Chapter 10
Electrocoagulation in Water Treatment

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10.1 Theoretical Aspect

10.1.1 Principle of Electrocoagulation

EC is a complicated process involving many chemical and physical phenomena that use consumable electrodes (Fe/Al) to supply ions into the water stream. It has been discovered over the last hundred years both in batch and continuous applications. During the late nineteenth century, EC has been applied in several large-scale water treatment plants in London (Matteson et al. 1995), while electrolytic sludge treatment plants were operated as early as 1911 in various parts of USA (Vik et al. 1984). Fe/Al is dissolved from the anode generating corresponding metal ions, which immediately hydrolyze to polymeric iron or aluminum hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions and precipitation or by physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electroflotation, sedimentation, and filtration. In conventional coagulation process, coagulating chemicals are added. By contrast, these coagulating agents are generated in situ in EC process. The basic process can be summarized in Fig. 10.1.

In the EC process, the destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions may be summarized as follows. (1) Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode. (2) Charge neutralization of the

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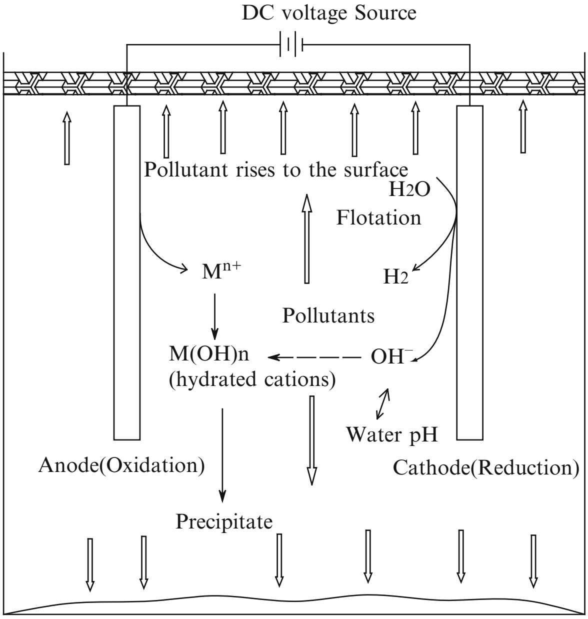

Fig. 10.1 Schematic diagram of a two-electrode electrocoagulation cell

ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic interparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process. (3) Floc formation: the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that are still remaining in the aqueous medium.

Water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and float the flocculated pollutants to the surface through natural buoyancy. In addition, the following physiochemical reactions may also take place in the EC cell (Paul 1996) (1) cathodic reduction of impurities present in wastewater; (2) discharge and coagulation of colloidal particles; (3) electrophoretic migration of the ions in solution; (4) electroflotation of the coagulated particles by O_2 and H_2 bubbles produced at the electrodes; (5) reduction of metal ions at the cathode; and (6) other electrochemical and chemical processes.

10.1.2 Reactions at the Electrodes and Electrodes Assignment

A simple electrocoagulation reactor is made up of one anode and one cathode. When a potential is applied from an external power source, the anode material undergoes

oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. The electrochemical reactions with metal M as anode may be summarized as follows:
At the anode:

$$M_{(s)} \rightarrow {M_{(aq)}}^{n+} + n\,e^{-} \tag{10.1}$$

$$2H_2O_{(1)} \rightarrow 4{H^{+}}_{(aq)} + O_{2(g)} + 4e^{-} \tag{10.2}$$

At the cathode:

$$ {M_{(aq)}}^{n+} + n\,e^{-} \rightarrow M_{(s)} \tag{10.3}$$

$$2H_2O_{(l)} + 2e^{-} \rightarrow 2H_{2(g)} + 2OH^{-} \tag{10.4}$$

If iron or aluminum electrodes are used, the generated ${Fe_{(ag)}}^{3+}$ or ${Al_{(aq)}}^{3+}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. These compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials (Jiang et al. 2002).

To improve the performances of an EC, it may be necessary to interchange the polarity of the electrode intermittently. Usually, a two-electrode EC cell is not suitable for wastewater treatment because of a workable rate of metal dissolution. The use of electrodes with large surface area is required and performance improvement has been achieved by using EC cells either with monopolar electrodes or with bipolar electrodes. The schematic diagram of monopolar and bipopar electrodes in series connections is shown in Fig. 10.2 (Golder et al. 2007). The parallel arrangement essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a DC power source. In a monopolar arrangement, each pair of "sacrificial electrodes" is internally connected with each other, and has no interconnection with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections. The experimental setup also requires a resistance box to regulate the flow of current and a multimeter to read the current values. The conductive metal plates or

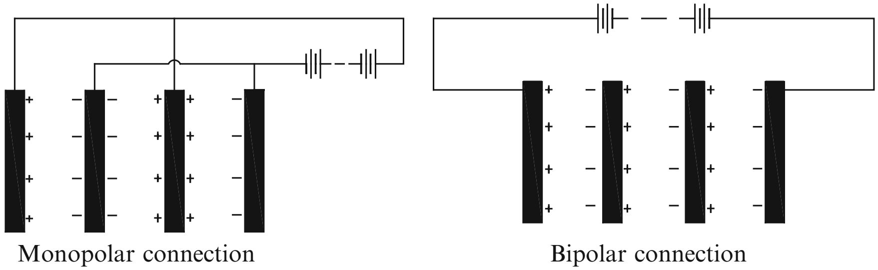

Fig. 10.2 Schematic diagram of a monopolar and bipolar electrodes in series connections

rods used in EC fabrication are commonly known as “sacrificial electrodes.” The sacrificial electrode and the cathode may be made up of the same or of different materials.

