Chemical Engineering Journal 317 (2017) 707–725

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Electrocoagulation treatment of arsenic in wastewaters: A comprehensive review

Peipei Song [a,b], Zhaohui Yang [a,b,*], Guangming Zeng [a,b], Xia Yang [a,b], Haiyin Xu [c], Like Wang [a,b], Rui Xu [a,b], Weiping Xiong [a,b], Kito Ahmad [a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, PR China
[c] College of Environmental Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, PR China

HIGHLIGHTS

- Electrocoagulation process for arsenic removal was evaluated.
- Transformation and characterization of EC products were investigated.
- Mechanism of As(III) oxidation and arsenic adsorption behavior were elucidated.
- Future research needs for arsenic removal by electrocoagulation were suggested.

ARTICLE INFO

Article history:
Received 11 November 2016
Received in revised form 10 January 2017
Accepted 16 February 2017
Available online 21 February 2017

Keywords:
Arsenic
Electrocoagulation
EC products
Electrocoagulation reactor configuration
As(III) oxidation
Adsorption behavior

ABSTRACT

Arsenic, classified as a carcinogen, is being subject to high concern due to its high toxicity especially in drinking water. Electrocoagulation (EC) has displayed a great potential as an effective and environmentally friendly method to remove arsenic from wastewaters. This review summarizes the recent development of arsenic removal in EC process including the effects of primary operating parameters, optimization of the EC performance, as well as the evaluation of EC reactor configurations. Production and characterization of EC products with respect to different electrodes are systematically discussed. Besides, this review sheds light on the debate about the mechanism involved in As(III) oxidation and further explores the arsenic adsorption behavior in EC process. Moreover, the performance of EC and other technologies are compared, and future research needs for arsenic removal in EC process are suggested accordingly. Overall, this review will contribute to deepening the understanding of EC process for arsenic removal and offer useful information to researchers in this field.

Contents

---

* Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
E-mail address: yzh@hnu.edu.cn (Z. Yang).

http://dx.doi.org/10.1016/j.cej.2017.02.086
1385-8947/

1. Introduction

Arsenic (As), a metalloid element in ⅤA group of the periodic table, is extensively consumed as semiconductor materials, alloys, pharmaceuticals, preservatives and so on. Owing to excessive mining and smelting, discharge of industrial wastewaters without treatment and widespread use of arsenic and its compounds, arsenic contamination in water becomes more and more serious, posing a great threat to the lives of more than 140 million people around the world [1–3]. Arsenic exposure can negatively influence the skin, liver, bladder, cardiovascular, gastrointestinal, respiratory and nervous systems. It has been reported that in Bangladesh, millions of people are suffering from the skin cancer or internal organs cancers, causing 1 in 5 deaths. 19.6 million people in China are also at risk of being affected by consumption of arsenic-contaminated groundwater [1–6]. Consequently, Arsenic removal from water is an important subject worldwide, and the need for a sustainable solution to arsenic removal is urgent.

To date, various technologies including chemical coagulation, adsorption, membrane filtration, reverse osmosis, oxidation and ion exchange have been proposed to remove arsenic from wastewaters [7,8]. However, they are subject to several drawbacks including time consuming, low removal efficiency, additional consumption of chemical reagents, high operating cost, as well as a great deal of secondary pollutants. Currently, electrocoagulation (EC) has attracted increasing attention due to its effectiveness in rapid removal of arsenic from wastewaters, since it involves not only electrochemical reactions occurring at the anode and cathode but also in-situ production of flocs or coagulants [7–10].

With the rapid development of electrocoagulation, it has been a lot of literatures about arsenic removal from wastewaters [11–14]. Most previous works are focused on the effects of operational parameters on EC process for arsenic removal, including initial concentration, pH, treatment time, current density, electrode material and so on. Some studies are reported to optimize the operating parameters, explore the potential mechanism, or evaluate the adsorption behavior involved in arsenic removal by electrocoagulation. The evaluation of EC reactor design and the characteristics of EC products which play an important role in arsenic removal are investigated only in few studies. To the authors' knowledge, up to now, none of them systematically summarizes the recent works, existing shortcomings, and future research of arsenic removal from wastewaters by electrocoagulation. Overall, a review with respect to the subject is still lacking.

Accordingly, the paper aims to outline the developments in the field of arsenic removal by electrocoagulation during the recent

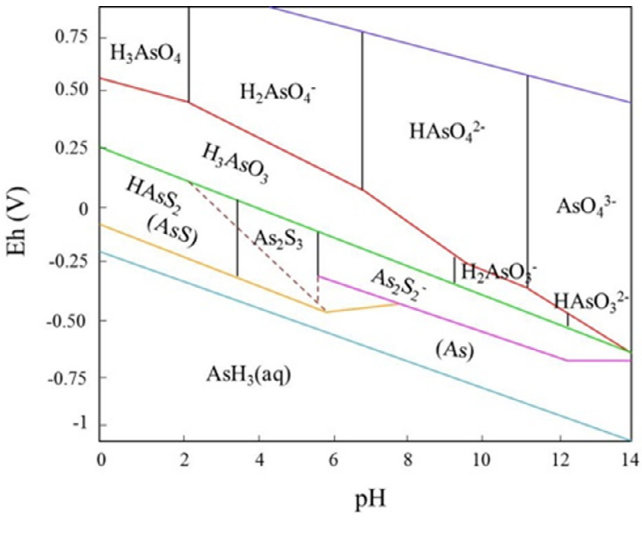

Fig. 1. Eh-pH diagram for aqueous As species [1].

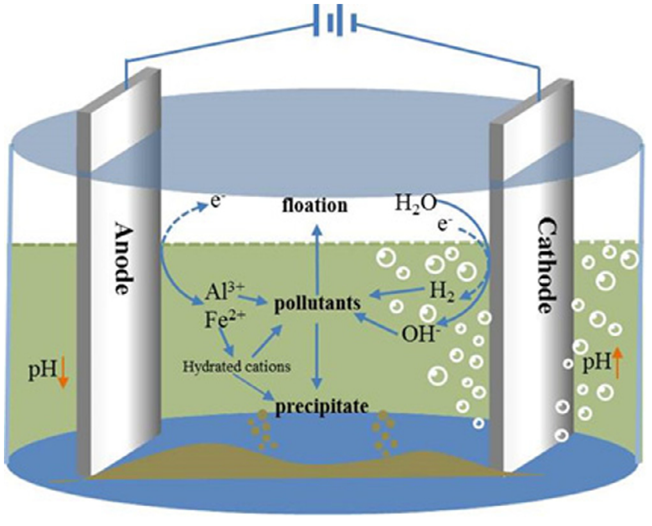

Fig. 2. The basic principle involved in EC process [13].

Table 1
Electrochemical reaction in EC process.

Anode	Cathode
$2H_2O - 4e^- = 4H^+ + O_2$ (g) (2.1)	$2H_2O + 2e^- = 2OH^- + H_2$ (g) (alkali solution) (2.3)
$4OH^- - 4e^- = 2H_2O + O_2$ (g) (2.2)	$2H_3O^+ + 2e^- = 2H_2O + H_2$ (g) (acid solution) (2.4)
	$2H_2O + O_2 + 4e^- = 4OH^-$ (2.5)
With Fe electrode	
$Fe(s) - 2e^- = Fe(aq)^{2+}$ (2.6)	$Fe(OH)_3 + OH^- = [Fe(OH)_4]^-$ (2.11)
$Fe^{2+} - e^- = Fe^{3+}$ (2.7)	$[Fe(OH)_4]^- + 2OH^- = [Fe(OH)_6]^{3-}$ (alkali solution) (2.12)
$Fe(aq)^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$ (2.8)	
$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$ (2.9)	
$Fe^{2+} + 3OH^- - e^- = FeOOH + H_2O$ (2.10)	
With Al electrode	
$Al(s) - 3e^- = Al(aq)^{3+}$ (2.13)	$Al(s) + 4OH^- = [Al(OH)_4]^- + 3e^-$ (alkali solution) (2.15)
$Al(aq)^{3+} + 3H_2O = Al(OH)_3 + 3H^+$ (2.14)	

years, and provides the future prospects of this topic. In this paper, the chemical and physical phenomena, influencing factors, and optimization of operating parameters involved in EC process are comprehensively discussed. Meanwhile, EC reactors at various configurations and the operating cost of EC process are systematically evaluated. Besides, the amount, production and transformation of EC products with different electrodes are deeply explored. It is noted that several conflicting theories of mechanism involved in As(III) oxidation do exist, which need to be urgently addressed in this review. Eventually, recommendations for further research of EC process for arsenic removal are proposed to inspire more exciting developments.

2. Theoretical background on arsenic and electrocoagulation

2.1. Arsenic

In general, arsenic exists mainly in the forms of arsenite (As(III)) and arsenate (As(V)) in water and wastewaters. As(V) are usually found under aerobic conditions, and As(III) are prevalent in anaerobic environment. The ionic form of arsenic species largely relies on pH and redox potential of the solution. As shown in Fig. 1, under reducing conditions, the dominant species of As(III) are neutrally charged H_3AsO_3 at pH 3–9, and negatively charged $H_2AsO_3^-$ at pH 9–11. Under oxidizing conditions, the ionic form of As(V) species is mainly negatively charged $H_2AsO_4^-$ at pH 3–7 and $HAsO_4^{2-}$ at pH 7–11 [1–3,6,9,13]. Under the conditions of extremely high reduced S concentration, dissolved arsenic-sulphide species are obvious in the solution. While As_2S_3, and other sulphide minerals containing arsenic appear in acidic and reducing conditions [6].

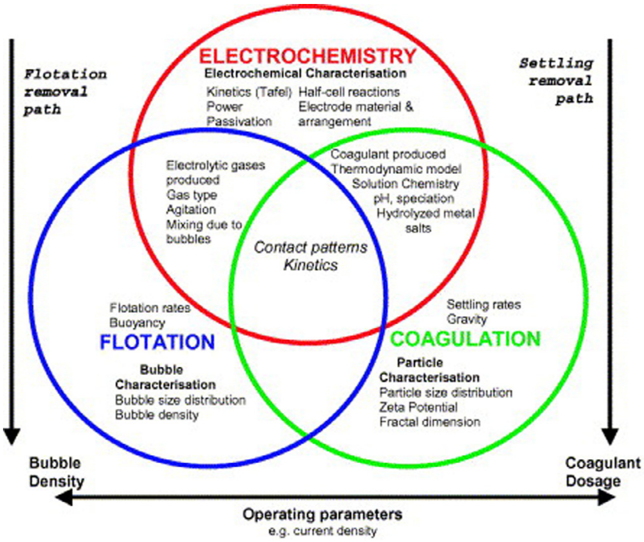

Fig. 3. Conceptual framework for EC as a 'synthesis' technology [23].

The toxicity of As(III) is 25–60 times higher than that of As(V). Long-term exposure to arsenic leads to high risks of skin cancer or internal organs cancers, even disturbs the cardiovascular and nervous system, ultimately resulted in death. Taking into consideration of the high toxicity, arsenic and its compounds have been regarded as the prime pollutant by US Environmental Protection Agency (USEPA) and Council of European Communities (CEC). Besides, the maximum allowable level of arsenic is set as 10 μg/L of drinking water by USEPA and World Health Organization (WHO) [1–3].

2.2. Electrocoagulation

Electrocoagulation was first reported to treat sewage in England at 1889, and used for wastewaters treatment in USA at 1946. However, owing to large capital investment and high power cost, the application of electrocoagulation was restricted [10]. Until the last few decades, with the rapid development of power industry and the increasing complexity of wastewaters components, there has been renewed interest in the application of electrocoagulation. As reported, with the continuous and in-depth study, electrocoagulation has been successfully applied to treat various wastewaters, such as textile industry effluent, restaurant wastewaters, electroplating wastewaters, laundry wastewaters, oily wastewaters, heavy metal contaminated wastewaters and so on [10,15–19].

Metal electrodes, usually aluminum or iron, are used in EC process. Electrocoagulation involves many chemical and physical phenomena as shown in Fig. 2, and electrochemical reactions in EC process are presented in Table 1. With a direct current, metallic cations such as Fe(II), Fe(III), or Al(III) are produced by anodic oxidation. They are gradually hydrolyzed and polymerized. To be specific, with Fe electrode, electro-generated ferrous and ferric ions initially form monomeric ions such as $FeOH^+$, $FeOH^{2+}$, $Fe(OH)_2^+$, and polymeric species such as $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$. Likewise, with Al electrode, electro-generated aluminium ions form various monomeric species such as $AlOH^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, and polymeric species such as $Al_6(OH)_{15}^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$. According to complex precipitation kinetics, these species subsequently form a series of iron or aluminum hydroxides/oxyhydroxides with large surface area such as $Fe(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, FeOOH, AlOOH and so on, to aggregate or absorb with the dissolved pollutants [25]. In polymeric species, Al_{13} polymer is considered to be the most active species responsible for coagulation [26]. Meanwhile, hydrogen bubbles are generated by cathodic reduction. These gas bubbles are extremely fine and uniform, which are able to capture the suspended substance, leading to additional removal of pollutants. These flocs with the characteristics of good stability, less bound water and large particle size are easily removed by filtration [12,20–24]. Accordingly, the basic principle of EC process may contain the following three aspects: (1) electrochemical reactions, including anodic oxidation and cathodic reduction; (2) flotation; and (3) coagulation or adsorption, as depicted in Fig. 3 [29].

EC is considered to be designed for any treatment capacity, and providing better removal performance of pollutants. In EC process, there is no need to add chemicals, since the electron is the primary reagent. EC is therefore identified as an environmental friendly technology. Compared with chemical coagulation, EC process generates lower quantity and more stable of sludge. However, there are some limitations in EC process. For example, an oxidation film which impedes current flow may be formed on the electrodes, and the operating cost of EC process is relatively high. As a result, developing an efficient and cost-effective EC treatment technology to remove pollutants from wastewaters is desirable.

3. Present and future perspectives of arsenic removal by electrocoagulation

3.1. Effects of primary operating parameters

It has been noted that several operating parameters influence the EC performance for arsenic removal. For example, pH is reported to influence the distribution of arsenic species and the surface charge of the complexes or coagulants generated in EC process. Arsenic valence state in aqueous solution seems to affect the difficulty of arsenic removal. To some extent, the existence of some anions may give rise to the inhibition of arsenic removal. Consequently, the influence of primary operating parameters on EC process for arsenic removal are thoroughly discussed and summarized in this review.

3.1.1. Electrode material

Different electrode materials have different electrochemical characteristic [30], selecting the suitable electrode material is vital to enhance arsenic removal efficiency in EC process [31].

As reported, electrodes applied for arsenic removal in EC process mainly refer to aluminium, iron, copper and zinc. With copper, zinc, iron, and brass plates as anode, the corresponding removal efficiency of arsenic is in the order of iron ≈ zinc > brass > copper, which may be due to the electrochemical intrinsic properties and the electrochemical reactions of metal electrodes [32]. EC process for arsenic removal with titanium, iron, or aluminum electrode demonstrate that iron plate as anode is more efficient than others under the condition of low current density. The plausible reasons for lower removal efficiency with aluminum electrode might be associated with higher solubility of aluminum salts, and the lower adsorption capacity of aluminum complexes in-situ generated in EC process [20,33,34]. EC process with aluminum electrode is more suitable for final purification. By comparison, iron electrode is considered to be more attractive to remove arsenic from various wastewaters in EC process [33].

