



Electrochemical technologies in wastewater treatment

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Abstract

This paper reviews the development, design and applications of electrochemical technologies in water and wastewater treatment. Particular focus was given to electrodeposition, electrocoagulation (EC), electroflotation (EF) and electrooxidation. Over 300 related publications were reviewed with 221 cited or analyzed. Electrodeposition is effective in recover heavy metals from wastewater streams. It is considered as an established technology with possible further development in the improvement of space-time yield. EC has been in use for water production or wastewater treatment. It is finding more applications using either aluminum, iron or the hybrid Al/Fe electrodes. The separation of the flocculated sludge from the treated water can be accomplished by using EF. The EF technology is effective in removing colloidal particles, oil & grease, as well as organic pollutants. It is proven to perform better than either dissolved air flotation, sedimentation, impeller flotation (IF). The newly developed stable and active electrodes for oxygen evolution would definitely boost the adoption of this technology. Electrooxidation is finding its application in wastewater treatment in combination with other technologies. It is effective in degrading the refractory pollutants on the surface of a few electrodes. Titanium-based boron-doped diamond film electrodes (Ti/BDD) show high activity and give reasonable stability. Its industrial application calls for the production of Ti/BDD anode in large size at reasonable cost and durability.

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1. Introduction

Using electricity to treat water was first proposed in UK in 1889 [1]. The application of electrolysis in mineral beneficiation was patented by Elmore in 1904 [2]. Electrocoagulation (EC) with aluminum and iron electrodes was patented in the US in 1909. The electrocoagulation of drinking water was first applied on a large scale in the US in 1946 [3,4]. Because of the relatively large capital investment and the expensive

electricity supply, electrochemical water or wastewater technologies did not find wide application worldwide then. Extensive research, however, in the US and the former USSR during the following half century has accumulated abundant amount of knowledge. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades. There are companies supplying facilities for metal recoveries, for treating drinking water or process water, treating various wastewaters resulting from tannery, electroplating, dairy, textile

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Nomenclature

a	specific electrode area (m^2/m^3)
A	area of electrode (m^2)
CE	current efficiency
d	net distance between electrodes (m)
E	constant in Eqs. (16) and (17) (V)
E_{eq}	equilibrium potential difference between an anode and a cathode (V)
F	Faraday constant (C/mol)
i	current density (A/m^2)
I	current (A)
K_1	constant in Eqs. (16) and (17)
K_2	constant in Eq. (17)
m	constant in Eq. (17)
M	molecular mass (g/mole)
n	constant in Eq. (17)
N	total electrode number of an electrocoagulation unit
U	total required electrolysis voltage of an electrocoagulation process (V)
U_0	electrolysis voltage between electrodes (V)
Y_{ST}	space–time yield
z	charge number

Greek letters

α	constant in Eq. (20)
$\eta_{\text{a,a}}$	anode activation overpotential (V)
$\eta_{\text{a,c}}$	anode concentration overpotential (V)
$\eta_{\text{a,p}}$	anode passive overpotential (V)
$\eta_{\text{c,a}}$	cathode activation overpotential (V)
$\eta_{\text{c,c}}$	cathode concentration overpotential (V)
κ	conductivity of water/wastewater treated (S/m)

processing, oil and oil-in-water emulsion, etc. Nowadays, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact. For some situations, electrochemical technologies may be the indispensable step in treating wastewaters containing refractory pollutants. In this paper, I shall examine the established technologies such as electrochemical reactors for metal recovery, electrocoagulation, electroflotation and electrooxidation. The emerging technologies

such as electrophotooxidation, electrodisinfection will not be discussed. In addition, I shall focus more on the technologies rather than analyzing the sciences or mechanisms behind them. For books dealing with environmentally related electrochemistry, the readers are referred to other publications [5–8].

Before introducing the specific technologies, let us review a few terminologies that are concerned by electrochemical process engineers. The most frequently referred terminology besides potential and current may be the *current density*, i , the current per area of electrode. It determines the rate of a process. The next parameter is *current efficiency*, CE, the ratio of current consumed in producing a target product to that of total consumption. Current efficiency indicates both the specificity of a process and also the performance of the electrocatalysis involving surface reaction as well as mass transfer. The space–time yield, Y_{ST} , of a reactor is defined as the mass of product produced by the reactor volume in unit time with

$$Y_{\text{ST}} = \frac{iaM}{1000 zF} \text{CE}. \quad (1)$$

The space–time yield gives an overall index of a reactor performance, especially the influence of the specific electrode area, a .