In a bipolar arrangement, the sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. The two monopolar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes. This cell arrangement provides a simple setup, which facilitates easy maintenance. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared with the parallel side beside it. The sacrificial electrodes are known as bipolar electrodes. It has been reported that EC cell with monopolar electrodes in series connection was more effective where aluminum electrodes were used as sacrificial and iron was used as anode and cathode. And, electrocoagulation with Fe/Al (anode/cathode) was more effective for the treatment process than Fe/Fe electrode pair (Modirshahla et al. 2007).

10.1.3 Electrode Passivation and Activation

Electrode passivation, specifically of aluminum electrodes, has been widely observed and recognized as detrimental to reactor performance. This formation of an inhibiting layer, usually an oxide on the electrode surface, will prevent metal dissolution and electron transfer, thereby limiting coagulant addition to the solution. Over time, the thickness of this layer increases, reducing the efficacy of the electrocoagulation process. The use of new materials, different electrode types and arrangements (Pretorius et al. 1991), and more sophisticated reactor operational strategies (such as periodic polarity reversal of the electrodes) have certainly let to significant reductions of impact passivation. In addition, addition of anions will also slow down the electrode passivation. The positive effect was as follows: $Cl^- > Br^- > I^- > F^- > ClO_4^- > OH^-$ and SO_4^{2-}. Specially, addition of a certain amount of Cl^- into the aqueous solution will inhibit the electrode passivation process largely. It is also necessary to rinse regularly the surface of the electrode plates. Generally, iron is used in wastewater treatment and aluminum is used in water treatment because there are a definite amount of metal ions required to remove a given amount of pollutants and iron is relatively cheaper. The aluminum plates are also finding application in wastewater treatment either alone or in combination with iron plates due to the high coagulation efficiency of Al^{3+}. When there are a significant amount of Ca^{2+} or Mg^{2+} ions in water, the cathode material is recommended to be stainless steel.

Apart from a technical focus on quantifying interactions between the foundation technologies and an economic focus on the relative cost of electrocoagulation, future research also needs to examine reliable means of reducing electrode passivation.

10.1.4 Comparison Between Electrocoagulation and Chemical Coagulation

Chemical coagulation and electrocoagulation have the same phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with metallic hydroxide ions and are agglomerated, followed by sedimentation or flotation. The difference between electrocoagulation and chemical coagulation is mainly in the way of which aluminum or iron ions are delivered (Zhu et al. 2005; Avsar et al. 2007). Electrocoagulation is a process consisting of creating metallic hydroxide flocks within the water by electrodissolution of the soluble anodes, usually made of iron or aluminum. In chemical coagulation, hydrolyzing metal salts, based on aluminum or iron, e.g., aluminum and ferric sulfates and chlorides, are very widely used as coagulants in water treatment. There are some advantages for EC compared to chemical coagulation, which are as follows:

1. In the chemical coagulation process, the hydrolysis of the metal salts will lead to a pH decrease and it is always needed to modulate the effluent pH. The chemical coagulation is highly sensitive to pH change and effective coagulation is achieved at pH 6–7. While in the electrocoagulation, the pH neutralization effect made it effective in a much wide pH range (4–9).
2. Flocs formed by EC are similar to chemical floc. But, EC floc tends to be much larger, contains less bound water, is acid resistant, and is more stable. In the chemical coagulation process, it is always followed by sedimentation and filtration. While in the electrocoagulation process, it can be followed by sedimentation or flotation. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected, and removed.
3. Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low-sludge producing technique.
4. Use of chemicals is avoided in EC process. Thus, it need not neutralize excess chemicals, and secondary pollution caused by chemical substances that are added can be avoided.
5. The EC process has the advantage of treating the water with low temperature and low turbidity. In this case, the chemical coagulation has difficulty in achieving a satisfying result.
6. EC requires simple equipment and is easy to be operated.

The disadvantages of EC are as follows. (1) The “sacrificial electrodes” are dissolved into wastewater as a result of oxidation, and need to be regularly replaced. (2) The passivation of the electrodes over time has limited its implementation. (3) The use of electricity may be expensive in many places. (4) High conductivity of the wastewater suspension is required (Yildiz et al. 2007).

10.2 Typical Designs of the EC Reactors

Electrocoagulation reactors have been built in a number of configurations. Each system has its own set of advantages and disadvantages. It is important to design the EC cell so that maximum efficiency can be achieved.

Among the electrocoagulation reactors, the first major distinction is whether a reactor was configured as a batch or a continuous system. It is clear that the majority of applications fall into the latter category, having a continuous feed of wastewater and operating under (pseudo) steady-state conditions. A key advantage for such reactor systems is that their coagulant requirements are essentially fixed, a major advantage in terms of both design and operation. Batch reactor applications typically operate with a fixed wastewater volume per treatment cycle, which suffer from the perceived disadvantage that those conditions within the reactor change with time.