In order to improve the EC performance, a range of electrodes made up of various materials are proposed [35]. It can be concluded that arsenic removal efficiency with combination of copper electrode is higher than aluminum or iron electrode alone [31]. More than 99% removal efficiency is obtained with hybrid Fe-Al electrodes as sacrificial electrodes [13,36], which seems to be promising for arsenic removal during the EC process.

3.1.2. Current density

Current density determines the generation rate of coagulant and gas bubbles, the size and distribution of flocs during the EC process. Therefore, current density is an important operation parameter influencing arsenic removal in EC process.

Almost all of the literatures about arsenic removal by electrocoagulation have discussed of the effects of current density [13,24,33–37]. From these studies, it can be concluded that arsenic removal efficiency is directly proportional to current density at the early stage of EC process, which can be explained by Faraday's law as follow:

$$C_{theo} = It_{EC}M/zFV \tag{3.1}$$

where C_{theo} (kg/m^3) is the theoretical amount of ions generated by anodic oxidation, I (A) is the current passed through the electrodes, t_{EC} (s) is the treatment time, z is the number of electrons; M (g/mol) is the atomic weight, F (96485 C/mol) is the Faraday's constant, and V (m^{-3}) is the volume of the treated wastewaters.

With the improvement of current density, the amounts of dissolved metal ions increase, resulting in more and more hydroxide cationic complexes. These complexes strongly adsorb or easily coprecipitate with pollutants. Meanwhile, the production rate of hydrogen increases and the size of bubbles becomes smaller, which enhances the flocculation performance and mass transfer in EC process. As a result, higher removal efficiency is obtained. However, a stagnation stage occurs in arsenic removal when the current density is higher than a certain value, which is due to that there are sufficient metal hydroxides/oxyhydroxides generated by anode oxidation and hydrolysis to remove arsenic [10,11]. Besides, the amount of Al_{13} which is regard as the most active species responsible for coagulation generated in EC process, is negatively correlated with the current density. As current density increases, higher Al (total) concentration in EC process with Al electrodes are generated. As a result, it may increase the opportunity of collision between Al_{13} polymer units, leading to the promotion of Al hydrolysis-polymerization as well as the formation of large polymer and Al precipitates [26–28]. Furthermore, with the increase of current density, it may be followed by electrode polarization and passivation [13,35], leading to the decline of current efficiency (C_E) and the loss of electrical energy.

$$C_E = (C_{elec,exp}/C_{elec,theo}) \times 100\% \tag{3.2}$$

According to Eq. (3.2), C_E is calculated as the ratio of the value of practical electrode consumption to the theoretical value. $C_{elec,exp}$ is defined as the experimental weight loss of the electrode before and after the EC process. The calculation of $C_{elec,theo}$ is based on Eq. (3.1). $C_E < 100\%$ possibly implies the polarization and passivation of electrode. However, the phenomenon that the current efficiencies for Fe and Al electrode are in the range of 106%–116% [21], presumably caused by the corrosion pitting, which refers to the holes on the surface of electrodes and results in a loss of ions.

It is also clear that the major operating cost in EC process is the consumption of electrical energy which is associated with current density and operating time as shown in Eq. (3.3).

$$C_{energy} = UIt_{EC}/V \tag{3.3}$$

where C_{energy} (kWh m^{-3}) is the consumption of electricity of per m^3, U (V) is the potential of the EC reactor.

Consequently, a compromise of the operating time and the current density is necessary to realize higher arsenic removal efficiency with lower operating cost. According to the literature [21], longer operating time with constant current density value contributes to higher arsenic removal efficiency and lower electric energy with iron electrode. Besides, the energy consumption of iron electrode is reported to be lower than that of aluminum electrode, since a higher value of potential is necessary for aluminum electrode to reach a certain current density. However, increasing current density shortened the operating time is beneficial to

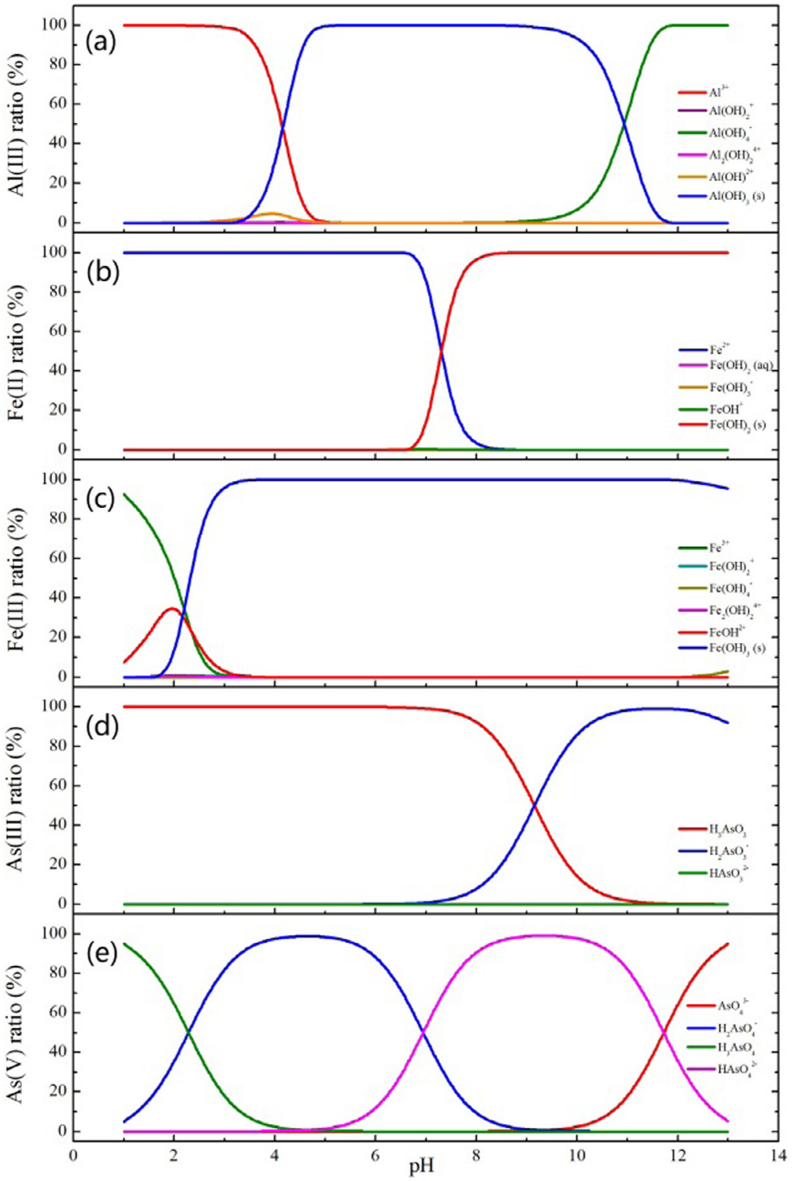

Fig. 4. Predominance zone diagrams for (a) Al(III), (b) Fe(II), (c) Fe(III), (d) As(III), and (e) As(V) species in solutions simulated by Visual MINTEQ version 3.0 [13].

acquire the maximum content of medium polymer species, such as Al_{13}, in EC process with Al electrodes [26]. As a result, an appropriate selection of current density need to take account for various factors such as treatment time, pH, or velocity, to ensure that arsenic removal in EC process is operated at the optimum conditions.

3.1.3. pH

In wastewaters treatment, pH has an important effect on many physical and chemical processes, especially for electrochemical process and chemical coagulation process.

The optimum removal efficiency of arsenic is taken place at pH of 6.5 with iron electrode and pH of 7.0 with aluminium electrode [38]. With hybrid Fe-Al electrodes, the optimum pH range is observed at 5.0–7.0, and arsenic removal efficiency is lower as pH increases [13]. The influence of pH on arsenic removal efficiency relies on the existing form in aqueous solution of Fe, Al, and As under different pH values as shown in Fig. 4. Positively charged colloid particles of ferrous hydroxide and ferric hydroxide are generated starting from pH about 7.0 and 3.0, respectively. While when pH is above 12.0, the amounts of ferric hydroxide decrease. Aluminum hydroxide is produced from pH about 4.0, and gradually dissolves at pH about 10.0. It is noted that pH 5.0–7.0 is an ideal pH range for the formation of Al_{13} polymer which is in favor of arsenic removal [26–28]. With respect to As(III), when the pH of solution is below 9.0, As (III) mainly exists in the form of neutral molecule H_3AsO_3, with the increase of pH, the amounts of negatively charged $H_2AsO_3^-$ increase. That is the reason why higher pH promotes As(III) removal in EC process, which agrees well with the data extracted from the model predicted by Li et al. [14]. In regard to As (Ⅴ), when pH value is lower than 3.0, neutral molecule H_3AsO_4 is primarily presented in the solution. At pH ranging from 3.0 to 7.0 and 7.0 to 11.0, the dominant ions in the solution are negatively charged $H_2AsO_4^-$ and $HAsO_4^{2-}$, respectively. With the increase of pH, the amounts of $HAsO_4^{2-}$ decrease while AsO_4^{3-} increase. The phenomenon that As(V) removal efficiency with iron electrode becomes lower as pH increases above 7.0, is associate with the isoelectric pH of EC products identified as lepidocrocite in EC process [11]. The isoelectric pH of lepidocrocite is measured about 7.0. When the pH of solution is lower than the isoelectric

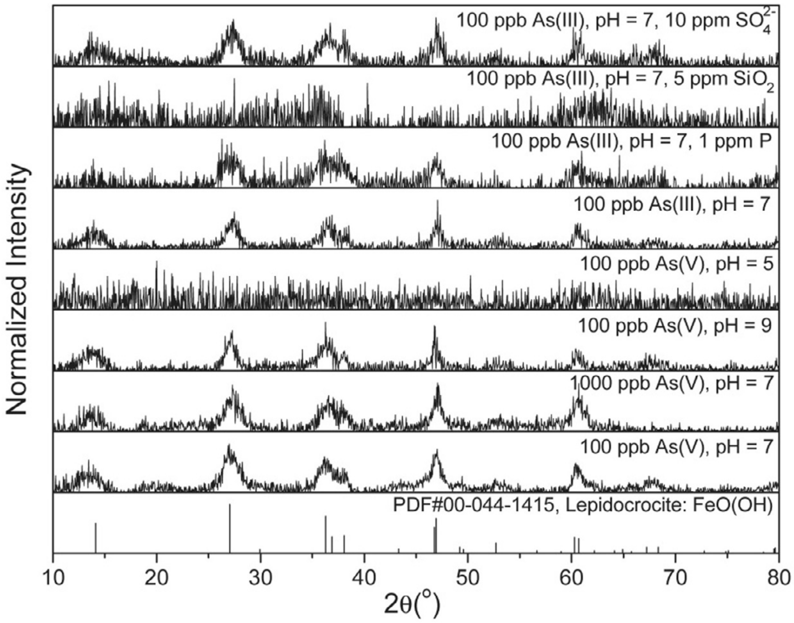

Fig. 5. X-ray diffraction patterns of solids with various coexisting ions in EC process [11].

value, the surfaces of EC products are positively charged, which is in favor of chemical contributions and electrostatic contributions to As(V) adsorption. When the pH of solution is higher than the isoelectric value, both the surfaces of EC products and As(V) species are negatively charged, leading to less favorable adsorption. Overall, whether electrostatic attraction or chemical contributions, EC products mainly metal hydroxides/oxyhydroxides with positive charge and arsenic species with negative charge are the optimum conditions for arsenic removal by electrocoagulation. Besides, it is noted that the final removal efficiency of arsenic is close to a constant value at pH ranging from 5.0 to 8.0 [11,20], which may be explained by that once sufficient metal hydroxides/oxyhydroxides are generated, very small amounts of dissolved arsenic is acquired in EC process regardless of the pH of the solution.

During the EC process, an obvious increase in final pH occurs with initial pH ranging from 3.0 to 7.0, which is correlated with the production of hydroxyl ions (OH^-) and hydrogen gas (H_2) by cathodic reduction according to Eqs. (2.3) and (2.4) [13]. However, when initial pH is higher than 9.0, the values of final pH reduce, which is possibly caused by hydrolysis reactions and consumption of hydroxyl ions according to Eqs. (2.8)–(2.12), (2.14) and (2.15) [11,20,21]. Accordingly, electrocoagulation can act as a pH neutralization technology, which is meaningful to practical application. It provides an advantage over other treatment methods that need to adjust pH values of the effluent, such as chemical coagulation [14,37].

3.1.4. Coexisting ions

There exist some anions such as nitrate, phosphate, silicate, sulfate, chloride, carbonate and fluoride in actual wastewaters. Investigation of the influence of anions on arsenic removal in EC process is important and meaningful to the practical application.

3.1.5. Phosphate

It has been reported that phosphate plays an inhibitory role in arsenic removal by electrocoagulation, and the inhibitory effect is more obvious at pH value of 6.5 or at higher concentration of phosphate [11,13,39]. Considering the increasing removal of phosphate and the decrease of arsenic removal efficiency, it can be inferred that phosphate probably competes with arsenic for adsorption sites of metal hydroxides/oxyhydroxides in EC process. Besides, because of the presence of phosphate in wastewaters, the oxidization rate of Fe(II) converted to Fe(III) becomes slower, leading to the decline in the rate at which the complexes is formed [11]. However, the identity of the metal hydroxides/oxyhydroxides formed in EC process is not affected, and no peaks for ferrous phosphate or ferric phosphate precipitates are detected by XRD characterization as shown in Fig. 5.

3.1.5.1. Silica. Some studies indicate that no significant inhibitory effect on arsenic removal efficiency is found when the solution containing dissolved silica [11][13][11,13]. It is noted that dissolved silica are also removed in EC process. This phenomenon is probably explained by that silica does not have a strong affinity with the metal hydroxides/oxyhydroxides as arsenic does. Although XRD analysis as shown in Fig. 5 displays that the presence of silica affects the identity and prevents the formation of iron oxides produced in EC process, the complexes namely metal hydroxides/oxyhydroxides newly generated is also able to be applied as sorbents for As removal.

However, the opposite phenomenon is taken place in other studies where 20 mg/L of dissolved silica significantly inhibits the adsorption of As(V), and the inhibitory effects become more remarkable as pH increases [40,41]. Plausible reasons for various observations are the discrepancies in the operating conditions and inhibitory mechanisms. It is assumed that the pathway associated with adsorption sites within internal pores of the metal hydroxides/oxyhydroxides is physically blocked by polymerization of silica [11]. In EC process with iron electrode, silicate, like phosphate, presumably affects the structure of iron hydroxides/oxyhydroxides by preventing FeO_6 corner-sharing linkages [42]. Besides, in the solution containing both phosphate and silica, As(V) and phosphate are firstly adsorbed, indicated by the simultaneous decreasing concentration of As(V) and phosphate, and then As(III) and silica begin to be removed at larger amounts of metal hydroxides/oxyhydroxides in-situ generated in EC process [14].

