3244.

[135] S. Hong, H. Zhang, C.M. Duttweiler, A.T. Lemley, Degradation of methyl *tertiary*-butyl ether (MTBE) by anodic Fenton treatment, J. Hazard. Mater. 144 (2007) 29–40.

[136] H.S. El-Desoky, M.M. Ghoneim, N.M. Zidan, Decolorization and degradation of Ponceau S azo-dye in aqueous solutions by the electrochemical advanced Fenton oxidation, Desalination 264 (2010) 143–150.

[137] Y. Sun, J.J. Pignatello, Photochemical reactions involved in the total mineralization of 2,4-D by iron(3+)/H_2O_2/UV, Environ. Sci. Technol. 27 (1993) 304–310.

[138] W. Chu, C.Y. Kwan, K.H. Chan, C. Chong, An unconventional approach to studying the reaction kinetics of the Fenton's oxidation of 2,4-dichlorophenoxyacetic acid, Chemosphere 57 (2004) 1165–1171.

[139] S.-S. Kim, J.-H. Kim, S.-J. Han, Application of the electrokinetic-Fenton process for the remediation of kaolinite contaminated with phenanthrene, J. Hazard. Mater. B118 (2005) 121–131.

[140] (a) Y. Zhong, X. Jin, R. Qiao, X. Qi, Y. Zhuang, Destruction of microcystin-RR by Fenton oxidation, J. Hazard. Mater. 167 (2009) 1114–1118; (b) N. K. Daud, U.G. Akpan, B.H. Hameed, Decolorization of sunzol black DN conc. in aqueous solution by Fenton oxidation process, effect of system parameters and kinetic study, Desalin. Water Treat. 37 (2012) 1–7.

[141] N. Modirshahla, M.A. Behnajady, F. Ghanbary, Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes, Dyes Pigm. 73 (2007) 305–310.

[142] S.S. Vaghela, A.D. Jethva, B.B. Metha, S.P. Dave, S. Adimurthy, G. Ramachandraiah, Laboratory studies of electrochemical treatment of industrial azo dye effluent, Environ. Sci. Technol. 39 (2005) 2848–2855.

[143] (a) B. Marselli, J. García-Gomez, P.A. Michaud, M.A. Rodrigo, Ch. Comninellis, Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes, J. Electrochem. Soc. 150 (2003) D79–D83; (b) S. Hammami, M.A. Oturan, N. Oturan, N. Bellakhal, M. Dachraoui, Comparative mineralization of textile dye indigo by photo-Fenton process and anodic oxidation using boron-doped diamond anode, Desalin. Water Treat. 45 (2012) 297–304.

[144] M. Panizza, G. Cerisola, Influence of anode material on the electrochemical oxidation of 2-naphthol. Part 2. Bulk electrolysis experiments, Electrochim. Acta 49 (2004) 3221–3226.

[145] M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, Electrochim. Acta 51 (2005) 191–199.

[146] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev. 109 (2009) 6541–6569.

[147] S.A.O. Galvão, A.L.N. Mota, D.N. Silva, J.E.F. Moraes, C.A. O. Nascimento, O. Chiavone-Filho, Application of the photo-Fenton process to the treatment of wastewaters contaminated with diesel, Sci. Total Environ. 367 (2006) 42–49.

[148] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends, Catal. Today 147 (2009) 1–59.

[149] (a) M.K. Ramseier, U. von Gunten, P. Freihofer, F. Hammes, Kinetics of membrane damage to high (HNA) and low (LNA) nucleic acid bacterial clusters in drinking water by ozone, chlorine, chlorine dioxide, monochloramine, ferrate (VI), and permanganate, Water Res. 45 (2011) 1490–1500; (b) V.K. Sharma, M. Sohn, G.A.K. Anquandah, N. Nesnas, Kinetics of the oxidation of sucralose and related carbohydrates by ferrate(VI), Chemosphere 87 (2012) 644–648; (c) G.A.K. Anquandah, V.K. Sharma, D.A. Knight, S.R. Batchu, P.R. Gardinali, Oxidation of trimethoprim by ferrate(VI): Kinetics, products, and antibacterial activity, Environ. Sci. Technol. 45 (2011) 10575–10581; (d) Z.-P. Wang, L.-Z. Huang, X.-N. Feng, P.-C. Xie, Z.-Z. Liu, Removal of phosphorus in municipal landfill leachate by photochemical oxidation combined with ferrate pre-treatment, Desalin. Water Treat. 22 (2010) 111–116; (e) P. Andrzejewski, J. Nawrocki, Mechanism of NDMA formation during ferrate or permanganate reactions with aqueous solutions of dimethylamine (DMA), Desalin. Water Treat. 23 (2010) 101–109.