The second major distinction between alternative reactor designs is the role of flotation. Reactors that do not exploit the separation of aggregated pollutant via electrochemically generated bubbles are regarded as "coagulation only" processes, while reactors that integrate flotation into their design and operation are classed as "coagulation and flotation" processes. Integrated units have two main pollutant removal paths – flotation and settling (Holt et al. 2002). Separation by settling is the more common option, with the fact that electrolytic gases are also being produced simultaneously with the dosing process often viewed as an unnecessary operational complication (Vik et al. 1984). The difference between pollutant removal by settling or flotation will seem to be the current density. A low current produces a low bubble density, leading to a low upward momentum-flux condition that encourages sedimentation over flotation. When the current is increased, the bubble density increases, which results in a greater upward momentum flux. Thus, the contaminants may be removed by flotation.

10.2.1 Liquid Flow Assignment

Generally, the liquid flow is in parallel connection (Fig. 10.3), which is easy to be fabricated. However, liquid flow is low in parallel connection and it is not beneficial for Al ion diffusion and Al coagulant formation as well as adsorption (Mameri et al. 1998). Additionally, if the Al ion cannot be transferred, the electrode will be passivated. Thus, overpotential will be increased and the electrical energy will be consumed. By contrast, the liquid flow rate in series connection will be increased (Fig. 10.3). Certainly, the flow rate cannot be increased too high in order to not to destroy the coagulant. The results of the treatment of a textile wastewater by EC process using various liquid flow assignments were reported. Two electrode materials, aluminum and iron, were connected in three modes namely, monopolar-parallel (MP-P), monopolar-serial (MP-S), and bipolar-serial (BP-S). For MP-P, anodes and cathodes are in parallel connection; the current is divided between all the electrodes in relation to the resistance of the individual cells. Hence, a lower potential

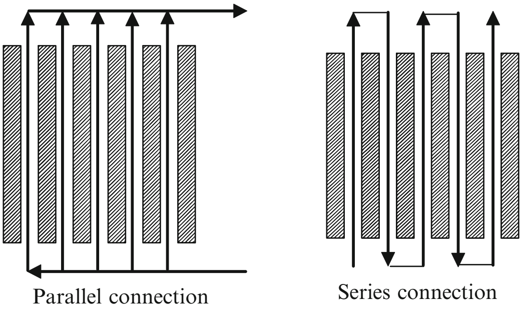

Fig. 10.3 Schematic diagram of liquid flow in parallel or series connection

difference is required in parallel connection, when compared with serial connections. For MP-S, each pair of sacrificial electrodes is internally connected with each other, because the cell voltages sum up a higher potential difference required for a given current. For BP-S, there is no electrical connection between inner electrodes, only the outer electrodes are connected to the power supply. Outer electrodes are monopolar and inner ones are bipolar. This connection mode has simple setup and has less maintenance cost during operation. COD and turbidity removals are selected as performance criteria. For a high COD removal, acidic medium is preferable for both electrode materials. And, process economy is as important as removal efficiencies during the process evaluation test. Various direct and indirect cost items including electrical, sacrificial electrodes, labor, sludge handling, maintenance, and depreciation costs have been considered in the calculation of the total cost. The results show that monopolar parallel mode is the most cost effective for both electrode types (Kobya et al. 2007).

10.3 Factors Affecting Electrocoagulation

10.3.1 Effect of Current Density or Charge Loading

Operating current density is very important in electrocoagulation because it is the only operational parameter that can be controlled directly. In this system, electrode spacing is fixed and current is a continuous supply. Current density directly determines both coagulant dosage and bubble generation rates and strongly influences both solution mixing and mass transfer at the electrodes.

In an EC experiment, the electrode or electrode assembly is usually connected to an external DC source. The amount of metal dissolved or deposited is dependent on the quantity of electricity passed through the electrolytic solution. A simple relationship between current density ($\mathrm{A\,cm^{-2}}$) and the amount of substances (M) dissolved ($\mathrm{g\ of\ M\,cm^{-2}}$) can be derived from Faraday's law:

$$w = \frac{itM}{Nf}, \tag{10.5}$$

where w is the quantity of electrode material dissolved (g of $\mathrm{M\,cm^{-2}}$), i the current density ($\mathrm{A\,cm^{-2}}$), t the time in s; M the relative molar mass of the electrode concerned, n the number of electrons in oxidation/reduction reaction, and f is the Faraday's constant, 96,500 $\mathrm{C\,mol^{-1}}$.

It is expected that there should be an agreement between the calculated amount of substances dissolved as a result of passing a definite quantity of electricity and the experimental amount determined. Usually a good agreement is obtained (Vik et al. 1984). One uncertainty is in the measurement of potential of the EC cell. The measured potential is the sum of three components:

$$\eta_{\mathrm{AP}} = \eta_{\mathrm{k}} + \eta_{\mathrm{Mt}} + \eta_{\mathrm{IR}}, \tag{10.6}$$

where η_{AP} is the applied overpotential (V), η_{k} the kinetic overpotential (V), η_{Mt} the concentration overpotential (V), and η_{IR} is the overpotential caused by solution resistance or IR drop (V).