3.1.5.2. Sulfate. Similarly, sulfate is also removed in EC process. However, no matter what the concentration is, the presence of sulfate in the solution almost does not influence the arsenic removal efficiency. Since the formation of metal hydroxides/oxyhydroxides is not affected, and sulfate does not adsorb as strongly as arsenic or phosphate does in EC process. As a result, it is not surprising that the performance of EC process is not influenced in the present of sulfate [11,13].

3.1.5.3. Chloride. Chloride addition slightly improves the arsenic removal efficiency. It may be due to that Cl^- can penetrate the passivation film formed on the surface of the anode, alleviating the obstructive effect on anodic dissolution [13,43]. Besides, electrode dissolution seems to be catalyzed by the pitting corrosion phenomenon in presence of high concentration of chloride ions [44]. Therefore, with the increased amounts of dissolved metal ions and metal hydroxides/oxyhydroxides coagulant, the presence of chloride ions enhances the arsenic removal efficiency. Besides, adding chloride gives rise to an obvious increase of conductivity, and thus the voltage and the power values reduce, leading to a significant decline in energy consumption. Accordingly, chloride addition avoids the generation of the passivation layer at the anode and prevents excessive ohmic drop in EC process.

3.1.5.4. Carbonate. The influence of carbonate on As(V) removal is considered to be dependent on the concentration of As(V). There is little impact on As(V) removal efficiency in presence of less than 5 mg/L carbonate ions [40,41]. However, when the concentration of carbonate is higher than 5 mg/L, As(V) removal efficiency significantly declines, which may be caused by the passivation of anode generated by large amount of ferrous ions and carbonate, hindering the process of electrodes dissolution.

3.1.5.5. Fluoride. As the fluoride ions increases from 0 to 5.0 mg/L, As(V) removal efficiency gradually decreases [40][33]. Like phosphate, fluoride is preferentially adsorbed as compared to As(V) with the increase of fluoride concentration in EC process. Accordingly, fluoride ions compete intensely with As(V) ions for the binding sites of metal hydroxides/oxyhydroxides during the EC process.

3.1.6. Oxidation state

As(III) is reported to be more toxic than As(V) [20,45], and As (III) is removed poorly form wastewaters by many conventional processes. As(V) presents better removal performance than As(III) during the EC process as observed as Kumar et al. [20]. Accordingly, converting As(III) to As(V) is priority to recommendation. In the experiments about As(III) wastewaters treatment [11], the concentration of dissolved As(V) enhances at the first stage and then reduces as the treatment time increases. The increase of As(V) concentration in treatment of wastewaters containing As(III) is explained by that As(III) is partly converted into As(V), indicating that oxidizing condition in EC process has a significant role in As (III) removal. In an aeration EC reactor with iron electrodes, as the aeration intensity increases from 0 L/min to 0.16 L/min, arsenic removal efficiency rises from 70% to 97%. While once above 0.16 L/min, arsenic removal efficiency reaches a plateau [13]. As the aeration intensity increases, As(III) in the solutions is favorably oxidized to As(V) which is easier to remove. In addition, Fe(II) dissolved by anodic oxidation is converted into Fe(III), whose capacity of forming iron hydroxides/oxyhydroxides and adsorption of arsenic is stronger. Meanwhile, under aeration environment, the necessary turbulent current condition is offered for the flocs to collide and contact with each other, ultimately leading to better performance of arsenic removal.

3.2. Optimization of the EC process

Experimental design is proved to be a powerful tool to evaluate the effects of operating parameters on EC performance. The objective of experimental design is mainly to search for the control factors influencing the EC performance [46,47]. Owing to the quickness and accuracy, Response Surface Method (RSM) is selected to investigate the combined effects of independent variables on responses, and to confirm the optimum operating conditions of the EC process. RSM is attempted to fit a model by least square method. Generally, it is divided into three steps: (1) design and experiments, (2) response surface modeling, and (3) optimization [48].

In RSM, the independent variables are denoted by $x_1, x_2, \ldots, x_k$, and the response is denoted by y. They can be related as follows [46,48,49]:

$$y = f(x_1, x_2, x_3 \ldots, x_k) + \varepsilon \tag{3.4}$$

where f is the response fuction, ε is the experimental error. A response surface is acquired by plotting the response of y. The form of f is given as the first and the second-order fuction, and y can be written as [48] [50] [51][48,50,51]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \varepsilon \tag{3.5}$$

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{3.6}$$

where y is the response variable, β_0, β_i, and β_{ii} are the offset term, χ_i and χ_j are the independent variables, β_{ij} is the term reflecting the interaction between χ_i and χ_j, i is the linear coefficient, and j is the quadratic coefficient.

According to Eq. (3.7), X_i is coded as x_i for statistical calculations:

$$x_i = (X_i - X_i^x)/\Delta X_i \tag{3.7}$$

where X_i and x_i are the actual and coded value of the ith independent variable, respectively. X_i^x is the actual value of the ith independent variable at the center point, and ΔX_i is the value of step change. Thus, y is represented by Eq. (3.8) [48–51]:

$$\begin{aligned} y = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 \\ & + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \end{aligned} \tag{3.8}$$

where β_0 is the model constant, β_1, β_2, β_3 and β_4 are linear coefficients,β_{11}, β_{22}, β_{33}, and β_{44} are the quadratic coefficients, β_{12}, β_{13}, β_{14}, β_{23}, β_{24} and β_{34} are the cross product coefficients.

To test the accuracy of the model, various parameters are critically examined in RSM. The adequacy of the RSM is justified through the analysis of variance (ANOVA) to evaluate the "goodness of fit". Terms regarded as statistically significant can be included while the non-significant terms are reduced by the way of reselecting the significant terms of the model. Among various parameters, larger magnitude of t-value indicates the importance of corresponding coefficient terms. Large F-values indicate that the regression model can describe the variation of the response. P value is used to estimate the model term. The term is deem to be statistically significant when P value is lower than 0.05, whereas P value higher than 0.10 is recognized as non-significant terms. Besides, the adequacy of the model can be checked by R^2 or Adj R^2.

Box Behnken Design (BBD), a three-level four factorial of RSM, can be employed to find the relationship between the independent variables and responses. In the study of Balasubramanian et al. [46], BBD was applied to evaluate the influence of operating parameters (current density, concentration, treatment time and pH) on the response (arsenic removal efficiency) with iron and aluminum electrode. Compared to the coefficients in the quadratic term, the linear coefficients of three variables including current density, electrolyte pH, and concentration were significant. A higher value of R^2 (0.89) was obtained, indicating that the response can be explained successfully by this model. In accordance to ANOVA, the second-order polynomial model acquired by BBD was adequate to represent the relationship between the variables and the response in EC process.

Central Composite Design (CCD), a 2^3 full factorial design of RSM with addition of six repetitive experiments of central point, is also conducted to evaluate the individual and combined effects of variables on the responses, and to optimize the operating variables. Three important independent variables (current density, concentration, and treatment time) along with responses of arsenic removal efficiency and the operating cost were systematically designed in EC process with Fe electrode by Kobya et al. [48]. R^2 (0.963 for arsenic removal efficiency and 0.965 for operating cost) and Adj R^2 (0.931 and 0.930) indicated that the model was significant and fitted well with experimental data. Prob > F values revealed that the individual and combined three independent variables were considered to be statistically significant for the response of arsenic removal efficiency, while only the individual and combined effects of two variables including treatment time and current density were highly significant for the response of the operating cost. Moreover, The model predicted that the maximum removal efficiency of arsenic (93.86%) and the minimum operating cost (0.0664 /m^3) were acquired in EC process at the optimum operating conditions of 112.3 μg/L initial concentration, 5.64 A/m^2 current density and 5 min treatment time. Song et al. [51] also established CCD design to investigate the influence of operating parameters (current density, aeration intensity, treatment time, and pH) on arsenic removal efficiency and the cell voltage, and determine the optimization of the EC performance with hybrid Fe-Al electrodes. Resulted showed that a second-order regression model fitted well with experimental data. Besides, the maximum amount of As (99.94%) was removed and the minimum cell voltage (3.23 V) was obtained at the optimum conditions of 0.47 A/dm^2 current density, 0.32 L/min aeration intensity, 20 min treatment time, and 7.0 pH. Experiments were also conducted to further verify the validity of the optimum conditions obtained from the proposed model.

Overall, it is clearly confirmed that RSM can be regarded as a suitable method to evaluate the individual and combined effects of variables on the responses, and to acquire the optimum operating conditions of arsenic removal during the EC process.

3.3. EC reactor configuration

EC reactor configuration significantly affects the EC performance, including the formation of flocs, the effectiveness of flotation, mixing/settling characteristics, bubble path, fluid flow regime and so on. It is noted that there is little discussion of the improvement of EC reactors in previous studies. Accordingly, it is crucial to design of the EC reactor for a specific process. In EC reactors, the following physical factors can be considered in the design phases: (1) operating mode; (2) reactor geometry; (3) electrode connection modes; (4) electrode distance; and (5) surface area to volume ratio [10,52].

3.3.1. Operating mode

The operating mode in EC process can be divided into batch and continuous operation.

The behavior in a batch EC reactor seems to be inherent dynamic, leading to a difficult mathematical modeling. Nevertheless, investigation and optimization of influencing factors in a batch EC reactor, such as the variation of pH, concentration, treatment time, the amounts of coagulation, current density and so on, are easier and relatively more accurate than that in a continuous reactor [10,48,51,53]. Furthermore, parametric optimization in the batch system can be also served as guidelines to operate a continuous EC reactor [54].

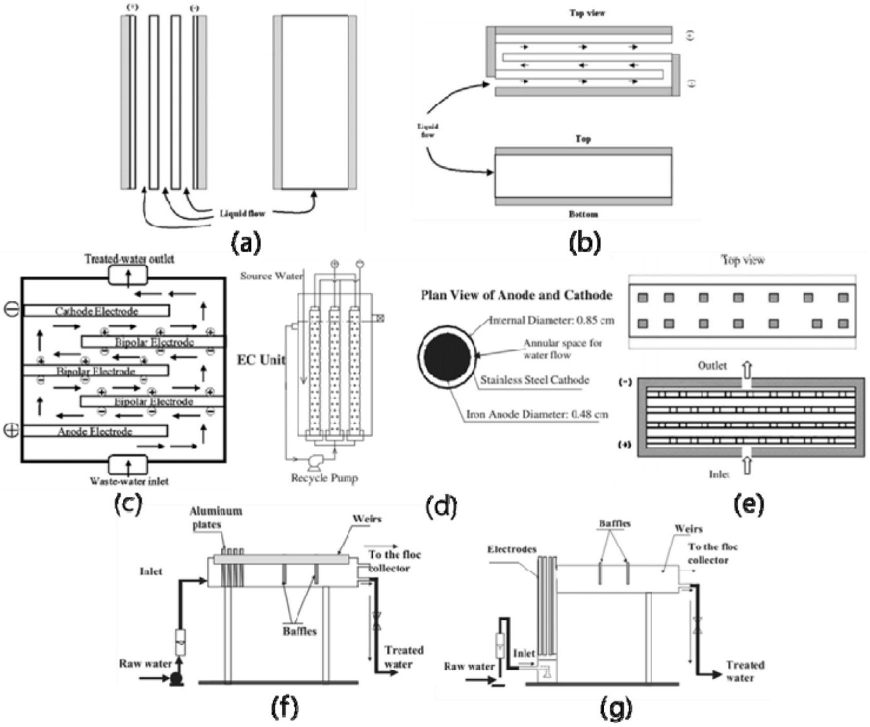

Fig. 6. Schematic diagram of different EC reactor designs. (a) Tall vertical-plate reactor, (b) Long horizontal plate reactor, (c) Short horizontal plate reactor, (d) Solid tube reactor and Perforated tube reactor, (e) Perforated plate reactor, (f) Up-flow EC reactor, and (g) Horizontal-flow EC reactor [32,51–58].

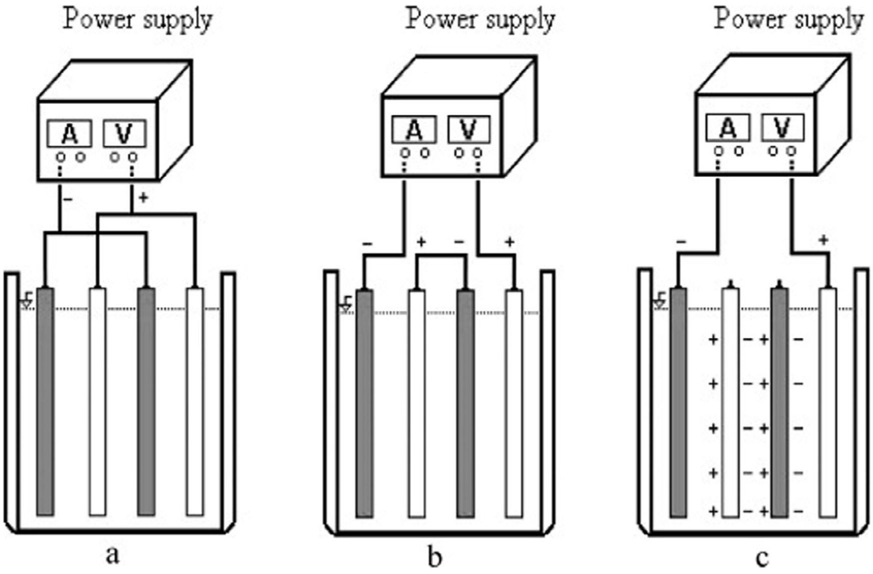

Fig. 7. Different electrode connection modes in EC process: (a) MP-P, (b) MP-S, and (c) BP-S [31].

The behavior in a continuous EC reactor seems to be stable in performance and inherently dynamic in operation. Moreover, it is easy to check the pollution load at different effluent flow rates. Electrode behaviors including the dissolution in the liquid and flocs generation or deposition, are additional benefits in a continuous reactor. The passivation and corrosion levels of electrodes in EC process can also be monitored with operating time [10,55]. A continuous system is considered to be more economical and stable than a batch system. Among three different continuous EC reactors including a turbulent flow reactor, a modified flow continuous reactor, and an airlift reactor, the airlift and modified flow reactor are more efficient in arsenic removal, and the lowest iron to arsenic ratio is obtained in turbulent flow reactor [56].

3.3.2. Reactor geometry

According to the different geometric configurations, EC reactors can be designed into a variety of forms with various degrees of treatment capacity [29,58–65]. Several common types of EC reactors are shown in Fig. 6.