2. Electrochemical reactors for metal recovery

The electrochemical recovery of metals has been practiced in the form of electrometallurgy since long time ago [9]. The earliest reported application of electrochemical phenomena in chemical subjects was supposed to be carried out by Pliny in protecting iron with lead electroplating [10]. The first recorded example of electrometallurgy was in mid-17th century in Europe [11]. It involved the recovery of copper from cupriferous mine water electrochemically. During the past two and half centuries, electrochemical technologies have grown into such areas as energy storage, chemical synthesis, metal production, surface treatment, etc. [12]. The electrochemical mechanism for metal recovery is very simple. It basically is the cathodic deposition as



The development of the process involves the improvement of CE as well as Y_{ST} .

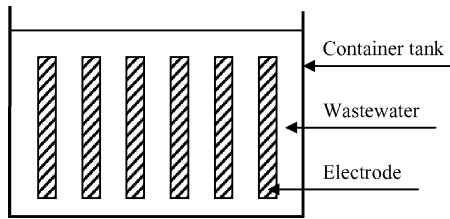


Fig. 1. Tank cell.

2.1. Typical reactors applied

There are quite a few types of reactors found applications in metal recovery, from very basic reactors such as tank cells, plate and frame cells, rotating cells, to complicated three-dimensional reactor systems like fluidized bed, packed bed cell, or porous carbon packing cells. Tank cells, Fig. 1, are one of the simplest and hence the most popular designs. It can be easily scaled up or down depending on the load of a process. The electrode can be arranged in mono-polar or bi-polar mode, Fig. 2. The main application of this type of reactor system is the recovery of metals from high concentration process streams such as effluents from the electroplating baths, ethants, and eluates of an ion-exchange unit [11]. The number of electrodes in a stack may vary from 10 to 100. The water flow is usually induced by gravity.

The plate and frame cell or sometimes called filter press, Fig. 3, is one of the most popular electrochemical reactor designs. It conveniently houses units with an anode, a cathode, and a membrane (if necessary) in one module. This module system makes the design, operation and maintenance of the reactor relatively

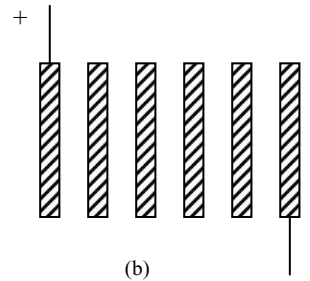
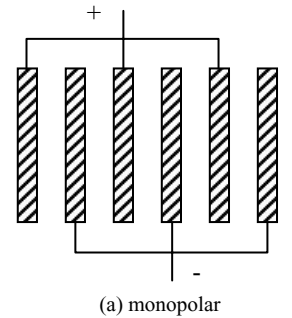


Fig. 2. Electrode arrangements.

simple [13]. In order to enhance mass transfer from the bulk to the electrode surface and also to remove the deposited metal powders from the cathode, the rotating cathode cell was designed and employed, Fig. 4 [14]. It was found that this system can reduce copper content from 50 to 1.6 ppm by using the systems in a cascade version [15]. The pump cell is another variant of rotating cathode cell, Fig. 5. By having a static anode and a rotating disk cathode, the narrow spacing between the electrodes allows the entrance of the

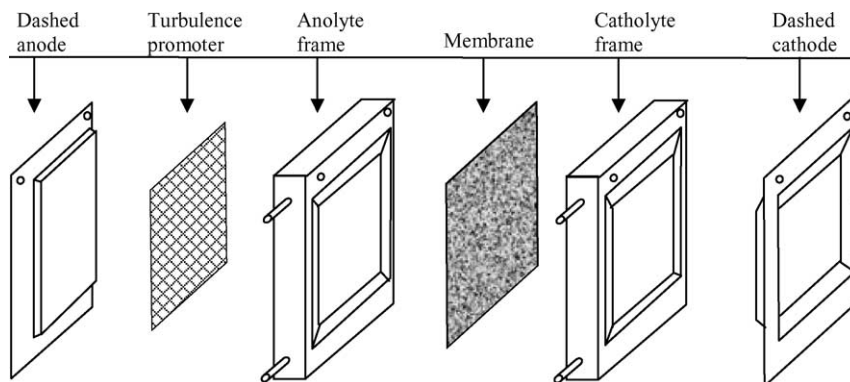


Fig. 3. Filter press reactor.