The IR drop is related to the distance (d in cm) between the electrodes, surface area (A in $\mathrm{m^2}$) of the cathode, specific conductivity of the solution (κ in $\mathrm{mS\,m^{-1}}$), and the current (I in A). The IR drop can be easily minimized by decreasing the distance between the electrodes and increasing the area of crossing section of the electrodes and the specific conductivity of the solution. The IR drop can be easily minimized by decreasing the distance between the electrodes and increasing the area of cross section of the electrodes and the specific conductivity of the solution. Concentration overpotential (η_{Mt}, V), also known as mass transfer or diffusion overpotential, is caused by the change in analytic concentration occurring in the proximity of the electrode surface due to electrode reaction. This overpotential is caused by the differences in electroactive species concentration between the bulk solution and the electrode surface. This condition occurs when the electrochemical reaction is sufficiently rapid to lower surface concentration of electroactive species below that of the bulk solution. The overpotential is small when reaction rate constant is much smaller than the mass-transfer coefficient. The mass-transport overpotential (η_{Mt}, V) can be reduced by increasing the masses of the metal ions transported from the anode surface to the bulk of the solution and can be achieved by enhancing the solution turbulence. It can also be overcome by passing electrolyte solution from anode to cathode at a higher velocity by using some mechanical means. With the increase in the current, both kinetic and concentration overpotential increase.

The current density is the key operational parameter, affecting not only the system's response time but also strongly influencing the dominant pollutant separation mode. The highest allowable current density may not be the most efficient mode of running the reactor. It is well known that the optimal current density will invariably involve a trade-off between operational costs and efficient use of the introduced coagulant. At the meantime, the current density depends on solution pH, temperature, flow rate, etc.

As summarized by Chen (2004), the supply of current to the electrocoagulation system determines the amount of $\mathrm{Al^{3+}}$ or $\mathrm{Fe^{2+}}$ ions released from the respective electrodes. For aluminum, the electrochemical equivalent mass is 335.6 mg $(\mathrm{Ah})^{-1}$. For iron, the value is 1,041 mg $(\mathrm{Ah})^{-1}$. In order for the electrocoagulation system to operate for a long period of time without maintenance, its current density is suggested to be 20–25 $\mathrm{A\,m^{-2}}$ unless there are measures taken for a periodical cleaning of the surface of electrodes. The current density selection should be made with other operating parameters such as pH, temperature, as well as flow rate to ensure a high current efficiency. The current efficiency for aluminum electrode can be 120–140% while that for iron is around 100%. The overall 100% current efficiency for aluminum is attributed to the pitting corrosion effect especially when there are chlorine ions present. The current efficiency depends on the current density as well as the types of the anions. Significantly enhanced current efficiency, up to 160%, was obtained when low-frequency sound was applied to iron electrodes (Kovatchva and Parlapanski 1999). The quality of the treated water depends on the amount of ions produced (mg) or charge loading, the product of current and time (Ah). Table 10.1 gives the values of the required $\mathrm{Al^{3+}}$ for treating some typical pollutants in water treatment (Kul'skii et al. 1978). The operating current density or charge loading can be determined experimentally if there are not any reported values available. There is a critical charge loading required. Once the charge loading reaches the critical value, the effluent quality does not show significant improvement for further current increase (Chen et al. 2000).

10.3.2 Effect of Conductivity

When the electrolytic conductivity is low, the current efficiency will decrease. And, high-applied bias potential is needed which will lead to the passivation of electrode and increase treatment cost. Generally, NaCl was added in order to increase the electrolytic conductivity. Active chloride will also produce in the $\mathrm{Cl^-}$ electrolysis, which will contribute to the water disinfection (Wong et al. 2002). And, the addition of $\mathrm{Cl^-}$ will also decrease the negative effect of $\mathrm{CO_3{}^{2-}}$ and $\mathrm{SO_4{}^{2-}}$. The presence of $\mathrm{CO_3{}^{2-}}$ and $\mathrm{SO_4{}^{2-}}$ will lead to the deposition of $\mathrm{Ca^{2+}}$ and $\mathrm{Mg^{2+}}$ and formation of oxide layer, which will decrease the current efficiency rapidly. It is

Table 10.1 The aluminum demand and power consumption for removing pollutants from water

		Preliminary purification		Purification	
Pollutant	Unit quantity	$\mathrm{Al^{3+}}$ (mg)	E $(\mathrm{Wh\,m^{-3}})$	$\mathrm{Al^{3+}}$ (mg)	E $(\mathrm{Wh\,m^{-3}})$
Turbidity	1 mg	0.04–0.06	5–10	0.15–0.2	20–40
Color	1 unit	0.04–0.1	10–40	0.1–0.2	40–80
Silicates	1 mg/$\mathrm{SiO_2}$	0.2–0.3	20–60	1–2	100–200
Irons	1 mg Fe	0.3–0.4	30–80	1–1.5	100–200
Oxygen	1 mg $\mathrm{O_2}$	0.5–1	40–200	2–5	80–800
Algae	1,000	0.006–0.025	5–10	0.02–0.03	10–20
Bacteria	1,000	0.01–0.04	5–20	0.15–0.2	40–80

therefore recommended that among the anions present, there should be 20% Cl^- to ensure a normal operation of electrocoagulation in water treatment. However, NO_3^- widely present in the water solution nearly has no effect on the EC process.