Among these types of EC reactors, tall vertical-plate reactor usually produces large amount of scale with the requirement of acid wash, resulting in generation of additional wastes. The electrodes in long horizontal plate reactor are impossible to remove once corrosion occurred. Short horizontal plate reactor is suitable for treatment high concentrations of pollutants. However, it is difficult to stop fluid leaks. In comparison to the horizontal flow reactor, the up-flow reactor generates more metal hydroxides/oxyhydroxides and provides higher flow residence time, resulting in the higher arsenic removal efficiency in EC process. Compared with the solid plates, perforated plates present better mass transfer, while they are subjected to be plugged causing electrical short circuits, and usually operated at high pressure. The parallel flows through abundant tubes in perforated tube reactor results in erosion and changes in flow rate [58–63].

In brief, the design of EC reactor geometry should be aim at enhancing the performance of EC process, cost-effective, and easily operable [10,29].

3.3.3. Electrode connection modes

According to different connection modes of electrodes, EC reactor can be divided into three configurations: monopolar serial (MP-S), monopolar parallel (MP-P), and bipolar-serial (BP-S). The electrode configuration scheme is presented in Fig. 7. In MP-P connection mode, the current is divided because of the parallel connection between anodes and cathodes. As a result, the total current is the sum of all the sub-current distributed in each unit while the voltage of each unit is equal in this configuration. Accordingly, in comparison with serial connection, the parallel connection mode requires a lower potential difference. In MP-S configuration, internal connection occurs in each pair of anodes. The cell voltage is divided by each unit, while the current is the same. Consequently, a given current is provided by a higher potential difference. In BP-S configuration, no connection occurs between inner electrodes, and only outermost electrodes are connected to the power supply. With a constant current passing through the inner plates, the neutral side is converted to the charged side by electrode polarization, which presents different polarity in comparison with the parallel side next to it. As a result, outer electrodes are monopolar plates while inner ones are bipolar plates. Each adjacent electrode pair can be regarded as a single unit. The cell voltage in BP-S arrangement is divided by each unit. BP-S connection mode provides a simple setup and requires less maintenance in EC application. The cost of BP-S connection mode is proved to be lower than that of MP-P connection mode with the same total output power. However, electric current in BP-S connection mode is easier to bypass the bipolar plates and flow in the solution of EC reactor, leading to the current loss [38,66–69].

With the enhancement of current density, arsenic removal efficiency increases for all types of electrode connection modes. Compared with MP-P and BP-S electrode connection mode, MP-S connection mode displays lower energy consumption [38]. Al electrode in bipolar mode facilitates the formation of monomeric and Al_{13} species, while monopolar mode has a higher yield of larger polymer or $Al(OH)_3(s)$ [26]. Besides, iron electrode connected in MP-S mode is regard as the most efficient connection in terms of removal efficiency and operating cost as compared to the rest for arsenic removal in EC process, which may be attribute to the better chemical coprecipitation performance and lower anodic over potential.

3.3.4. Electrode distance

Since electrode distance can affect the water motion, turbulence, mass transfer, size of EC reactor, and energy consumption,

Table 2
Operating costs of arsenic removal by electrocoagulation in published studies.

Water type	Electrode	Reactor	R.E. (%)	C.D. (A/m^2)	Time (min)	O.C. ($/m^3)	Reference
C_0 (As(III)) 150 μg/L, pH 6.5	Fe	Batch	93.5%	2.5	12.5	0.02	[21]
C_0 (As(III)) 150 μg/L, pH 7.0	Al	Batch	95.7%	2.5	15	0.017	[21]
C_0 (As(III)) 500 μg/L, pH 7.0, Aeration intensity 0.32 L/min	Fe-Al	Batch	99.94%	4.7	20	0.078	[51]
C_0 (As) 150 μg/L, pH 7.0	Fe-Al-Al-Fe	Batch	96%	2.5	1	0.0026	[54]
C_0 (As) 150 μg/L, pH 7.0, Flow rate 0.05 L/min	Fe-Al-Al-Fe	Continuous flow	96.07%	2.5	3	0.0118	[54]
C_0 (As) 150 μg/L, pH 6.5	Fe	Batch	98.3%	7.5	2.5	0.022	[38]
C_0 (As) 150 μg/L, pH 7.0	Al	Batch	96.1%	7.5	4	0.028	[38]
C_0 (As) 25–50 μg/L, Flow rate 30 L/min, pH 5.5–7.1, Conductivity 600–4000 μS	Fe	Continuous flow	> 99%	5	1	0.002	[81]
C_0 (As) 25–50 μg/L, pH 6.8–7.1	Fe	Continuous flow	96.19%–99.92%	–	–	0.11	[11]
C_0 (As) 112.3 μg/L, pH 6.5	Fe	Batch	93.86	5.64	5	0.0797	[48]

R.E. Removal efficiency; C.D. Current density; O.C. Operating cost.

it is also an important factor to be investigated in arsenic removal by electrocoagulation.

At the optimum electrode distance, the flotation of hydrogen bubbles is more stable and the flocs are easier to be floated [71]. With larger electrode distance, there is a decrease in mass transfer and the movement of participant species, leading to the decline of the reaction rate. However, when the electrode distance is lower than the optimum value, arsenic removal efficiency also decreases, which is related to the obstructive mass transfer in EC reactor, causing an increase of electrolyte resistance and instability of arsenic removal [10].

Electrical resistance (IR drop) significantly affects the electrochemical measurements as shown in Eq. (3.9) [70–73].

$$\eta_{IR} = Id/Ak \tag{3.9}$$

where η_{IR} (U) is the electrical resistance (IR drop), I (A) is the current, d (m) is the electrode distance, A (m^2) is the electrode active surface, k (mS/m) is the conductivity of the solution.

From the above equation, it is known that IR drop is proportional to the electrode distance. It enhances with the improvement of electrode distance, further leading to the increment of energy consumption as shown in Eq. (3.10).

$$U = E_A + \eta_A - E_C + \eta_C + \eta_{IR} \tag{3.10}$$

where U (V) is the voltage in EC reactor, E_A (V) is the reversible anodic potential, E_C (V) is the reversible cathodic potential, η_A (V) is the anodic overvoltage, η_C (V) is the cathodic overvoltage, and η_{IR} (V) is the electrical resistance (IR drop).

Usually, a smaller distance between anode and cathode is desirable, which not only favors the reduction of the operating time but also reduces the energy consumption of EC process. Accordingly, providing just sufficient turbulence, mass transfer within the electrodes, and lower energy consumption in EC reactor can be applied as the criterion to select the optimal electrode distance value for EC process.

3.3.5. Electrode area to volume ratio (A/V)

The ratio of electrode surface area to EC reactor volume (A/V), an important parameter for scale-up systems, has significant effects on the amount of EC products such as metal hydroxides/oxyhydroxides, and the generation or path length of bubbles. It has been reported that the appropriate A/V ratio of EC reactors applied for arsenic removal in scale up is in the range of 6.5 to 50 (m^2/m^3) [57,64]. When A/V is higher or lower than the magnitude, arsenic removal efficiency declines [59].

Besides the parameters mentioned above, other dimensionless parameters taken into account for appropriate proportion and sizes of the EC reactors in scale-up systems are as follows: (1) Reynolds number, indication of the fluid flow regime; (2) Froude number, indication of buoyancy; (3) Weber criteria, indication of the surface tension; (4) Gas saturation similarity; and (5) Geometric similarity [74].

In conclusion, there are so many parameters to be considered in design phases of EC reactor to ensure the better EC performance for different types of wastewaters. These parameters are more or less lack of assessment of the processes such as electrochemical reactions or hydrodynamic process involved in electrocoagulation, further limiting more efficient EC reactor design. Consequently, it is urgent to establish a more consistent and rigorous approach to evaluate the design characteristics of EC reactors, which will be discussed later in this review.

3.4. Operating cost

Operating cost (OC) is also another important factor influencing the practical application of arsenic removal by electrocoagulation [75]. Table 2 summarized the operating costs of arsenic removal in EC process with different conditions in published studies. Various direct and indirect cost items of EC process include utility (mainly electrical energy) costs, materials (mainly sacrificial electrodes) costs, chemicals costs, as well as sludge treatment, maintenance, labors, and depreciation costs [54] Among these, electrode costs, energy consumption, and chemicals costs are considered as major cost items, as shown in Eq. (3.11) [21,38,76].

$$Operating cost = aC_{energy} + bC_{electrode} + cC_{chemicals} \tag{3.11}$$

where C_{energy} calculated by Eq. (3.12) is the consumption in kWh energy per m^3. $C_{electrode}$ calculated by Eq. (3.1) is the consumption in kg electrode per m^3, and $C_{chemicals}$ is the consumption in kg chemicals per m^3 of treated wastewaters. *a*, *b*, and *c* stand for the unit prices of electrical energy (€/kWh), electrode material (€/kg), and chemicals (€/kg), respectively.

$$C_{electrode} = It_{EC}M/Z \tag{3.12}$$

where $C_{ECreactor}$ is calculated by Eq. (3.3), C_{pump} is calculated by Eq. (3.13).

$$C_{pump} = \rho gQht/V \tag{3.13}$$

where ρ (kg/m^3) is the density of solution, *t* (h) is the treatment time, g (9.81 m/s^2) is the gravitational constant, *h* (m) is the pump height, and *V* (m^3) is the volume of treated wastewaters.

Obviously, it can be inferred that the consumption of energy and electrode are in direct proportion to the current and treatment time as shown in the Eqs. (3.12) and (3.1), respectively. Under the same arsenic removal efficiency, improvement of the cell current in EC reactor causes a corresponding reduction of the reaction time, and an increase in reaction time implies the decrease of the cell current. Therefore, a compromise of the treatment time and cell current is the key to reduce the consumption of energy and electrode in EC process. CCD can be established to optimize the treatment time and current density to obtain the highest removal efficiency of arsenic and the lowest energy consumption in EC process [51].

Various factors are observed to influence the operating cost. It has been reported that high conductivity is in favor of reducing energy consumption and improving EC performance, although it causes a small increase in chemicals consumption [13,43,44,77]. With the enhancement of initial arsenic concentration, the operating cost increases. Unit operating cost for aluminum electrode is calculated to be less expensive than that of iron electrode [21]. It has revealed that the electrode connection modes significantly affect the operating cost of EC process in the sequence of MP-P > BP-S > MP-S for both Fe and Al electrodes [38]. The effects of four factors (electrode distance (d), electrode area to volume ratio (A/V), liquid motion driving mode (LM), and current density (I)) on energy and electrode consumption are in the sequence of d > LM > A/V > I and I > A/V > d > LM, respectively, for arsenic removal from groundwater in EC process[70].

Therefore, the operation cost of arsenic removal in EC process is not only related to the types of arsenic contaminated wastewaters and the operating parameters of EC process, but also associated with the configuration of EC reactors.

3.5. EC products

The characteristics of EC products are dependent on the composition of wastewaters and operating conditions in EC process.

3.5.1. The amount of EC products

With the increase of current density or treatment time, anodic dissolution is favored, resulting in higher amount of EC products as shown in Eq. (3.1). Under the influence of electrode connection mode, the lowest amount of EC products is achieved in MP-S connection mode for ion or aluminum electrode [38]. For various hybrid Fe-Al electrodes in MP-S connection mode, Fe-Al-Al-Al hybrid electrode pair displays the lowest amount of EC products, while the highest amount of EC products is generated with Al-Fe-Fe-Al connection mode [54].

3.5.2. Characteristics of EC products

Analysis of EC products is not only beneficial to acquire the identity of the EC products, but also in favor of further understanding the mechanism involved in arsenic removal by electrocoagulation. EC products can be identified by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) or Extended X-ray absorption fine structure (EXAFS), Transmission mossbauer spectroscopy (TMS), Raman spectroscopy and so on. Characteristic of EC products in arsenic removal varies depending on the electrode material.

3.5.2.1. Al electrode. With Al electrode, SEM image displays that EC products are of irregular shape with 150– 500 μm size when current density is ranging from 4 to 6 mA/cm^2. Low standard deviations of EDS imply that the samples are homogeneous [73]. The chemical speciation of FT-IR analysis involved in EC products includes aluminum hydroxide and/or aluminum oxyhydroxide, which is similar to the aluminum oxide film reported in the previous studies [36,78,79]. The alumina of the oxide film is identified as γ-alumina, whose property lies between crystalline and amorphous alumina [36]. It has been revealed that H and H_2O during the generation of EC products are tend to together with the cyclic compound composed of oxygen and aluminum atoms, leading to the formation of cyclic aluminic acid trihydrate [36,78–80]. XRD analysis of EC products displays completely shallow and broad peak diffraction peaks. The phase of EC products is regarded as amorphous or very poorly crystalline in nature indicated by Bragg reflections in the form of low intensity and broad humps. Besides, aluminum hydroxide flocs are proved to bound more water, chemically or physically, than iron hydroxide flocs [21]. Additional studies are required to explore the clear arsenic transformation in EC process with Al electrode.

3.5.2.2. Fe electrode. With Fe electrode, the structure of EC products is proved to be mainly amorphous with 20–50 μm size by the analysis of SEM image [38]. EDS analysis of EC products indicates that the surface of EC products is partially covered with arsenic, confirming arsenic removal from the solution. According to FT-IR analysis, OH stretching, hydroxyl bending, magnetite, Fe-O vibration band, lepidocrocite, and overtones of hydroxyl bending are identified in EC products, which is consistent with the result of Raman bands. Both amorphous phases represented by lepidocrocite and well crystalline phases represented by magnetite are detected by XRD pattern [36,38,81], and the predominant phase in EC products is identified as lepidocrocite (γ-FeOOH) [11,82]. EXAFS analysis can be applied to explore the local coordination environment and determine the short-ranged structure of iron and arsenic [42]. Regardless of various values of current density, iron and arsenic K-edge EXAFS spectra seem to be similar. Shell-by-shell fits of the Fe K-edge EXAFS spectra suggests that the edge-sharing FeO_6 octahedra is the main phase in EC products, and the corner-sharing FeO_6 octahedra is absent, indicating that EC products are able to make effective combination with arsenic. Shell-by-shell fits of As K-edge EXAFS spectra reveals that arsenic, originally in existence of both As(III) and As(V), becomes corner-sharing As(V) surface compounds with mainly binuclear structure on EC products. The specific coordination geometry as shown in Fig. 8 prevents the formation of FeO_6 corner-sharing linkages [42]. Accordingly, EXAFS analysis provides insights into the reactivity and structure of EC products, and offers a better understanding of arsenic removal with iron electrode in EC process [42,83,84].

Various conditions for the generation and transformation of EC products generated in Fe(0) EC process are summarized in Fig. 9

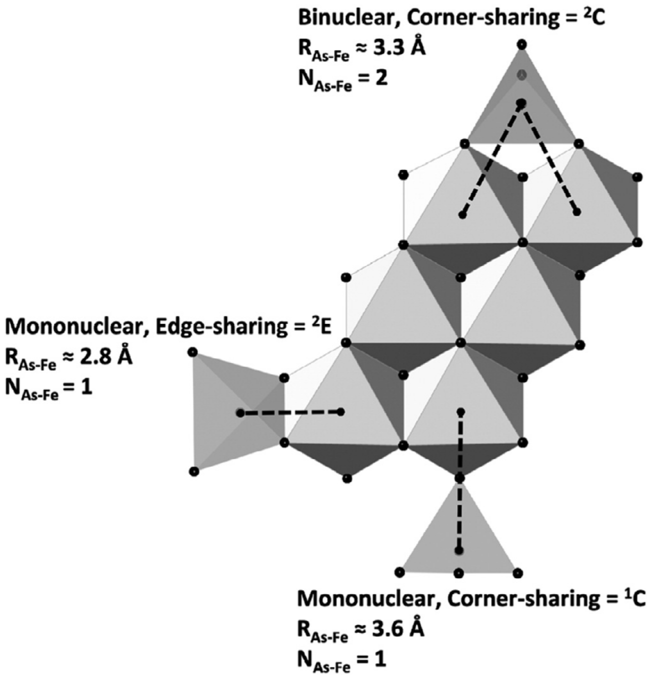

Fig. 8. Possible inner-sphere coordination geometries of AsO_4 tetrahedra bound to a cluster of FeO_6 octahedra [35].