[150] C.A. Murray, S.A. Parsons, Advanced oxidation processes: Flowsheet options for bulk natural organic matter removal, Water Sci. Technol.: Water Supply 4 (2004) 113–119.

[151] (a) J. Kim, I. Song, S. Lee, P. Kim, M. Lee, Y. Choung, Novel pilot plant-scale graywater treatment system using titanium ball, membrane and advanced oxidation process, Desalin. Water Treat. 10 (2009) 153–157; (b) W.K. Lafi, M. Al-Anber, Z.A. Al-Anber, M. Al-Shannag, A. Khalil, Coagulation and advanced oxidation processes in the treatment of olive mill wastewater (OMW), Desalin. Water Treat. 24 (2010) 251–256.

[152] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84.

[153] (a) E. Önder, A.S. Koparal, Ü.B. Öğütveren, An alternative method for the removal of surfactants from water: Electrochemical coagulation, Sep. Purif. Technol. 52 (2007) 527–532; (b) E. Yüksel, İ.A. Şengil, M. Özacar, The removal of sodium dodecyl sulfate in synthetic wastewater by peroxi-electrocoagulation method, Chem. Eng. J. 152 (2009) 347–353.

[154] G. Roa-Morales, E. Campos-Medina, J. Aguilera-Cotero, B. Bilyeu, C. Barrera-Díaz, Aluminum electrocoagulation with peroxide applied to wastewater from pasta and cookie processing, Sep. Purif. Technol. 54 (2007) 124–129.

[155] P.C. Singer, D.A. Reckhow, Chemical oxidation, in: R.D. Letterman (Ed.), A Handbook of Community Water Supplies, fifth ed., AWWA/McGraw-Hill, New York, NY, 1999 (Chapter 12), pp. 12.1–12.51.

[156] A.J. Bard, Standard Potential in Aqueous Solution, Marcel Decker, New York, NY, 1985, p. 63.

[157] (a) M. Ksibi, Chemical oxidation with hydrogen peroxide for domestic wastewater treatment, Chem. Eng. J. 119 (2006) 161–165; (b) T. Scheers, L. Appels, B. Dirkx, L. Jacoby, L. Van Vaeck, B. Van der Bruggen, J. Luyten, J. Degrève, J. Van Impe, R. Dewil, Evaluation of peroxide based advanced oxidation processes (AOPs) for the degradation of ibuprofen in water, Desalin. Water Treat. 50 (2012) 189–197.

[158] L. Li, R.K. Goel, Role of hydroxyl radical during electrolytic degradation of contaminants, J. Hazard. Mater. 181 (2010) 521–525.

[159] J. Grimm, D. Bessarabov, R. Sanderson, Review of electro-assisted methods for water purification, Desalination 115 (1998) 285–294.

[160] R. Goel, J. Flora, J. Ferry, Mechanisms for naphthalene removal during electrolytic aeration, Water Res. 37 (2003) 891–901.

[161] O.J. Murphy, G.D. Hitchens, L. Kaba, C.E. Verostko, Direct electrochemical oxidation of organics for wastewater treatment, Water Res. 26 (1992) 443–451.

[162] L. Li, Y. Liu, Ammonia removal in electrochemical oxidation: Mechanisms and pseudo kinetics, J. Hazard. Mater. 161 (2009) 1010–1016.