10.3.3 Effect of Temperature

The water temperature will also influence the electrocoagulation process. Al anode dissolution was investigated in the water temperature range from 2 to 90°C. The Al current efficiency increase rapidly when the water temperature increase from 2 to 30°C. The temperature increase will speed up the destructive reaction of oxide membrane and increase the current efficiency. However, when the temperature was over 60°C, the current efficiency began to decrease. In this case, the volume of colloid $Al(OH)_3$ will decrease and pores produced on the Al anode will be closed. The above factors will be responsible for the decreased current efficiency.

10.3.4 Effect of pH

The pH of solution plays an important role in electrochemical and chemical coagulation process (Chen et al. 2000). Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerization reaction of electrochemically dissolved Al^{3+}. The formation of Al^{3+} single-core coordination compounds can be described as follows:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \tag{10.7}$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2{}^+ + H^+ \tag{10.8}$$

$$Al(OH)_2{}^+ + H_2O \rightarrow Al(OH)_3 + H^+ \tag{10.9}$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4{}^- + H^+ \tag{10.10}$$

With the extension of hydrolysis of Al^{3+}, multicore coordination compounds and $Al(OH)_3$ precipitate can be formed.

$$Al^{3+} \rightarrow Al(OH)_n{}^{3-n} \rightarrow Al_2(OH)_2{}^{4+} \rightarrow Al_{13}\,\text{complex} \rightarrow Al(OH)_3 \tag{10.11}$$

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

In the chemical coagulation process, pH is needed to be adjusted because the pH of solution will decrease with the addition of coagulants. In the electrochemical coagulation, the evolution of H_2 at the cathode will increase the OH^- concentration. Thus, pH in the aqueous solution will increase when the pH of original water is in the range of 4–9. However, when the pH of the original water is higher than 9, the pH of the treated water will decrease. Compared with the chemical coagulation, electrocoagulation can neutralize the pH of the treated water to some extent via following reactions.

$$\mathrm{Al} + 3\mathrm{H}^+ \rightarrow \mathrm{Al}^{3+} \tag{10.12}$$

$$\mathrm{Al}^{3+} + 3\mathrm{H_2O} \rightarrow \mathrm{Al(OH)_3} + 3\mathrm{H}^+ \tag{10.13}$$

$$\mathrm{Al(OH)_3} + \mathrm{OH}^- \rightarrow \mathrm{Al(OH)_4}^- \tag{10.14}$$

Under acid conditions, CO_2 can be purged with the evolution of H_2 and O_2. Particularly, Al dissolution occurs by (10.4)–(10.24). And, the formed $Al(OH)_3$ also dissolve, reaction (10.12) occurs to the left easily. These reactions are responsible for the increase of solution's pH. At high pH, reaction (10.13) occurs to the right easily, Ca^{2+} and Mg^{2+} can precipitate with $Al(OH)_3$. At higher pH, reaction (10.14) proceeds. These processes are responsible for the decrease of aqueous pH.

10.4 Application of Electrocoagulation in Water Treatment

EC is a process consisting of creating metallic hydroxides flocs within the wastewater by electrodissolution of soluble anodes, usually made of iron or aluminum. It was found that anodized aluminum was more effective than the aluminum ion introduced in the form of aluminum sulfate solution. In water and wastewaters treatment, electrocoagulation has been widely used to treat potable water, urban wastewater, oil wastes, textile wastewater, suspended particles, chemical and mechanical polishing waste, fluoride containing water, and heavy metal containing solutions (Hu et al. 2005; Adhoum et al. 2004; Yildiz et al. 2007; Kumar et al. 2004; Gomes et al. 2007; Parga et al. 2005; Golder et al. 2007; Hansen et al. 2007; Mollah et al. 2004; Wu et al. 2008). The removal of surfactants can also be achieved efficiently by using electrochemical coagulation not depending on the type of surfactant. Removal efficiency of nearly 100% has been achieved for the solution of $300\,\mathrm{mg\,L^{-1}}$ in a short time of 4 min (Onder et al. 2007). The treatability of waters containing high concentration of NOMs using iron cast electrodes has been explored based on removal efficiency by electrocoagulation method. Effects of initial humic substance concentration, applied potential, and supporting electrolyte type on the electrocoagulation have been investigated. It can be concluded that electrocoagulation is an effective method for the treatment of waters containing MOMs (Yildiz et al. 2007). Here, we take the removal of arsenic, dyes, and heavy metal from water as examples to explain the EC process and its mechanism in water treatment.

10.4.1 Arsenic Removal from Water by EC

Arsenic in drinking water is a worldwide concern due to its toxicity and carcinogenicity. In order to minimize these health risks, the World Health Organization (WHO) has set a guideline limit of $10\,\mu\mathrm{g\,L^{-1}}$ in drinking water. In natural water, arsenic is primarily present in inorganic forms and exists in two predominant species, arsenate (As(V)) and arsenite (As(III)). As(V) is the major arsenic species in well-oxygenated water, whereas As(III) is the dominant arsenic in groundwater.