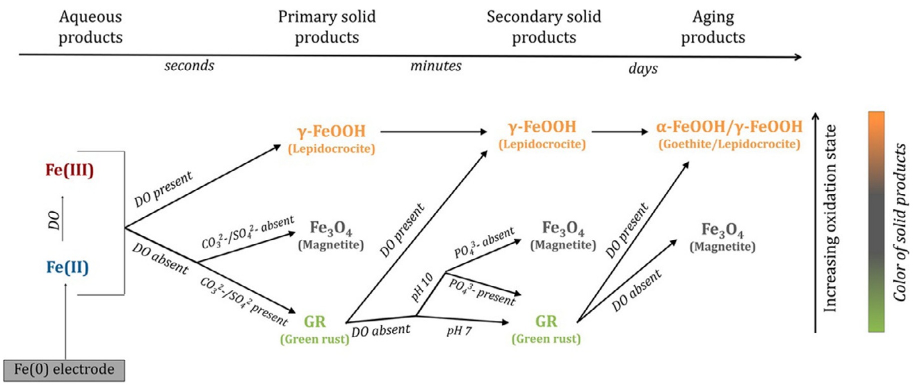

Fig. 9. Schematic diagram of the formation pathways of mixed-valent Fe hydr(oxide) phases generated by Fe(0) electrocoagulation [78].

[85]. In the present of dissolved oxygen (DO), EC products initially form as lepidocrocite (γ-FeOOH) within seconds and minutes, and the transformation from lepidocrocite to goethite (α-FeOOH) is observed with aging time. When DO is absent or very low, mixed-valent EC products, including magnetite and green rust (GR), generate in Fe(0) EC process. The production of magnetite as a primary product is detected in the absence of DO and intermediates such as CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}. In the presence of intermediates, GR generates as a precursor for lepidocrocite formation in aerobic environment and for magnetite formation in anaerobic environment. The transformation of GR with a smaller crystallite size into magnetite is slower and complicated depending on some parameters including electrolyte composition, pH, as well as aging conditions, which probably results in a loss of surface area. Additional studies are required to explore arsenic removal involved in the transformation of GR into magnetite, which is essential to optimize arsenic removal.

3.5.2.3. Hybrid Fe-Al electrode. With hybrid Fe-Al electrode, primarily amorphous and ultrafine structure at μm scale on the surface is observed by SEM image. EDS analysis of EC products confirms arsenic removal from the solution and reveals that the mass ratio between Fe and Al is about 5:4 [36]. XRD analysis verifies that the predominant phases of iron and aluminum hydroxide/oxyhydroxides are lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4), diaspore (γ-AlOOH), and bayerite ($Al(OH)_3$) respectively [13]. Some studies also confirms the formation of mansfieldite and symplesite [36,54]. XPS analysis indicates that Fe2p peaks are usually broad and presumably contain a mixture of iron species. With the concentration of arsenic increases, a slight shift to lower binding energy is taken place in Al2p peaks. There are two different peaks at 44.5 eV and 46.7 eV in As3d signal, which are identified as As(III) and As(V), respectively. It implies that at higher concentration (1000 ppm arsenic solution), As(III) is not only partly oxidized to As(V) in EC process for As(III) removal, but also removed by adsorption onto the flocs without transformation into As(V) [36].

Compared with Fe electrode, the crystallinity of lepidocrocite and magnetite significantly reduces, which is characterized by the diffractogram of EC products with hybrid Fe-Al electrodes, and several hydroxyl groups between aluminum and iron hydroxide/oxyhydroxides phases appear according to FT-IR analysis. It is probably attribute to the ionic replacement of iron by aluminum, confirming by Mossbauer spectroscopic analysis. Due to smaller ionic radius of aluminum, isomorphous substitution seems to disrupt the crystallization and leads to a larger surface area, which provides an alternative mechanism of arsenic removal with hybrid Fe-Al electrodes in EC process [36,86,87].

3.6. Mechanism involved arsenic removal in EC process

3.6.1. As(III) and As(V) removal in EC process

3.6.1.1. As(III) removal. Opinions are varied with regard to the mechanism involved in As(III) removal by electrocoagulation [88]. Some studies propose that As(III) is removed by adsorption onto metal hydroxides/oxyhydroxides and no significant As(III) oxidation is observed in EC process [39]. While some studies indicates that As(III) oxidation followed with As(V) adsorption onto the metal hydroxides/oxyhydroxides occurs in As(III) removal by electrocoagulation [11,20]. Besides, there is also an argument on the pathways of As(III) converted into As(V) in EC process. Some studies assume the possible generation of Cl_2 which is potential to oxidize As(III) [39,89–91], and some researchers propose the intermediate iron-containing species [11,92,93]. As we all know, As(III) is of higher mobility and solubility, and more toxic than As(V) [1]. Moreover, As(V) adsorption capacity is 3–20 times than that of As(III) in EC process [39]. Therefore, pre-oxidation of As (III) and subsequent adsorption of As(V) are the best way to remove As(III) by electrocoagulation [14,89]. Thus, it is urgent to shed light on the debate concerning the mechanism involved in As(III) oxidation during the EC process.

(1) As(III) oxidation in EC process

In comparison of As(III) and As(V) adsorption capacities based on the study of Lakshmanan et al. [39], no As(III) oxidation occurs in As(III) removal during the EC process. Contrary to the above phenomenon, some researches show that the concentration of As(V) initially improved and then reduced with the increase of treatment time in As(III) removal by electrocoagulation, which implies that more than 25% of As(III) are transformed into As(V) in EC process [11]. The declining concentrations of both As(V) and the total arsenic are attribute to the adsorption by metal hydroxides/oxyhydroxides in-situ generated in EC process [11,21]. In the absent of chloride and DO, As(III) is assumed to convert to As(V) by the electrodes or an intermediate as the oxidant [11,21,88]. Whereas studies shows that significantly less As(III) (<20%) is oxidized even at higher current density in EC process without chloride and dissolved oxygen, indicating As (III) oxidation by electrodes is not the main oxidative pathway [39]. It is also proposed that Fe(II) together with Fe(III) oxyhydroxides, form an Fe(IV) intermediate as rate enhancing species. However, detailed researches are recommended to further determine the feasibility of As(III) oxidation by Fe(IV) intermediate or explore the clear mechanism involved in As(III) oxidation during the EC process. In order to accelerate the oxidation rate, oxidation mediums such as dissolved oxygen (DO) or chlorine (Cl_2) are explored.

(2) As(III) oxidation with DO in EC process

DO may be produced as a result of the possible side reaction at the anode. However, the amount of oxygen is so small that it is not sufficient to oxidize As(III), especially in the presence of Fe(II). Accordingly, DO is supplied with pure oxygen or air injection. As expected, As(III) is favorably converted to As(V) with increasing aeration intensity [13]. It is also assumed that the oxidation rate is promoted by reactive intermediates represented as Fe(IV) generated in the oxidation of Fe(II). It plays a significant role in the rapid oxidation of As(III) as shown in Eq (3.14)(3.19) [92–95].

$$\mathrm{Fe}(II) + \mathrm{O_2} \rightarrow \mathrm{O_2^-} + \mathrm{Fe}(III) \quad (3.14)$$

$$\mathrm{Fe}(II) + \mathrm{O_2^-} + 2\mathrm{H^+} \rightarrow \mathrm{Fe}(III) + \mathrm{H_2O_2} \quad (3.15)$$

$$\mathrm{Fe}(II) + \mathrm{H_2O_2} \rightarrow \mathrm{intermediate(INT)} \quad (3.16)$$

$$\mathrm{(INT)} \rightarrow \mathrm{Fe}(IV) \quad (3.17)$$

That is to say,

$$3\mathrm{Fe}(II) + \mathrm{O_2} \rightarrow \mathrm{Fe}() + 2\mathrm{Fe(III)} \quad (3.18)$$

$$\mathrm{Fe(IV)} + \mathrm{As(III)} \rightarrow \mathrm{Fe(III)} + \mathrm{As}(V) \quad (3.19)$$

As(III) oxidation with DO is considered to be highly dependent on the iron/charge dosage rate in EC process using iron electrode. A lower iron/charge dosage rate is proved to be beneficial to As(III) oxidation, because the amount of DO required for the oxidation of Fe(II) is low. Nonetheless, the lower iron dosage rate results in a smaller number of iron hydroxides/oxyhydroxides and longer treatment time for arsenic removal. Conversely, with the iron/charge dosage rate increases, the oxidation behavior of As(III) during the EC process is analogous to chemical coagulation, where Fe (II) is added at one time, leading to lower As(III) oxidation. It is also reported that the intermediate oxidant relies on the pH of the solution, with the most likely oxidant being Fe(IV) at near-neutral pH [42,96]. When the pH value is lower than 6.8, nearly 90% of total iron are in the presence of Fe(II), and the oxidation rate of Fe(II) is slower, causing stronger competition for the intermediate oxidant. However, when pH value is higher than 7.8, almost complete oxidation of Fe(II) are obtained, and a large number of As(III) are oxidized to As(V) owing to the relatively weak competition from Fe(II) [14,94,95].

Overall, Fe(II) and reactive intermediates in continuous supply during the EC process with DO is better than the disposable dosing of Fe(II) salt. DO addition not only improves the reaction rate of As (III) oxidation, but also offers a necessary turbulent current condition for flocs to be in full collision and contact, finally resulting in better As(III) removal performance.

(3) As(III) oxidation with Cl_2 in EC process

Cl_2 production and As(III) oxidation in EC process are related to the electrode material when chloride ions exist in the solution.

With iron electrode as anode, It is not surprising that there is no occurrence of Cl_2 considering the existence of Fe(II) in outlet of EC reactor. Even if it is, it is used up attribute to Cl_2 demand of the Fe (0) and Fe(II) in EC process [39]. With graphite electrode as anode, Cl_2 generation is observed in the solution containing 71 mg/L chloride ions. Although the amount of Cl_2 generated by anodic oxidation in EC process is only 2%–5% of theoretical amount calculated according to Faraday's law, complete oxidation of As(III) is possible. With a combination of iron and graphite electrodes as anodes in the same EC reactor, no significant As(III) oxidation occurs due to approximately the same removal efficiency of both As(III) and the total arsenic. Besides, no Cl_2 generation is detected in the outlet of EC reactor, which is presumed due to the fact that Cl_2 once produced is immediately consumed by Fe(0) and Fe(II) during the EC process. However, the two-stage EC process is a result of almost complete As(III) oxidation in the first stage where Cl_2 is generated by anodic oxidation with graphite electrode, and subsequent As(V) removal by iron hydroxides/oxyhydroxides produced at iron anode in the second stage, which is highly recommended for As(III) removal during the EC process [39].

3.6.1.2. As(V) removal. When the concentration of As(V) is low (μg/L level), no As(V)-Al/Fe precipitates such as mansfieldite or symplesite are expected to form. As(V) is proposed to be removed by ligand exchange in EC process as reported in most previous studies [11]. As(V) substitutes for hydroxyl group of iron or aluminum hydroxides/oxyhydroxides, contributing to insoluble surface compounds as expressed in Eqs. (3.20)(3.23).

$$2\mathrm{FeOOH_{(S)}} + \mathrm{H_2AsO_4^-} \rightarrow \mathrm{(FeO)_2HAsO_4^-} + \mathrm{H_2O} + \mathrm{OH^-} \quad (3.20)$$

$$3\mathrm{FeOOH_{(S)}} + \mathrm{HAsO_4^{2-}} \rightarrow \mathrm{(FeO)_3AsO_{4(S)}} + \mathrm{H_2O} + 2\mathrm{OH^-} \quad (3.21)$$

$$mAl^{3+}_{(aq)} + (3\mathrm{m} - \mathrm{n})\mathrm{OH^-} + \mathrm{nHAsO^{2-}_{4(aq)}} \rightarrow \mathrm{Al_m(OH)_{(3m-n)}(HAsO_4)_{n(s)}} \quad (3.22)$$

$$\equiv \mathrm{Al} - \mathrm{OH_{(S)}} + \mathrm{HAsO^{2-}_{4(aq)}} \rightarrow \equiv \mathrm{Al} - \mathrm{OAs(O)_2(OH)^-_{(S)}} + \mathrm{(OH)^-_{(aq)}} \quad (3.23)$$

$$\mathrm{Al(OH)}_{3(S)} + AsO^{3-}_{4(aq)} \rightarrow [Al\mathrm{(OH)_3}\mathrm{As}O_4^{3-}]_{(S)} \quad (3.24)$$

where the symbol of $\equiv$ is applied to indicate the bonding of cations to the surface of metal hydroxides/oxyhydroxides [21,39,54].

Although few As(V)-Al/Fe precipitates such as mansfieldite or symplesite are found in EC process containing higher As(V) concentration (1000 ppm) [36,81], adsorption onto iron or aluminum hydroxides/oxyhydroxides is still the dominant removal mechanism of As(V) during the EC process.

3.6.2. Adsorption behavior of arsenic in EC process q_e

As mentioned above, arsenic is assumed to be mainly adsorbed onto the surface of iron or aluminum hydroxides/oxyhydroxides in-situ generated in EC process. Therefore, arsenic removal is analogous to conventional adsorption method except the production of flocs. As a result, adsorption kinetics, adsorption isotherms, and adsorption thermodynamics are recommended to further explore the adsorption behavior of arsenic removal by electrocoagulation.

According to Faraday's Law, the amount of flocs or coagulants mostly being iron or aluminum hydroxides/oxyhydroxides can be calculated stochiometrically as the following equations [97,98]:

$$q_e = (C_0 - C_e)V/W \quad (3.25)$$

$$W = ItM/(zF) \quad (3.26)$$

where (mg/g) is the amount of arsenic adsorbed at equilibrium, C_0 (mg/L) is the initial concentration, C_e (mg/L) is the equilibrium concentration, V (L) is the volume of the solution, and W (g) is the mass of adsorbent [98].

The suitability of the adsorption models is tested by chi-square (χ^2) [98,99]:

$$\chi^2 = (q_e^{exp} - q_e^{cal})^2/q_e^{cal} \quad (3.27)$$

where q_e^{exp} (mg/g) is the adsorption capacity of experimental equilibrium, and q_e^{cal} (mg/g) is the adsorption capacity of calculated equilibrium by Eq. (3.24). χ^2 is used to measure the goodness of fit between q_e^{exp} and q_e^{cal}. Generally, the most suitable model should possess a higher linear regression correlation coefficient of R^2 and a lower chi-square of χ^2 [100].