[163] R. Amadelli, L. Armelao, A.B. Velichenko, N.V. Nikolenko, D.V. Girenko, S.V. Kovalyov, F.I. Danilov, Oxygen and ozone evolution at fluoride modified lead dioxide electrodes, Electrochim. Acta 45 (1999) 713–720.

[164] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, Electrochim. Acta 39 (1994) 1857–1862.

[165] C.A. Basha, E. Chithra, N.K. Sripriyalakshmi, Electro-degradation and biological oxidation of non-biodegradable organic contaminants, Chem. Eng. J. 149 (2009) 25–34.

[166] R. Amadelli, A. De Battisti, D. Girenko, S. Kovalyov, A. Velichenko, Electrochemical oxidation of trans-3,4-dihydroxycinnamic acid at PbO_2 electrodes: Direct electrolysis and ozone mediated reactions compared, Electrochim. Acta 46 (2000) 341–347.

[167] (a) A.R. Khataee, V. Vatanpour, A.R.A. Ghadim, Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO_2, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: A comparative study, J. Hazard. Mater. 161 (2009) 1225–1233; (b) L. Mansouri, L. Bousselmi, Degradation of diethyl phthalate (DEP) in aqueous solution using TiO_2/UV process, Desalin. Water Treat. 40 (2012) 63–68.

[168] (a) K. Nielson, D.W. Smith, Ozone-enhanced electroflocculation in municipal wastewater treatment, J. Environ. Eng. Sci. 4 (2005) 65–76; (b) C.-H. Wu, C.-L. Chang, C.-Y. Kuo, Decolorization of Procion Red MX-5B in electrocoagulation (EC), UV/TiO_2 and ozone-related systems, Dyes Pigm. 76 (2008) 187–194.

[169] S. Song, Z. He, J. Qiu, L. Xu, J. Chen, Ozone assisted electrocoagulation for decolorization of C.I. Reactive Black 5 in aqueous solution: An investigation of the effect of operational parameters, Sep. Purifi. Technol. 55 (2007) 238–245.

[170] M. Hernández-Ortega, T. Ponziak, C. Barrera-Díaz, M.A. Rodrigo, G. Roa-Morales, B. Bilyeu, Use of a combined electrocoagulation–ozone process as a pre-treatment for industrial wastewater, Desalination 250 (2010) 144–149.

[171] P. Asaithambi, M. Susree, R. Saravanathamizhan, M. Matheswaran, Ozone assisted electrocoagulation for the treatment of distillery effluent, Desalination 297 (2012) 1–7.

[172] (a) Z.Q. He, S. Song, J.P. Qiu, J. Yao, X.Y. Cao, Y.Q. Hu, J.M. Chen, Decolorization of C.I. Reactive Yellow 84 in aqueous solution by electrocoagulation enhanced with ozone: Influence of operating conditions, Environ. Technol. 28 (2007) 1257–1263; (b) D. Ghernaout, M.W. Naceur, B. Ghernaout, A review of electrocoagulation as a promising coagulation process for improved organic and inorganic matters removal by electrophoresis and electroflotation, Desalin. Water Treat. 28 (2011) 287–320.

[173] D. Ghernaout, M.W. Naceur, Ferrate(VI): *In situ* generation and water treatment—a review, Desalin. Water Treat. 30 (2011) 319–332.

[174] D. Ghernaout, B. Ghernaout, On the controversial effect of sodium sulphate as supporting electrolyte on electrocoagulation process: A review, Desalin. Water Treat. 27 (2011) 243–254.

[175] A.H. Mahvi, S.J.A.D. Ebrahimi, A. Mesdaghinia, H. Gharibi, M.H. Sowlat, Performance evaluation of a continuous bipolar electrocoagulation/electrooxidation–electroflotation (ECEO–EF) reactor designed for simultaneous removal of ammonia and phosphate from wastewater effluent, J. Hazard. Mater. 192 (2011) 1267–1274.

[176] S. Cotillas, J. Llanos, P. Cañizares, S. Mateo, M.A. Rodrigo, Optimization of an integrated electrodisinfection/electrocoagulation process with Al bipolar electrodes for urban wastewater reclamation, Water Res. 47 (2013) 1741–1750.