EC is a simple, efficient, and promising method to remove arsenic form water. Arsenic removal efficiencies with different electrode materials follow the sequence: iron > titanium > aluminum. The process was able to remove more than 99% of arsenic from an As-contaminated water and met the drinking water standard of $10\,\mu\mathrm{g\,L^{-1}}$ with iron electrode. Compared with the iron electrodes, aluminum electrodes obtained lower removal efficiency. The plausible reason for less arsenic removal by aluminum in comparison to iron could be that the adsorption capacity of hydrous aluminum oxide for As(III) is much lower in comparison to hydrous ferric oxides. Comparative evaluation of As(III) and As(V) removal by chemical coagulation (with ferric chloride) and electrocoagulation has been done. The comparison revealed that EC has better removal efficiency for As(III), whereas As(V) removal by both processes was nearly same (Kumar et al. 2004).

Gomes et al. (2007) reported that As(III) ions are partly converted to As(V) during EC process. Crystalline iron oxides (magnetite, iron oxide), iron oxyhydroxide (lepidocrocite), aluminum hydroxide (bayerite), and aluminum oxyhydroxide (diaspore), as well as some interaction between the two phases were generated during the EC process. They also indicated the presence of amorphous or ultrafine particular phase in the floc. The substitution of Fe^{3+} ions by Al^{3+} ions in the solid surface has been observed also, which indicated a removal mechanism of arsenic in these metal hydroxides and oxyhydroxides by providing larger surface area for arsenic adsorption via retarding the crystalline formation of iron oxides. Electrocoagulation of As (V) in wastewaters is a promising remediation tool. Experiments with three different process designs showed the possibility of removing arsenic as adsorbed to or co-precipitate with iron(III)hydroxide. Applying electrocoagulation with a modified flow and an air lift reactor, in both cases practically all arsenic was eliminated from a $100\,\mathrm{mg\,As(V)\,L^{-1}}$ solution with current densities of around $1.2\,\mathrm{A\,dm^{-2}}$ (Parga et al. 2005).

10.4.2 Other Heavy Metal Removal from Water by EC

Most of the metals such as copper, nickel, chromium, silver, and zinc are harmful when they are discharged without treatment. The most widely used method for the treatment of metal polluted wastewater is precipitation with NaOH and coagulation with $FeSO_4$ or $Al_2(SO_4)_3$ with subsequent time-consuming sedimentation. Other methods include adsorption, ion exchange, and reverse osmosis. Each method has its disadvantages. EC is a promising method to remove heavy metal from water and has the advantages of simple equipment, easy operation, high removal efficiency, high removal rate, and no need pH adjustment.

Take the treatment of electroplating wastewater containing Cu^{2+}, Zn^{2+}, and Cr(VI) as an example. When using aluminum as electrode, Cu^{2+}, Zn^{2+}, and Cr(VI) could be effectively removed by the EC process when the pH was kept between 4 and 8. The removal rates of copper and zinc were found to be five times quicker than chromium because of a difference in the removal mechanisms. Coprecipitation of $Cu(OH)_2$ and $Zn(OH)_2$ may play a dominant role in the removal mechanism of the corresponding metallic ions. For Cr(VI), it was firstly reduced to Cr(III) at the cathode surface and then removed by coprecipitated process to $Cr(OH)_3$. When the pH was higher than 8, a dramatic decrease of the removal efficiency of chromium is observed, while removal yields of Cu^{2+} and Zn^{2+} remained very high. At alkaline pH between 8 and 10, $Cr_2O_7{}^{2-}$ ions are converted to soluble chromate ($CrO_4{}^{2-}$) anions, which can explain the low removal rate.

When using Fe as electrode, Fe^{2+} was formed by direct electrochemical reduction at the anode surface. Simultaneously, higher oxidized metal compounds like Cr(VI) may be reduced to Cr(III) by Fe^{2+} in acidic solution, as (10.15)–(10.17).

$$Fe \rightarrow Fe^{2+} + 2e \tag{10.15}$$

$$Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \tag{10.16}$$

$$CrO_4{}^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \tag{10.17}$$

On the cathode, in addition to the formation of H_2, Cr(VI) can be directly reduced to Cr(III) on the cathodes, which can be expressed as (10.18)–(10.20).

$$2H^+ + 2e \rightarrow H_2 \tag{10.18}$$

$$Cr_2O_7{}^{2-} + 6e + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \tag{10.19}$$

$$CrO_4{}^{2-} + 3e + 8H^+ \rightarrow Cr^{3+} + 4H_2O \tag{10.20}$$

Additionally, H_2 formed at the cathode increase the pH of the wastewater thereby inducing precipitation of Cr^{3+} and Fe^{3+} as corresponding hydroxides $Cr(OH)_3$ and $Fe(OH)_3$ (Golder et al. 2007).

10.4.3 Dye Removal from Water by EC

Dye is a ubiquitous class of synthetic organic pigments. The traditional treatment methods for dye effluents include physical–chemical method and biological process. The biological methods are cheap and simple to apply, but cannot be applied to most textile wastewaters because most commercial dyes are toxic to the organisms used in the process and result in sludge bulking. The EC technique is considered to be an effective tool for treatment of textile wastewaters with high removal efficiency.