Table 3
Parameters of pseudo second order kinetic model in published studies.

Electrode	C_0 (mg/L)	q_e^{exp} (mg/g)	q_e^{cal} (mg/g)	k (g/(mg min))	R^2	Reference
Al alloy	1.0	0.948	0.899	0.450	0.9997	[41]
Fe	0.15	–	5.2	0.1431	0.99	[21]
Al	0.075	–	12.8	0.0242	0.98	[21]
Mild steel	1.25	1.186	1.186	0.3881	0.9994	[40]

Table 4
Parameters of Langmuir isotherm model in published studies.

Electrode	C_0 (mg/L)	q_{max} (mg/g)	k_L (L/mg)	R_L	R^2	Reference
Al alloy	0.5	55.959	0.0171	0.9831	0.9995	[41]
Mild steel	5–70	1937.5	0.0032	–	0.998	[107]
Al	25–75	4800	0.002	–	0.992	[46]
Mild steel	0.5–1.5	30.844	0.0895	0.9889	0.9992	[40]

3.6.2.1. Adsorption kinetics. To investigate the possible rate-limiting steps in adsorption process, chemical reactions as well as mass transport in EC process, adsorption kinetic models widely used as pseudo first order kinetic model, pseudo second order kinetic model, Elovich model, and intra-particle diffusion model are employed.

Under different initial concentrations with iron or aluminum electrode, the correlation coefficient value of R^2 is in the order of pseudo second order kinetic > pseudo first order kinetic > intra-particle diffusion > Elovich model, and q_e^{exp} agrees well with q_e^{cal}. Therefore, experimental data follows better with pseudo second order kinetic model than others [21,40,101]. The relationship of t/q_t vs t exhibits a linear behavior derived from pseudo second order kinetic model. As the initial concentration increases, the adsorbent capacity rises. While when the amounts of the dissolved metal ions enhance, the value of q_t declines [21,101]. Table 3 summarizes parameters of pseudo second order kinetic model in published studies. A good fitting with the empirical model of pseudo second order kinetic model suggests that chemisorption involving valence forces through the sharing or exchange of electrons between the adsorbent of metal hydroxides/oxyhydroxides and arsenic ions is the main rate-limiting step [100,102–106].

3.6.2.2. Adsorption isotherms. Langmuir, Freundlich, Dubinin-Redushkevich, and Frumkin isotherm models are employed to evaluate the correlation for adsorption isothermal equilibrium curves in arsenic removal during the EC process [46,77,107].

It can be concluded that under different initial arsenic concentrations, the regression coefficient values of R^2 decline in sequence of the Langmuir, Freundlich, Dubinin- Redushkevich, and Frumkin isotherm model, indicating that Langmuir isotherm model provides a good fit to experimental data with iron or aluminum electrode [46,101,107]. Table 4 summarizes parameters of Langmuir isotherm model in published studies. Namely, the adsorption behavior of arsenic on metal hydroxides/oxyhydroxides electrochemically generated in EC process follows a monolayer adsorption reaction. R_L, the equilibrium constant of Langmuir isotherm model, between 0 and 1, confirming the favorable arsenic adsorption during the EC process [46,100,107,108].

3.6.2.3. Adsorption thermodynamics. To assess the effects of temperature on adsorption behavior of arsenic during the EC process, thermodynamic parameters including Gibbs free energy change (ΔG), enthalpy change (ΔH), as well as entropy change (ΔS) are explored at various temperatures [100,108].

During the EC process, arsenic adsorption on metal hydroxides/oxyhydroxides is spontaneous and thermodynamically favorable indicated by the negative value of ΔG. The positive values of ΔH and ΔS, deriving from the slope and intercept of the van't Hoff linear plots of $\ln K_C$ vs $1/T$, respectively, implies that the adsorption process is endothermic in nature, and confirms the increased randomness of the solution interface during arsenic adsorption on the adsorbent [109,110]. Besides, the adsorption capacity increases as the enhancement of the temperature, which is possibly due to the activation of adsorbent surface or the enlargement of pore size [100,101,107,108].

3.7. Compared with other technologies for arsenic removal

Numerous remediation methods based on conventional technologies (eg. chemical coagulation, reverse osmosis, adsorption, bioflocculation, oxidation and ion exchange) and advanced technologies (eg. modified adsorption, biological process, electrocoagulation, DCMD, RO + MD) have been applied for arsenic removal from wastewaters [122–144]. These technologies are systematically and critically reviewed in this paper with attention to their performance, advantages as well as disadvantages as displayed in Table 5.

Either As(III) or As(Ⅴ) is removed directly in most of the conventional technologies. Obviously, compared with others, chemical coagulation is considered to be more effective and economical [39,111,7]. The common coagulants as iron salts and aluminum salts are used for arsenic removal in chemical coagulation process. As reported, As(V) removal efficiency can be achieved up to 99% while As(III) removal efficiency is only up to 40–50%. As a result, chemical coagulation is beneficial to As(V) removal but inefficient for As(III) removal [8,34,39,112]. Moreover, continuous requirement of chemicals, pH adjustment, large volumes of sludge, as well as the generation of the secondary pollutants have hampered the practical application of chemical coagulation [20].

In the past decades, efforts have been in direction of enhancing the removal efficiency of As especially As(III) and reducing the operating cost by modified traditional methods represented by modified adsorption or exploration of new methods with acceleration of As(III) oxidation [7]. For example, a novel adsorbent of Fe-Mn binary oxide (FMBO) material, combination of manganese dioxide with oxidation property and iron oxides with high adsorption capacity, is developed [113]. It is proved to be an attractive adsorbent for As(III) removal. However, cyclic utilization of FMBO becomes more difficult especially when FMBO is well dispersed into the water as nanoparticles, which need to be further modified [114–116]. A native As(III)-oxidizing bacterium named as As7325 is used to remove As(III) from groundwater [118]. 2300 μg/L As (III) are completely oxidized within 1 d under aerobic environment, and 1000 μg/L As(V) are removed at 6 d by As7325 cell pellets. The process is so time-consuming and strict with the

Table 5
Overall performances of technologies for As removal.

Technologies	Performance	Advantage	Disadvantage	Reference
Chemical coagulation	R.E. of As(V) achieved up to 99%, while R.E. of As(III) is only 40–50%.	R.E. for As(V) is high; Effective for the system with hard water and applicable for large water volume; Simple and low operating costs.	Poor As(III) removal; Continuous requirement of chemicals; pH adjustment; Large volumes of sludge	[34,7,112]
Reverse osmosis	> 90% As(V)can be removed from wastewaters.	Higher water quality; Treatment of a wide range of dissolved salts; No generation of toxic sludge.	R.E. for As(III) is very low; Higher operating costs; Requirement of membrane monitoring; Complicated pretreatment steps are often required; R.E. is low for high As contaminated wastewater.	[7,122,123]
Ion exchange	> 90% As can be removed from wastewaters.	R.E. is not dependent on the pH and initial As concentration; As removal is moderately effective.	As(III) is removed with prior oxidation; Interferences from other anions; It is easy to be blocked. Higher operating costs;	[7,124,125]
Adsorption	> 90% As(V) can be removed from wastewaters.	Comparatively cheap and commercially available; High R.E. of As(V).	Poor As(III) removal; Interferences from competitive anions; Adsorbent is difficult to remove and further environmental contamination may be possible	[7,126–129]
Bioflocculation	R.E. of As(V) is more than 90%.	Low operating costs; No secondary pollutants generation.	Low R.E. of As(III); Complicated and time-consuming process.	[130,132]
Oxidation (eg. O_3, H_2O_2, TiO_2)	Higher oxidation of As(III) to As(V) is achieved.	Simple process; Low operating costs; Applicable for large water volume.	Additional technology is essential for As(V) removal; Toxic chemicals or carcinogens may be produced as by-products	[119,134–139]
Advanced adsorption (eg. FMBO, ZVI)	Higher R.E. for both As(III) and As(V).	Modified adsorbent possesses higher surface area and pore volume; Simultaneous oxidation of As(III) and adsorption of As(V); Low operating costs.	Cyclic utilization is more difficult especially when the adsorbent is well dispersed into the water as nanoparticles.	[113–117,140]
Electrocoagulation	> 99% As can be removed from wastewater.	High R.E. of As; Easy to automatic control and Low maintenance costs; No addition of chemicals; No generation of the secondary pollutants; Low operating costs; Treatment of various wastewaters.	Oxidation film formed on the electrode hinders the flow of electric current; Sacrificial anodes need to be replaced periodically; In operating costs, the energy consumption is relatively high.	[9,13,14,20,21,31]
Direct contact membrane distillation (DCMD)	> 99% removal of As from groundwater	High R.E. of As(III) and As(V); No need for chemicals treatment and high pressure requirement; No generation of sludge;	Increasing concentration has an adverse effect on the process and As removal; High energy consumption; Polarization effect occurs.	[141–143]
Biological process(eg. As7325)	Higher R.E. for As removal.	As(III) is oxidized to As(V) with less toxicity and more affinity; Effective biosorptive capacity for As(V); Low operating costs.	The stability of the retained As(V) in the biomass in a more complicated water system requires further investigation; It is time-consuming and strict with operating conditions	[118,120,131,144]
Reverse osmosis + membrane distillation (RO + MD)	> 99% of As are removed.	High R.E. of As(III) and As(V); No generation of sludge; Compared with other RO process, he process is relatively costly.	Feed water flow rate significantly affects As removal; The process requires high energy consumption; Not suitable for treatment of wastewaters containing high As concentration.	[121]

R.E. Removal efficiency.

operating conditions although it provides a potential alternative for As(III) removal from groundwater [119,120]. Effective removals of both As(V) and As(III) without oxidant agents occurs by reverse osmosis followed with membrane distillation (RO + MD) technology. However, the process is significantly affected by the flow rate, and requires high amount of energy. Besides, it is not suitable for treatment of wastewaters containing high As concentration [8,121].

Among these advanced technologies, electrocoagulation displays its specific advantages. With oxidizing medium such as DO or chloride ions, As(III) are rapidly converted into As(V), and more than 99% As(III) removal efficiency is obtained in EC process with hybrid Fe-Al electrodes [13]. Accordingly, whether As(III) or As(V) removal, electrocoagulation presents better treatment performance [11]. Besides, additional advantages including lower quantity of sludge, no addition of the chemicals, no requirement of pH adjustment, easy to automatic control and so on, give rise to widespread application of electrocoagulation in treatment of various wastewater.

Recent work on arsenic removal by electrocoagulation are concentrated on batch scale of evaluation of EC performance at various operating conditions or investigation of arsenic adsorption behavior in EC process, but lack of application in larger scales. It also suffers from some limitations or drawbacks such as passive oxide films formed easily on the electrode and high energy consumption hindering its development in extensive application. Besides, modeling of multiphysics field in EC process is necessary to systematically estimate the feasibility of EC reactor design, and to enhance the configuration of EC reactors for future applications. Extensive studies are therefore carried out to overcome the above limitations and design a more efficient EC reactor, providing a deep understanding of EC process.

3.8. Future recommendations for arsenic removal by electrocoagulation

Based on this review, the primary aspects of future researches on arsenic removal in EC process are proposed as follows:

(1) Among the factors limiting widespread application of electrocoagulation, electricity consumption, as one of the major operating cost in EC process, should be given priority. Since large scales and continuous operation of EC process for arsenic removal from wastewaters require considerable power. With the rapid development of green energy, application of renewable energy sources such as solar energy, biochemical fuel cell, as well as wind energy for continuous EC operation is considered to be cost effective and environmentally friendly [88]. As a result, the technology of green energy coupling with electrocoagulation seems to be promising in large scale of arsenic removal from wastewaters by electrocoagulation.

(2) In order to solve the problems such as passivation encountered in operation of EC process, the configuration of EC reactor is required to be optimized. In EC systems, a range of physical phenomena are related to the interaction of multiphysics field including flow field, electric field as well as temperature field, which can be mathematically described by partial differential equations (PDEs). On the basis of the finite element method, COMSOL Multiphysics provides solutions by solving PDE or PDEs for one type of physics or multiphysics modeling.

Among a series of physical interfaces, Computational fluid dynamic (CFD) module, on the basis of conservation laws of mass, momentum and energy, turns out to be accurate to describe the hydrodynamics of EC process by defining specific initial values and boundary conditions. Electrochemistry module, on the basis of Faraday's law, Nernst-Planck equation, and current conservation equation in the electrolyte, can accomplish the simulation of potential and current distributions, and the transport of chemical species in the electrolyte. Heat transfer module, on the basis of the law of conservation of energy, is able to perform computations with respect to conduction or convection in EC process. Unparalleled capability in COMSOL Multiphysics is that the physical interfaces of CFD module, electrochemistry module, and heat transfer module can be seamlessly coupled for a full multiphysics simulation, which simplifies the assessment of the impacts of EC reactors configurations. This approach is not only beneficial to design an efficient and energy-saving EC reactor, but also in favor of further understanding of the EC performance [145–148].

(3) In EC process with Al electrode, Al_{13} polymer has been considered to be the most active species responsible for coagulation. However, the effects of Al_{13} polymer formation and distribution on arsenic removal, as well as arsenic transformation in EC process have been not yet clear, which requires further investigation. In EC process with hybrid Fe-Al electrodes, although some studies have been carried out to improve arsenic removal efficiency, little research has been focused on production and transformation of EC products with hybrid Fe-Al electrodes, which is associated with the removal mechanism of arsenic. Besides, the electrochemical pathways in EC process and the influence of primary factors on the phase and morphology of EC products with hybrid Fe-Al electrodes are not well documented. Accordingly, it is necessary to apply multiple characterization techniques to explore the effects of Al_{13} polymer on arsenic removal, and identify arsenic transformation and the phases of EC products in different chemical environments.

4. Conclusions

Arsenic removal by electrocoagulation has attracted increasing attention in recent years. This review outlines the effects and optimization of operating parameters on arsenic removal efficiency and operation costs, mainly including electrode material, current density, pH, coexisting ions and oxidation state. The physical factors such as continuous or batch operation, reactor geometry, electrode connection modes, electrode distance as well as surface area to volume ratio (A/V) are considered to design an efficiency and energy-saving EC reactor. Besides, this review summarizes the characteristics of EC products with various electrodes by multiple characterization techniques. Furthermore, As(III) oxidation in EC process at different chemical environments are comprehensively clarified, and the adsorption behavior of arsenic removal in EC process is further explored. Compared with other technologies, electrocoagulation turns out to be an environmentally friendly and effective method for arsenic removal from wastewaters. However, it is subject to some limitations such as high energy consumption in large scales and difficulty of EC reactor design, which seriously impeding its wide application. As a result, further studies are recommended to overcome the drawbacks to enlarge the practical application and deeply explore the EC performance of arsenic removal.

Acknowledgements

We are grateful for the financial support of National Natural Science Foundation of China (Grants Nos. 51578223, 51378189 and 51521006).