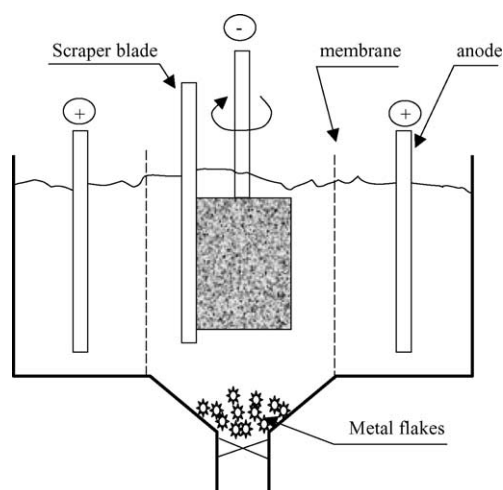


Fig. 4. Rotating cylinder electrode.

effluent. The metals were electrically won and scraped as powders [16–18]. Another design employs rotating rod cathodes in between inner and outer anodes. Besides metal recovery, it is also possible to have the anodic destruction of cyanides if necessary [19].

Since the metal deposition happens at the surface of the cathode, it is necessary to increase the specific surface area in order to improve the space–time yield. Fluidized bed electrode was therefore designed, Fig. 6 [20]. The cathode was made of conductive particles in contact with a porous feeder electrode. The electrode can give a specific area of $200 \text{ m}^2/\text{m}^3$. Because of the fluidization of the particles by the water flow, the elec-

trical contact is not always maintained thus the current distribution is not always uniform and the ohmic drop within the cell is high. In order to improve the contact between the electrode feeder and cathode particles, a large number of additional rod feeders was used [21]. Inert particles were also employed in fluidized bed reactor to improve mass transfer rate in a ChemElec commercial design. Tumbling bed electrodes, Fig. 7, are also available.

The packed bed cell overcomes the sometimes non-contacting problem met in fluidized bed, Fig. 8 [22,23]. Carbon granules were packed in a cell. The anode was separated by a diaphragm. The recently developed packed bed reactor by EA Technology Ltd. (UK) and marketing by Renovare International Inc. (US), RenoCell, Fig. 9, claims to excel in competition with many existing technologies. This three-dimensional porous, carbon cathode provides 500 times more plating area than conventional two-dimensional cells [24]. In order for dilute metal pollutants to deposit properly on the cathode, it is suggested to seed metal powders by having concentrated metal solution at the beginning of the recovery process. Control of pH in the feed tank of a recirculating electrolyte is important to avoid precipitation of the metal.

For example, “100 l of a solution containing 19 ppm nickel in a 0.1 M Na_2SO_4 matrix were electrolyzed in the cell under conditions at 40°C and pH 4 and using a current density of 200 A/m^2 (based on geometric area). The nickel concentration was reduced from 19

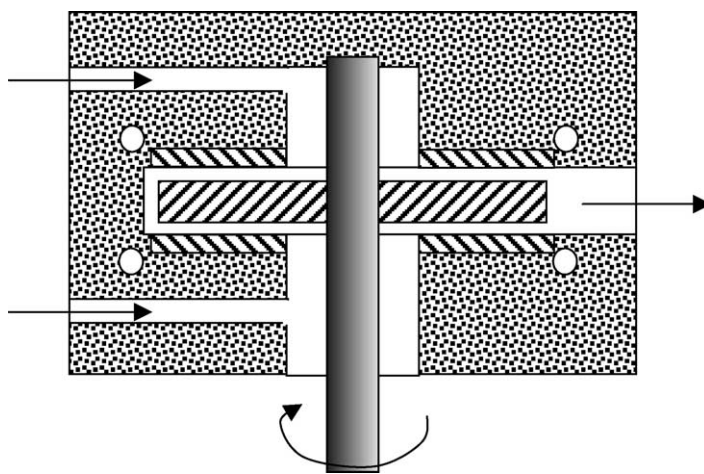


Fig. 5. Pump cell.