A number of authors have reported the treatments of textile dye wastewater by EC technique (Mollah et al. 2004; Wu et al. 2008). There are two mechanisms for the dye decolorization (1) precipitation and (2) adsorption. At low pH, the precipitation is dominant. At pH > 6.5, the adsorption is the main process.

Precipitation:

$$\text{Dyes} + \text{Monomeric Al} \rightarrow [\text{Dyes Monomeric Al}]\ (\text{s})\ \text{pH} = 4.0 - 5.0 \quad (10.21)$$

$$\text{Dyes} + \text{Polymeric Al} \rightarrow [\text{Dyes Polymeric Al}](\text{s})\ \text{pH} = 5.0 - 6.0 \quad (10.22)$$

Adsorption:

$$\text{Dyes} + \text{Al(OH)}_{3(\text{s})} \rightarrow\rightarrow [\text{particle}] \quad (10.23)$$

$$[\text{Dyes Polymeric Al}]_{(\text{s})} + \text{Al(OH)}_{3(\text{s})} \rightarrow\rightarrow\rightarrow [\text{particles}] \quad (10.24)$$

Freshly formed amorphous $Al(OH)_3(s)$ "sweep flocs" have large surface areas which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation.

Iron and aluminum are used as sacrificial electrode materials in the treatment of textile wastewater by EC. In acidic medium, COD and turbidity removal efficiencies of aluminum are higher than those of iron, while in neutral and weakly alkaline medium iron is more efficient. High conductivity is in favor of high process performances and low operating cost. For the same turbidity and COD removal efficiencies, iron requires a lower current density than aluminum. Operating time and current density exhibit similar effects on the process performances and the operating cost. The energy consumption is lower with iron, while the electrode consumption is lower generally with aluminum. If anode potential is sufficiently high, secondary reactions may occur, including direct oxidation of organic compounds and of $Cl^- \leftarrow$ ions present in wastewater.

The dye removal efficiency decreased with increase in the initial concentration. In a bipolar EC reactor with iron electrodes, using NaCl as electrolyte, the removal efficiency of orange II decreased from 90.4 to 55% with the increase in the initial dye concentration from 10 to 50 mg L^{-1} at constant voltage of 40 V and a current strength of 159.5 A m^{-2}. The high treatment efficiency is considered to be due to chemical coagulation involving maghemite (γ-Fe_2O_3) and/or magnetite (Fe_3O_4) produced in the system as well as electrooxidation. The results of XRD analyses of the residue confirmed the presence of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) in EC process (Canizares et al. 2006). Misawa et al. (199) reported that either goethite (α-FeOOH) or magnetite (Fe_3O_4) is produced depending upon the pH of the environment. At acidic condition, γ-Fe_2O_3 was formed; in slightly basic and strongly basic condition Fe_3O_4 and α-FeOOH were formed, respectively by the (10.25)–(10.26).

$$6\text{Fe(OH)}_{2(\text{s})} + \text{O}_{2(\text{aq})} \rightarrow 2\text{Fe}_3\text{O}_{4(\text{s})} + 6\text{H}_2\text{O} \quad (10.25)$$

$$4\text{Fe(OH)}_{2(\text{s})} + \text{O}_{2(\text{aq})} \rightarrow 4\alpha{-}\text{FeOOH}_{(\text{s})} + 2\text{H}_2\text{O} \quad (10.26)$$

As for the acid red 14 removal by EC, 95% color removal and 85% COD removal were obtained when the pH ranged from 6 to 9, time of electrolysis was approximately 4 min and current density was approximately $80\,\mathrm{A\,m^{-2}}$. The results also showed that an EC cell with monopolar electrodes had higher color removal efficiency than an EC cell with bipolar electrodes. Furthermore, within an EC cell, the series connection of the monopolar electrodes was more effective for the treatment process than the parallel connection in color removal (Daneshvar et al. 2004).

EC has the advantage of consumed less material and produced less sludge, and the pH of the medium was more stabilized than that of chemical coagulation for similar COD and turbidity removal levels. Cost calculations for dye removal by EC show that, in the case of iron electrode, operating cost is approximately 0.1 US$ per kg COD removed, and for aluminum, it is 0.3 US$ per kg COD removed. Electrode consumption cost accounts nearly 50% of the total cost for iron, and 80% of the total cost for aluminum (Bayramoglu et al. 2004). This paper presents the comparative results with respect to electrode configurations on the economic performance of treatment of textile wastewater by EC process. Aluminum and iron electrode materials were used as sacrificial electrode in parallel and series connection modes. Various direct and indirect cost items including electrical, sacrificial electrodes, labor, sludge handling, maintenance, and depreciation costs were considered in the calculation of the total cost per m^3 of wastewater taken from a textile plant with a capacity of 1,000 m^3 per day. The results showed that MP-P was the most cost effective for Fe and Al electrodes.

10.5 A New Bipolar EC–EF Process for Wastewater Treatment

The separation of the flocculated sludge formed by EC process can be accomplished by precipitation or flotation (Yavuz 2007; Szpyrkowicz 2007). However, preliminary experiment showed that the hydrogen gas produced at the aluminum cathode in an electrocoagulation cell was not so fine that could float only about 60% of the total solids. In our research group, a combinative bipolar EC–EF process was developed to treat laundry wastewater (Ge et al. 2004).