References

[1] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.
[2] N. Singh, D. Kumar, A. Sahu, Arsenic in the environment: effects on human health and possible prevention, J. Environ. Biol. 28 (2007) 359–365.
[3] M.M. Karim, Arsenic in groundwater and health problems in Bangladesh, Water Res. 34 (2000) 304–310.
[4] L. Rodríguez-Lado, G. Sun, M. Berg, Q. Zhang, H. Xue, Q. Zheng, C.A. Johnson, Groundwater arsenic contamination throughout China, Science 341 (2013) 866–868.
[5] M. Argos, T. Kalra, P. Rathouz, Y. Chen, B. Pierce, F. Parvez, T. Islam, A. Ahmed, M. Rakibuz-Zaman, R. Hasan, G. Sarwar, V. Slavkovich, A. van Geen, J. Graziano, H. Ahsan, Arsenic exposure from drinking water, and all-cause and chronic-disease mortalities in Bangladesh (HEALS): a prospective cohort study, Lancet 376 (2010) 252–258.
[6] W.R. Cullen, K.J. Reimer, Arsenic speciation in the environment, Chem. Rev. 89 (1989) 713–764.
[7] P. Mondal, C.B. Majumder, B. Mohanty, Laboratory based approaches for arsenic remediation from contaminated water: recent developments, J. Hazard. Mater. 137 (2006) 464–479.
[8] P. Mondal, S. Bhowmick, D. Chatterjee, A. Figoli, B. Van der Bruggen, Remediation of inorganic arsenic in groundwater for safe water supply: a critical assessment of technological solutions, Chemosphere 92 (2013) 157–170.
[9] G. Ungureanu, S. Santos, R. Boaventura, C. Botelho, Arsenic and antimony in water and wastewater: overview of removal techniques with special reference to latest advances in adsorption, J. Environ. Manage. 151 (2015) 326–342.
[10] O. Sahu, B. Mazumdar, P.K. Chaudhari, Treatment of wastewater by electrocoagulation: a review, Environ. Sci. Pollut. R. 21 (2014) 2397–2413.
[11] W. Wan, T.J. Pepping, T. Banerji, S. Chaudhari, D.E. Giammar, Effects of water chemistry on arsenic removal from drinking water by electrocoagulation, Water Res. 45 (2011) 384–392.
[12] M.M. Emamjomeh, M. Sivakumar, Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes, J. Environ. Manage. 90 (2009) 1663–1679.
[13] P. Song, Z. Yang, H. Xu, J. Huang, X. Yang, L. Wang, Investigation of influencing factors and mechanism of antimony and arsenic removal by electrocoagulation using Fe-Al electrodes, Ind. Eng. Chem. Res. 53 (2014) 12911–12919.
[14] L. Li, C.M. van Genuchten, S.E. Addy, J. Yao, N. Gao, A.J. Gadgil, Modeling As (III) oxidation and removal with iron electrocoagulation in groundwater, Environ. Sci. Technol. 46 (2012) 12038–12045.

[15] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, Electrocoagulation of potable water, Water Res. 18 (1984) 1355–1360.

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

[17] C.A. Basha, S.J. Selvi, E. Ramasamy, S. Chellammal, Removal of arsenic and sulphate from the copper smelting industrial effluent, Chem. Eng. J. 141 (2008) 89–98.

[18] B. Merzouk, B. Gourich, A. Sekki, K. Madani, C. Vial, M. Barkaoui, Studies on the decolorization of textile dye wastewater by continuous electrocoagulation process, Chem. Eng. J. 149 (2009) 207–214.

[19] C.L. Lai, S.H. Lin, Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication, Chem. Eng. J. 95 (2003) 205–211.

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

[21] M. Kobya, U. Gebologlu, F. Ulua, S. Oncela, Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes, Electrochim. Acta 56 (2011) 5060–5070.

[22] Z. Zaroual, M. Azzi, N. Saib, E. Chaînet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, J. Hazard. Mater. 131 (2006) 73–78.

[23] E. Bazrafshan, L. Mohammadi, A. Ansari-Moghaddam, A.H. Mahvi, Heavy metals removal from aqueous environments by electrocoagulation process-a systematic review, J. Environ. Health 13 (2015) 1.

[24] J.H. Qu, H.J. Liu, Electrochemical Principles and Techniques in Water Treatment, Science Press, Beijing, 2007, pp 205-209.

[25] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, J. Hazar. Mater. 100 (2003) 163–178.

[26] C. Hu, S. Wang, J. Sun, H. Liu, J. Qu, An effective method for improving electrocoagulation process: optimization of Al 13 polymer formation, Colloids Surface. A 489 (2016) 234–240.

[27] C. Hu, H. Liu, G. Chen, J. Qu, Effect of aluminum speciation on arsenic removal during coagulation process, Sep. Purif. Technol. 86 (2012) 35–40.

[28] M. Mechelhoff, G.H. Kelsall, N.J. Graham, Electrochemical behaviour of aluminium in electrocoagulation processes, Chem. Eng. Sci. 95 (2013) 301–312.

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

[30] I. Linares-Hernández, C. Barrera-Díaz, G. Roa-Morales, B. Bilyeu, F. Ureña-Núñez, Influence of the anodic material on electrocoagulation performance, Chem. Eng. J. 148 (2009) 97–105.

[31] J.A. Gomes, M.S. Rahman, K. Das, S. Varma, D.A. Cocke, Comparative electrochemical study on arsenic removal using iron, aluminum, and copper electrodes, ECS Trans. 25 (2010) 59–68.

[32] A. Maldonado-Reyes, C. Montero-Ocampo, O. Solorza-Feria, Remediation of drinking water contaminated with arsenic by the electro-removal process using different metal electrodes, J. Environ. Mon. 9 (2007) 1241–1247.

[33] E. Lacasa, P. Canizares, C. Sáez, F.J. Fernández, M.A. Rodrigo, Removal of arsenic by iron and aluminium electrochemically assisted coagulation, Sep. Purif. Technol. 79 (2011) 15–19.

[34] J.G. Hering, P.Y. Chen, J.A. Wilkie, M. Elimelech, Arsenic removal by ferric chloride, J. Am. Water Works Assoc. 88 (1996) 155–167.

[35] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)-science and applications, J. Hazard. Mater. 84 (2001) 29–41.

[36] J.A.G. Gomes, P. Daida, M. Kesmez, M. Weir, H. Moreno, J.R. Parga, G. Irwin, H. McWhinney, T. Grady, E. Peterson, D.L. Cocke, Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products, J. Hazar. Mater. 139 (2007) 220–231.

[37] USEPA, Technologies and costs for removal of arsenic from drinking water, Tech. Report no. EPA-815-r-00–028. USEPA, 2000.

[38] M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas, M.S. Oncel, Treatment of potable water containing low concentration of arsenic with electrocoagulation: Different connection modes and Fe-Al electrodes, Sep. Purif. Technol. 77 (2011) 283–293.

[39] D. Lakshmanan, D.A. Clifford, G. Samanta, Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation, Water Res. 44 (2010) 5641–5652.

[40] S. Vasudevan, J. Lakshmi, G. Sozhan, Studies relating to removal of arsenate by electrochemical coagulation: optimization, kinetics, coagulant characterization, Sep. Sci. Technol. 45 (2010) 1313–1325.

[41] S. Vasudevan, J. Lakshmi, G. Sozhan, Studies on the removal of arsenate by electrochemical coagulation using aluminum alloy anode, Clean Soil Air Water 38 (2010) 506–515.

[42] C.M. van Genuchten, S.E. Addy, J. Peña, A.J. Gadgil, Removing arsenic from synthetic groundwater with iron electrocoagulation: an Fe and As K-edge EXAFS study, Environ. Sci. Technol. 46 (2012) 986–994.

[43] M. Kobya, E. Senturka, M. Bayramoglub, Treatment of poultry slaughterhouse wastewaters by electrocoagulation, J. Hazard. Mater. 133 (2006) 172–176.

[44] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res. 37 (2003) 4513–4523.

[45] X.G. Meng, G.P. Korfiatis, S.B. Bang, K.W. Bang, Combined effects of anions on arsenic removal by iron hydroxides, Toxicol. Lett. 133 (2002) 103–111.

[46] N. Balasubramanian, T. Kojima, C. Srinivasakannan, Arsenic removal through electrocoagulation: kinetic and statistical modeling, Chem. Eng. J. 155 (2009) 76–82.

[47] R. Saravanathamizhan, N. Mohan, N. Balasubramanian, V. Ramamurthi, C. Ahmed Basha, Evaluation of electro oxidation of textile effluent using response surface technique, Clean Soil Air, Water 35 (2007) 355–361.

[48] M. Kobya, E. Demirbas, U. Gebologlu, M.S. Oncel, Y. Yildirim, Optimization of arsenic removal from drinking water by electrocoagulation batch process using response surface methodology, Desalin. Water Treat. 51 (2013) 6676–6687.

[49] R.H. Myers, D.C. Montgomery, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, second ed., John Wiley and Sons, New York, NY, 2002.

[50] T. Olmez, The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology, J. Hazard. Mater. 162 (2009) 1371–1378.

[51] P. Song, Z. Yang, H. Xu, J. Huang, X. Yang, F. Yue, L. Wang, Arsenic removal from contaminated drinking water by electrocoagulation using hybrid Fe-Al electrodes: response surface methodology and mechanism study, Desalin. Water Treat. 57 (2016) 4548–4556.

[52] S. Mahesh, B. Prasad, I.D. Mall, I.M. Mishra, Electrochemical degradation of pulp and paper mill wastewater. Part 2. Characterization and analysis of sludge, Ind. Eng. Chem. Res. 45 (2006) 5766–5774.

[53] H.K. Hansen, P. Nunez, C. Ji, Removal of arsenic from wastewaters by airlift electrocoagulation. Part 1: batch reactor experiments, Sep. Sci. Technol. 43 (2008) 212–224.

[54] M. Kobya, A. Akyol, E. Demirbas, M.S. Oncel, Removal of arsenic from drinking water by batch and continuous electrocoagulation processes using hybrid Al-Fe plate electrodes, Environ. Prog. Sustainable 33 (2014) 131–140.

[55] Z.H. Yang, H.Y. Xu, G.M. Zeng, Y.L. Luo, X. Yang, J. Huang, P.P. Song, The behavior of dissolution/passivation and the transformation of passive films during electrocoagulation: influences of initial pH, Cr (VI) concentration, and alternating pulsed current, Electrochim. Acta 153 (2015) 149–158.

[56] O. Levenspiel, Chemical reaction engineering, Ind. Eng. Chem. Res. 38 (1999) 4140–4143.

[57] H.K. Hansen, P. Nunez, D. Raboy, I. Schippacasse, R. Grandon, Electrocoagulation in wastewater containing arsenic: comparing different process designs, Electrochim. Acta 52 (2007) 3464–3470.

[58] Y.A. Mollah Mohammad, M. Paul, A.G.G. Jewel, M. Kesmez, J. Parga, L.C. David, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. 114 (2004) 199–210.

[59] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, Water Res. 32 (1998) 1604–1612.

[60] D. Mills, A new process for electrocoagulation, J. Am. Water Works Asssoc. 92 (2000) 34.

[61] M.Y.A. Mollah, S.R. Pathak, P.K. Patil, M. Vayuvegula, T.S. Agrawal, J.A. Gomes, D.L. Cocke, Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes, J. Hazard. Mater. 109 (2004) 165–171.

[62] J.Q. Jiang, N.J.D. Graham, C.M. André, G.H. Kelsall, N.P. Brandon, Laboratory study of electro-coagulation-flotation for water treatment, Water Res. 36 (2002) 4064–4078.

[63] J.Q. Jiang, N.J.D. Graham, C.M. André, G.H. Kelsall, N.P. Brandon, M.J. Chipps, Comparative performance of an electrocoagulation/flotation system with chemical coagulation/dissolved air flotation: a pilot-scale trial, Water Sci. Technol. Water Supply 2 (2002) 289–297.

[64] P. Holt, G. Barton, C. Mitchell, Electrocoagulation as a wastewater treatment, The third annual Australian environmental engineering research event 1000 (1999) 41-46.

[65] F. Walsh, G. Mills, Electrochemical methods for pollution control, Chem. Technol. Eur. 1 (1994) 13–18.

[66] M. Asselin, P. Drogui, H. Benmoussa, J.F. Blais, Effectiveness of electrocoagulation process in removing organic compounds from slaughterhouse wastewater using monopolar and bipolar electrolytic cells, Chemosphere 72 (2008) 1727–1733.

[67] N. Modirshahla, M.A. Behnajady, S. Kooshaiian, Investigation of the effect of different electrode connections on the removal efficiency of Tartrazine from aqueous solutions by electrocoagulation, Dyes Pigm. 74 (2007) 249–257.

[68] A.K. Golder, A.N. Samanta, S. Ray, Removal of Cr^{3+} by electrocoagulation with multiple electrodes: bipolar and monopolar configurations, J. Hazard. Mater. 141 (2007) 653–661.

[69] M. Kobya, M. Bayramoglu, M. Eyvaz, Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections, J. Hazard. Mater. 148 (2007) 311–318.

[70] J.F. Martinez-Villafane, C.M. Ocampo, A.M. Garcia-Lara, Energy and electrode consumption analyses of electrocoagulation for the removal of arsenic from underground water, J. Hazard. Mater. 172 (2009) 1617–1622.

[71] E. Mohora, S. Rončević, B. Dalmacija, J. Agbaba, M. Watson, E. Karlović, M. Dalmacija, Removal of natural organic matter and arsenic from water by electrocoagulation/flotation continuous flow reactor, J. Hazard. Mater. 235 (2012) 257–264.

[72] C. Phalakornkule, S. Polgumhang, W. Tongdaung, Performance of an electrocoagulation process in treating direct dye: batch and continuous upflow processes, World Acad. Sci. Eng. Technol. 57 (2009) 277–282.