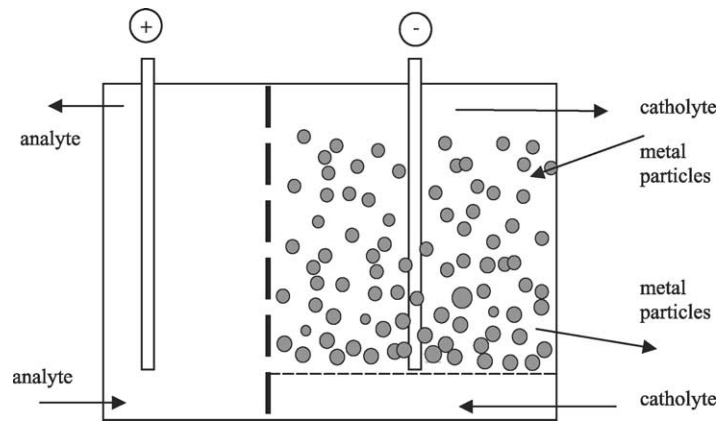


Fig. 6. Fluidized bed reactor.

to 5 ppm in 120 min.” The circulation flowrate was 20 l/min. Four grams per liter of boric acid was added as buffer agent [24]. The deposited metals can be removed from a felt cathode in a stripping cell using the carbon felt electrode as an anode. This system can work on single metal as well as metal mixtures. The circulating flowrate can vary between 15 and 30 l/min. The current density is preferably between 100 and 300 A/m² based on geometric area. In exceptional cases where very high acidity or alkalinity exists, a current density between 300 and 800 A/m²

may be applied. The RenoCell unit can be used alone, or in series or parallel depending on the quantity and quality of the effluent.

2.2. Electrode materials

The anode electrode materials for metal recovery can be steel or dimensionally stable anodes (DSA®). The latter was made of a thin layer of noble metal oxides on titanium substrate [25]. It has been used extensively in electrochemical industry. More on this material will be discussed later on in Section 4. The

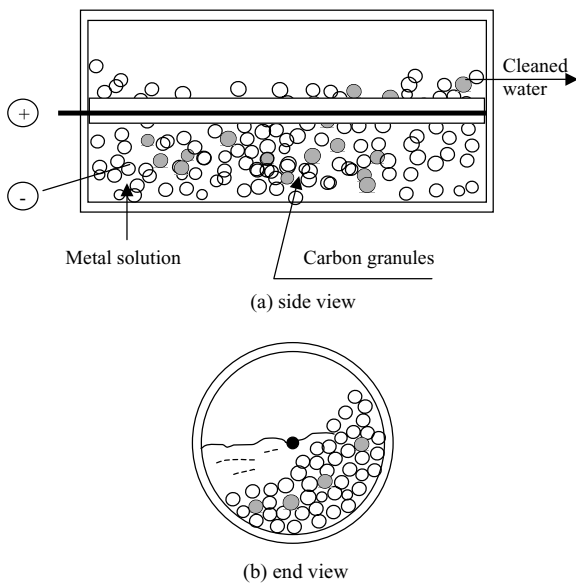


Fig. 7. Tumbling bed electrodes.

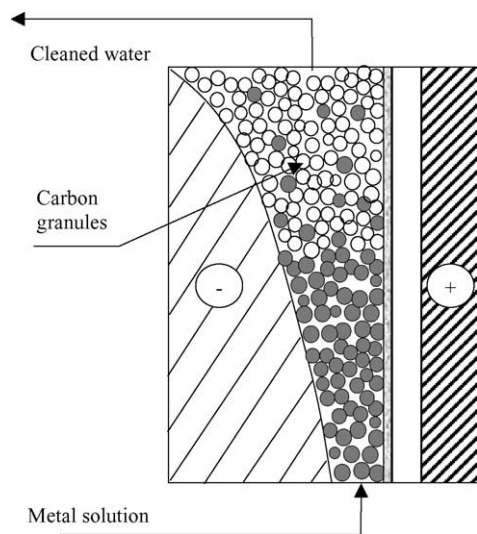


Fig. 8. Fixed bed reactor.

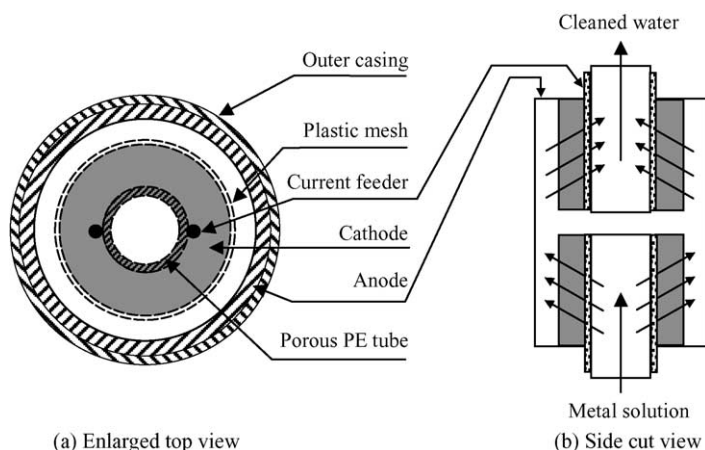


Fig. 9. Design of a RenoCell.

cathode materials can be the metal to be recovered or graphite, carbon fibers, etc. The cathode electrode feeder can be steel or titanium.