Figure 10.4 showed the flowchart of the experimental EC–EF system in our research work. In the bipolar EC–EF unit, three aluminum plates placed between two titanium electrodes having opposite charges will undergo anodic reactions on the positive side while on the negative side cathodic reactions take place. The objectives of using this bipolar EC–EF reactor were to neutralize pollutant charge, generate ultrafine bubbles, and separate the coagulated flocs from water.

The main anodic reactions are as follows:

Ti anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \tag{10.27}$$

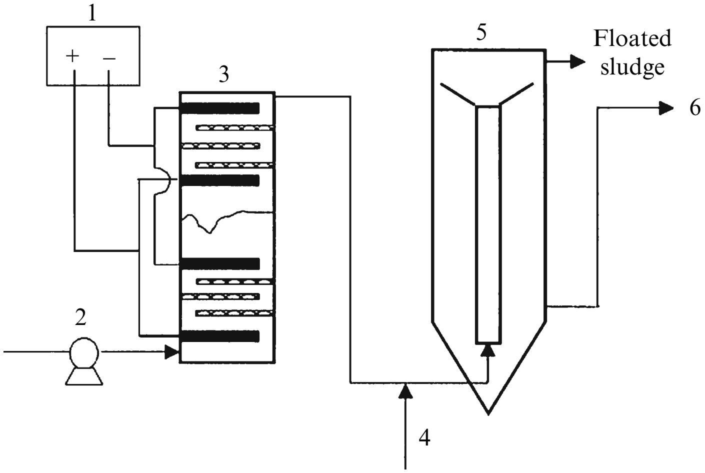

Fig. 10.4 Flowchart of the experimental system: (1) DC power supply, (2) pump, (3) electrochemical cell (*solid bar*: Ti electrode and *space bar*: Al electrode), (4) polymer electrolyte injection, (5) separator, and (6) effluent

Al positive side:

$$Al \rightarrow Al^{3+} + 3e \tag{10.28}$$

The hydrolysis and polymerization of Al^{3+} under appropriate pH conditions subsequently give rise to the formation of such species as $Al(OH)^{2+}$, ${Al_2(OH)_2}^{4+}$, $Al(OH)_3$, and charged hydroxo cationic complexes, which can effectively remove pollutants. In this study, titanium metal is chosen as anode material mainly for its cheapness and high stability. Some materials with high oxygen evolution have also been reported. When there are some Cl^- in the solution, some reactions will occur on the anode by (10.29)–(10.31).

$$2Cl^- \rightarrow Cl_2 + 2e \tag{10.29}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{10.30}$$

$$HClO \rightarrow H^+ + ClO^- \tag{10.31}$$

It is generally believed that there are three possible mechanisms involved in the process: electrocoagulation, electroflotation, and electrooxidation. However, it can be suggested that, during the bipolar EC–EF process, bipolar aluminum electrodes are mainly responsible for electrocoagulation.

The process successfully removed turbidity, COD, phosphate, and MBAS simultaneously in the pH range of 5–9. The COD removal was greater than 70%. And the removal efficiencies of MBAS, turbidity, and P-phosphate could be reached above 90%. Based on the laboratory test of laundry wastewater, $1.5\,m^3\,h^{-1}$ pilot scale EC–EF equipment was manufactured and mounted on a mobile truck. The

Table 10.2 Pilot scale field test results

	Harbin, Heilongjiang		Wuxi, Jiangsu		Shunyi, Beijing	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Conductivity (μS)	1,904–786	956–675	830–712	719–655	1,159–897	735–589
pH	9.56–7.83	8.15–7.24	10.68–9.77	8.73–7.92	9.35–8.45	8.09–7.77
Turbidity (NTU)	583–471	12.3–8.26	78.0–32.2	11.2–10.5	810–225	4.25–1.41
COD $\left(\mathrm{mg\,L^{-1}}\right)$	1,090–785	45.6–32.4	65.9–31.8	11.2–5.3	890–628	71.2–59.3
MBAS $\left(\mathrm{mg\,L^{-1}}\right)$	72.3–64.5	11.2–9.6	14.6–8.3	2.9–1.7	72.5–57.6	8.9–5.8

equipment mainly consisted of an EC–EF tank and a separator. The field test results are shown in Table 10.2. As for the laundry wastewater of Shunyi (Beijing), when polyaluminum chloride (10% Al_2O_3) was used, the dosage was $1,200\,\mathrm{mg\,L^{-1}}$, equal to $63.5\,\mathrm{mg\,L^{-1}}$ Al^{3+}, to achieve the same residual turbidity. The settled sludge amounted to nearly 40% of the total volume. For the electrochemical process (32 V/30 A, $1.5\,\mathrm{m^3\,h^{-1}}$), the Al^{3+} consumption was $6.72\,\mathrm{mg\,L^{-1}}$. Table 10.1 also indicated that the pH of the treated wastewater was neutralized and the electrical conductivity was reduced. It can be seen that the bipolar EC–EF process was different from other coagulation/flotation processes.

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