[73] C. Wang, W.L. Chou, Y.M. Kuo, Removal of COD from laundry wastewater by electrocoagulation/electroflotation, J. Hazard. Mater. 164 (2009) 81–86.
[74] I.A. Zolotukhin, A pilot-scale system for the treatment of mine water by electro-coagulation/flotation, Sov. J. Water Chem. Tech. 11 (1989) 147–151.
[75] J.C. Donini, J. Kan, J. Szynkarczuk, T.A. Hassan, K.L. Kar, The operating cost of electrocoagulation, Can. J. Chem. Eng. 72 (1994) 1007–1012.
[76] M. Kobya, S. Delipinar, Treatment of the baker's yeast wastewater by electrocoagulation, J. Hazard. Mater. 154 (2008) 1133–1140.
[77] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, Sep. Purif. Technol. 37 (2004) 117–125.
[78] J.B. Dixon, S.B. Weed (Eds.), Minerals in Soil Environments, 2nd ed., Soil Science Society of America, Madison, WI, 1989, pp. 331–378.
[79] http://www.mc.mat.shibaura-it.ac.jp/~plaza/chap211.html, (accessed in June, 2005).
[80] A. Guzmán, J.L. Nava, O. Coreño, I. Rodríguez, S. Gutiérrez, Arsenic and fluoride removal from groundwater by electrocoagulation using a continuous filter-press reactor, Chemosphere 144 (2016) 2113–2120.
[81] J.R. Parga, D.L. Cocke, J.L. Valenzuela, J.A. Gomes, M. Kesmez, G. Irwin, M. Weir, Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera Mexico, J. Hazard. Mater. 124 (2005) 247–254.
[82] A. Maldonado-Reyes, C. Montero-Ocampo, J. Medina-Garcia, S. Bolado-Rodríguez, J. Alvárez-Benedí, A. Herrera-Vazquez, V.M. Castaño, Electrocoagulation removal of As from water: the role of phases formation, Water Air Soil Pollut. 226 (2015) 1–6.
[83] B.M. Toner, C.M. Santelli, M.A. Marcus, R. Wirth, C.S. Chan, T. McCollom, W. Bach, K.J. Edwards, Biogenic iron oxyhydroxide formation at mid-ocean ridge hydrothermal vents: Juan de Fuca Ridge, Geochim. Cosmochim. Acta 73 (2009) 388–403.
[84] G. Ona-Nguema, G. Morin, F. Juillot, G. Calas, G.E. Brown, EXAFS analysis of arsenite adsorption onto two-line ferrihydrite, hematite, goethite, and lepidocrocite, Environ. Sci. Technol. 39 (2005) 9147–9155.
[85] K.L. Dubrawski, C.M. van Genuchten, C. Delaire, S.E. Amrose, A.J. Gadgil, M. Mohseni, Production and transformation of mixed-valent nanoparticles generated by Fe (0) electrocoagulation, Environ. Sci. Technol. 49 (2015) 2171–2179.
[86] Y. Masue, R. Loeppert, T. Kramer, Adsorption, Desorption and Stabilization Behavior of Arsenic on Ferrihydrite and Al-substituted Analogs. Progress Report, Department of Soil and Crops Sciences, Texas A&M University: College Station, TX, 2004.
[87] T. Satapanajaru, S.D. Comfort, P.J. Shea, Enhancing metolachlor destruction rates with aluminum and iron salts during zerovalent iron treatment, J. Environ. Qual. 32 (2003) 1726–1734.
[88] W. Wan, Arsenic removal from drinking water by electrocoagulation, 2010.
[89] J. Kim, A.B. Velichenko, G.V. Korshin, Effect of selected water quality parameters on electrochemical oxidation of arsenite in drinking water, Proc. Annu. AWWA Conf., 2002.
[90] M. Han, J. Song, A. Kwon, Preliminary investigation of electrocoagulation as a substitute for chemical coagulation, Water Sci. Technol. 2 (2002) 73–76.
[91] X.M. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Separ. Purif. Technol. 19 (2000) 65–76.
[92] K.J. Bisceglia, K.J. Rader, R.F. Carbonaro, K.J. Farley, J.D. Mahony, D.M. DiToro, Iron(II)-catalyzed oxidation of arsenic(III) in a sediment column, Environ. Sci. Technol. 39 (2005) 9217–9222.
[93] K. Amstaetter, T. Borch, P. Larese-Casanova, A. Kappler, Redox transformation of arsenic by Fe(II)-activated goethite (alpha-FeOOH), Environ. Sci. Technol. 44 (2010) 102–108.
[94] M.C. Ciardelli, H.F. Xu, N. Sahai, Role of Fe(II), phosphate, silicate, sulfate, and carbonate in arsenic uptake by coprecipitation in synthetic and natural groundwater, Water Res. 42 (2008) 615–624.
[95] N. Sahai, Y.J. Lee, H.F. Xu, M. Ciardelli, J.F. Gaillard, Role of Fe(II) and phosphate in arsenic uptake by coprecipitation, Geochim. Cosmochim. Ac. 71 (2007) 3193–3210.
[96] S.J. Hug, O. Leupin, Iron-catalyzed oxidation of arsenic (III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction, Environ. Sci. Technol. 37 (2003) 2734–2742.
[97] İ.A. Şengil, Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes, J. Hazard. Mater. 137 (2006) 1197–1205.
[98] M.H. Isa, E.H. Ezechi, Z. Ahmed, S.F. Magram, S.R.M. Kutty, Boron removal by electrocoagulation and recovery, Water Res. 51 (2014) 113–123.
[99] C.S. Sundaram, N. Viswanathan, S. Meenakshi, Defluoridation chemistry of synthetic hydroxyapatite at nanoscale: equilibrium and kinetic studies, J. Hazard. Mater. 155 (2008) 206–215.
[100] P. Song, Z. Yang, G. Zeng, X. Yang, H. Xu, J. Huang, L. Wang, Optimization, kinetics, isotherms, and thermodynamics studies of antimony removal in electrocoagulation process, Water Air Soil Pollut. 226 (2015) 1–12.
[101] A.M. García-Lara, C. Montero-Ocampo, Improvement of arsenic electro-removal from underground water by lowering the interference of other ions, Water Air Soil Pollut. 205 (2010) 237–244.
[102] Y.A. Aydin, N.D. Aksoy, Adsorption of chromium on chitosan: optimization, kinetics and thermodynamics, Chem. Eng. J. 151 (2009) 188–194.
[103] X.M. Dou, D. Mohan, X.Q. Zhao, C.U. Pittman, Antimonate removal from water using hierarchical macro-mesoporous amorphous alumina, Chem. Eng. J. 264 (2015) 617–624.
[104] X.J. Guo, Z.J. Wu, M.C. He, X.G. Meng, X. Jin, N. Qiu, J. Zhang, Adsorption of antimony onto iron oxyhydroxides: adsorption behavior and surface structure, J. Hazard. Mater. 276 (2014) 339–345.
[105] M. Vithanage, A.U. Rajapaksha, X.M. Dou, N.S. Bolan, J.E. Yang, Y.S. Ok, Surface complexation modeling and spectroscopic evidence of antimony adsorption on ironoxide-rich red earth soils, J. Colloid Interface Sci. 406 (2013) 217–224.
[106] C. García-Gómez, M.L. Rivera-Huerta, F. Almazán-García, A. Martín-Domínguez, I.C. Romero-Soto, V.A. Burboa-Charis, P. Gortáres-Moroyoqui, Electrocoagulat- ed metal hydroxide sludge for fluoride and arsenic removal in aqueous solution: characterization, kinetic, and equilibrium studies, Water Air Soil Pollut. 227 (2016) 1–16.
[107] N. Balasubramanian, T. Kojima, C.A. Basha, C. Srinivasakannan, Removal of arsenic from aqueous solution using electrocoagulation, J. Hazard. Mater. 167 (2009) 966–969.
[108] P. Ganesan, J. Lakshmi, G. Sozhan, S. Vasudevan, Removal of manganese from water by electrocoagulation: adsorption, kinetics and thermodynamic studies, Can. J. Chem. Eng. 91 (2013) 448–458.
[109] B. Manna, U.C. Ghosh, Adsorption of arsenic from aqueous solution on synthetic hydrous stannic oxide, J. Hazard. Mater. 144 (2007) 522–531.
[110] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydride: kinetics, equilibrium and adsorption envelopes, Environ. Sci. Tech. 32 (1998) 344–349.
[111] G. Ghurye, D.A. Clifford, A.R. Tripp, Pilot study of coagulation microfiltration for arsenic removal from groundwater, J. Am. Water Works Assoc. 96 (2004) 143–152.
[112] R.C. Cheng, S. Liang, H.C. Wang, M.D. Beuhler, Enhanced coagulation for arsenic removal, J. Am. Water Works Assoc. 86 (1994) 79–90.
[113] G. Zhang, J. Qu, H. Liu, R. Liu, R. Wu, Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal, Water Res. 41 (2007) 1921–1928.
[114] X. Li, K. He, B. Pan, S. Zhang, L. Lu, W. Zhang, Efficient As (III) removal by macroporous anion exchanger-supported Fe-Mn binary oxide: behavior and mechanism, Chem. Eng. J. 193 (2012) 131–138.
[115] G. Zhang, H. Liu, R. Liu, J. Qu, Adsorption behavior and mechanism of arsenate at Fe–Mn binary oxide/water interface, J. Hazard. Mater. 168 (2009) 820–825.
[116] G. Zhang, J. Qu, H. Liu, R. Liu, G. Li, Removal mechanism of As (III) by a novel Fe-Mn binary oxide adsorbent: oxidation and sorption, Environ. Sci. Technol. 41 (2007) 4613–4619.
[117] X. Luo, C. Wang, S. Luo, R. Dong, X. Tu, G. Zeng, Adsorption of As(III) and As(V) from water using magnetite Fe_3O_4-reduced graphite oxide-MnO_2 nanocomposites, Chem. Eng. J. 187 (2012) 45–52.
[118] A.C. Kao, Y.J. Chu, F.L. Hsu, V.H.C. Liao, Removal of arsenic from groundwater by using a native isolated arsenite-oxidizing bacterium, J. Contam. Hydrol. 155 (2013) 1–8.
[119] J.K. Myoung, N. Jerome, Oxidation of arsenate in ground water using ozone and oxygen, Sci. Total Environ. 247 (2000) 71–79.
[120] A. Ito, J.I. Miura, N. Ishikawa, T. Umita, Biological oxidation of arsenite in synthetic groundwater using immobilised bacteria, Water Res. 46 (2012) 4825–4831.
[121] F. Macedonio, E. Drioli, Pressure-driven membrane operations and membrane distillation technology integration for water purification, Desalination 223 (2008) 396–409.
[122] P. Xu, M. Capito, T.Y. Cath, Selective removal of arsenic and monovalent ions from brackish water reverse osmosis concentrate, J. Hazard. Mater. 260 (2013) 885–891.
[123] R.Y. Ning, Arsenic removal by reverse osmosis, Desalination 143 (2002) 237–241.
[124] J. Kim, M.M. Benjamin, Modeling a novel ion exchange process for arsenic and nitrate removal, Water Res. 38 (2004) 2053–2062.
[125] E. Korngold, N. Belayev, L. Aronov, Removal of arsenic from drinking water by anion exchangers, Desalination 141 (2001) 81–84.
[126] S. Dixit, J.G. Hering, Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility, Environ. Sci. Technol. 37 (2003) 4182–4189.
[127] B.A. Manning, S. Goldberg, Adsorption and stability of arsenic (III) at the clay mineral-water interface, Environ. Sci. Technol. 31 (1997) 2005–2011.
[128] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.
[129] S.H. Yoon, J.H. Lee, S.E. Oh, J.E. Yang, Photochemical oxidation of As(III) by vacuum-UV lamp irradiation, Water Res. 42 (2008) 3455–3463.
[130] H. Zhao, C. Zhong, H. Chen, J. Yao, L. Tan, Y. Zhang, J. Zhou, Production of bioflocculants prepared from formaldehyde wastewater for the potential removal of arsenic, J. Environ. Manage. 172 (2016) 71–76.
[131] A. Sarı, Ö.D. Uluozlü, M. Tüzen, Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (Maugeotia genuflexa) biomass, Chem. Eng. J. 167 (2011) 155–161.
[132] J. Lin, C. Harichund, Industrial effluent treatments using heavy-metal removing bacterial bioflocculants, Water SA 37 (2011) 265–270.
[133] D.L. Huang, G.M. Zeng, C.L. Feng, S. Hu, X.Y. Jiang, L. Tang, H.L. Liu, Degradation of lead-contaminated lignocellulosic waste by Phanerochaete chrysosporium and the reduction of lead toxicity, Environ. Sci. Technol. 42 (2008) 4946–4951.
[134] P.K. Dutta, A.K. Ray, V.K. Sharma, F.J. Millero, Adsorption of arsenate and arsenite on titanium dioxide suspensions, J. Colloid Interface Sci. 278 (2004) 270–275.

[135] T. Luo, J. Cui, S. Hu, Y. Huang, C. Jing, Arsenic removal and recovery from copper smelting wastewater using TiO_2, Environ. Sci. Technol. 44 (2010) 9094–9098.

[136] L. Tang, G.M. Zeng, G.L. Shen, Y.P. Li, Y. Zhang, D.L. Huang, Rapid detection of picloram in agricultural field samples using a disposable immunomembrane-based electrochemical sensor, Environ. Sci. Technol. 42 (2008) 1207–1212.

[137] Y. Li, J.R. Liu, S.Y. Jia, J.W. Guo, J. Zhuo, P. Na, TiO_2 pillared montmorillonite as a photoactive adsorbent of arsenic under UV irradiation, Chem. Eng. J. 191 (2012) 66–74.

[138] H.V. Aposhian, R.A. Zakharyan, M.D. Avram, M.J. Kopplin, M.L. Wollenberg, Oxidation and detoxification of trivalent arsenic species, Toxicol. Appl. Pharm. 193 (2003) 1–8.

[139] M.J. Kim, J. Nriagu, Oxidation of arsenite in groundwater using ozone and oxygen, Sci. Total Environ. 247 (2000) 71–79.

[140] H. Zhu, Y. Jia, X. Wu, H. Wang, Removal of arsenic from water by supported nano zero-valent iron on activated carbon, J. Hazard. Mater. 172 (2009) 1591–1596.

[141] D. Qu, J. Wang, D. Hou, Z. Luan, B. Fan, C. Zhao, Experimental study of arsenic removal by direct contact membrane distillation, J. Hazard. Mater. 163 (2009) 874–879.

[142] P. Pal, A.K. Manna, Removal of arsenic from contaminated groundwater by solar-driven membrane distillation using three different commercial membranes, Water Res. 44 (2010) 5750–5760.

[143] S. Yarlagadda, V.G. Gude, L.M. Camacho, S. Pinappu, S. Deng, Potable water recovery from As, U, and F contaminated ground waters by direct contact membrane distillation process, J. Hazard. Mater. 192 (2011) 1388–1394.

[144] L. Yang, X. Li, Z. Chu, Y. Ren, J. Zhang, Distribution and genetic diversity of the microorganisms in the biofilter for the simultaneous removal of arsenic, iron and manganese from simulated groundwater, Bioresour. Technol. 156 (2014) 384–388.

[145] A. Vázquez, I. Rodríguez, I. Lázaro, Primary potential and current density distribution analysis: a first approach for designing electrocoagulation reactors, Chem. Eng. J. 179 (2012) 253–261.

[146] A. Vázquez, J.L. Nava, R. Cruz, I. Lázaro, I. Rodríguez, The importance of current distribution and cell hydrodynamic analysis for the design of electrocoagulation reactors, J. Chem. Technol. Biotechnol. 89 (2014) 220–229.

[147] M.R. Cruz-Díaz, E.P. Rivero, A. Torres-Mendoza, F.J. Almazán-Ruiz, I. González, Experimental and modelling study for electrocoagulation cell used to remove high organic loads in wastewater, Electrochem. Soc. 18 (2014), 933-933.

[148] E.J. Dickinson, H. Ekström, E. Fontes, COMSOL Multiphysics®: Finite element software for electrochemical analysis, A mini-review, Electrochem. Commun. 40 (2014) 71–74.