2.3. Application areas

The electrochemical recovery of metals can be used in the metal surface finishing industry. It has to bear in mind that it is unable to provide a complete solution to the industry's waste management problems because it cannot treat all the metals either technically or economically. The electrolytic recovery of metals here involves two steps: collection of heavy metals and stripping of the collected metals. The collection step involves plating and the stripping can be accomplished chemically or electrochemically. Nowadays, metal powders can be formed on the surface of carbon cathodes. Therefore, physical separation is sufficient. The metals recovered can be of quite high purity.

Another application is in the printed circuit board manufacturing industry. Because of the well-defined process, the treatment can be accomplished relatively easily for this industry. For dilute effluent, an ion-exchange unit can be used to concentrate the metal concentration. For high concentration streams, they can be treated directly using a recovery system as in metal surface finishing industry. Application of metal recovery should be very much useful in metal winning in mining industry especially in the production of precious metals such as gold [11].

3. Electrocoagulation

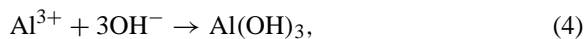
Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from respectively aluminum or iron electrodes. The metal ions generation takes place at the anode, hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water. This process sometimes is called electroflocculation. It is schematically shown in Fig. 10. The electrodes can be arranged in a mono-polar or bi-polar mode. The materials can be aluminum or iron in plate form or packed form of scraps such as steel turnings, millings, etc.

The chemical reactions taking place at the anode are given as follows.

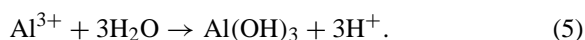
For aluminum anode:



at alkaline conditions



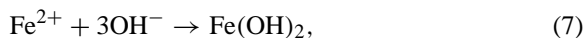
at acidic conditions



For iron anode:



at alkaline conditions



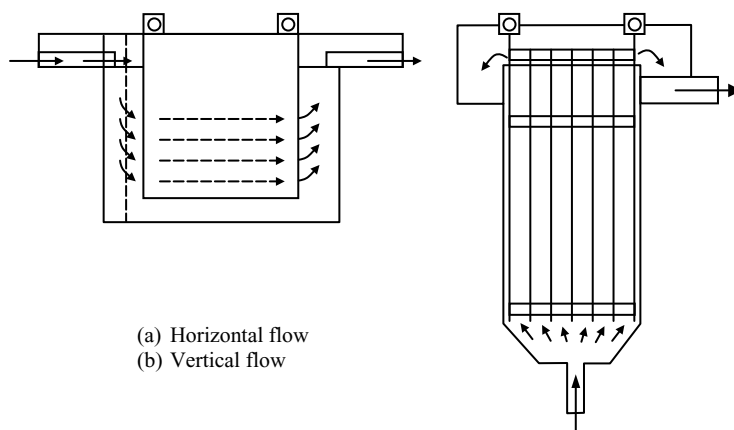
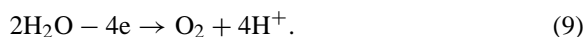


Fig. 10. Electrocoagulation units.

at acidic conditions



In addition, there is oxygen evolution reaction



The reaction at the cathode is



The nascent Al^{3+} or Fe^{2+} ions are very efficient coagulants for particulates flocculating. The hydrolyzed aluminum ions can form large networks of Al-O-Al-OH that can chemically adsorb pollutants such as F^- [26]. Aluminum is usually used for water treatment and iron for wastewater treatment. The advantages of electrocoagulation include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation.

3.1. Factors affecting electrocoagulation

3.1.1. Current density or charge loading

The supply of current to the electrocoagulation system determines the amount of Al^{3+} or Fe^{2+} ions released from the respective electrodes. For aluminum, the electrochemical equivalent mass is 335.6 mg/(Ah). For iron, the value is 1041 mg/(Ah). A large current means a small electrocoagulation unit. However, when too large current is used, there is a

high chance of wasting electrical energy in heating up the water. More importantly, a too large current density would result in a significant decrease in current efficiency. 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 A/m² 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 flowrate to ensure a high current efficiency. The current efficiency for aluminum electrode can be 120–140% while that for iron is around 100%. The over 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 [27].

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 1 gives the values of the required Al^{3+} for treating some typical pollutants in water treatment [28]. 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

Table 1

The aluminum demand and power consumption for removing pollutants from water

Pollutant	Unit quantity	Preliminary purification		Purification	
		Al ³⁺ (mg)	E (Wh/m ³)	Al ³⁺ (mg)	E (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/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 O ₂	0.5–1	40–200	2–5	80–800
Algae	1000	0.006–0.025	5–10	0.02–0.03	10–20
Bacteria	1000	0.01–0.04	5–20	0.15–0.2	40–80

value, the effluent quality does not show significant improvement for further current increase [29].

3.1.2. Presence of NaCl

Table salt is usually employed to increase the conductivity of the water or wastewater to be treated. Besides its ionic contribution in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO₃[−], SO₄^{2−}. The existence of the carbonate or sulfate ions would lead to the precipitation of Ca²⁺ or Mg²⁺ ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency. It is therefore recommended that among the anions present, there should be 20% Cl[−] to ensure a normal operation of electrocoagulation in water treatment. The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections [30].

3.1.3. pH effect

The effects of pH of water or wastewater on electrocoagulation are reflected by the current efficiency as well as the solubility of metal hydroxides. When there are chloride ions present, the release of chlorine also would be affected. It is generally found that the aluminum current efficiencies are higher at either acidic or alkaline condition than at neutral. The treatment performance depends on the nature of the pollutants with the best pollutant removal found near pH of 7. The power consumption is, however, higher at

neutral pH due to the variation of conductivity. When conductivity is high, pH effect is not significant.

The effluent pH after electrocoagulation treatment would increase for acidic influent but decrease for alkaline influent. This is one of the advantages of this process. The increase of pH at acidic condition was attributed to hydrogen evolution at cathodes, reaction [10] by Vik et al. [31]. In fact, besides hydrogen evolution, the formation of Al(OH)₃ near the anode would release H⁺ leading to decrease of pH. In addition, there is also oxygen evolution reaction leading to pH decrease. When there are chlorine ions, there are following chemical reactions taking place:



Hence, the increase of pH due to hydrogen evolution is more or less compensated by the H⁺ release reactions above. For the increase in pH at acidic influent, the increase of pH is believed to be due to CO₂ release from hydrogen bubbling, due to the formation of precipitates of other anions with Al³⁺, and due to the shift of equilibrium towards left for the H⁺ release reactions. As for the pH decrease at alkaline conditions, it can be the result of formation of hydroxide precipitates with other cations, the formation of Al(OH)₄[−] by [29].



The pollutants removal efficiencies were found to be the best near neutral pH using aluminum electrode. When iron electrode was used in textile printing and dyeing wastewater treatment, alkaline influent was

found to give better color as well as COD removals [32].

3.1.4. Temperature

Although electrocoagulation has been around for over 100 years, the effect of temperature on this technology was not very much investigated. For water treatment, the literatures from former USSR [33] show that the current efficiency of aluminum increases initially with temperature until about 60 °C where a maximum CE was found. Further increase in temperature results in a decrease in CE. The increase of CE with temperature was attributed to the increased activity of destruction of the aluminum oxide film on the electrode surface. When the temperature is too high, there is a shrink of the large pores of the $\text{Al}(\text{OH})_3$ gel resulting in more compact flocs that are more likely to deposit on the surface of the electrode. Similar to the current efficiency, the power consumption also gives a maximum at slightly lower value of temperature, 35 °C, for treating oil-containing wastewater [34]. This was explained by the opposite effects of temperature on current efficiency and the conductivity of the wastewater. Higher temperature gives a higher conductivity hence a lower energy consumption.

3.1.5. Power supply

When current passes through an electrochemical reactor, it must overcome the equilibrium potential difference, anode overpotential, cathode overpotential and ohmic potential drop of the solution [7]. The anode overpotential includes the activation overpotential and concentration overpotential, as well as the possible passive overpotential resulted from the passive film at the anode surface, while the cathode overpotential is principally composed of the activation overpotential and concentration overpotential. Therefore,

$$U_0 = E_{\text{eq}} + \eta_{\text{a,a}} + \eta_{\text{a,c}} + \eta_{\text{a,p}} + |\eta_{\text{c,a}}| + |\eta_{\text{c,c}}| + \frac{d}{\kappa}i. \quad (15)$$

It should be noted that the passive overpotential highly depends on the electrode surface state. For the new non-passivated electrodes, the passive overpotential can be neglected and Eq. (15) simplifies to:

$$U_0 = E + \frac{d}{\kappa}i + K_1 \ln i, \quad (16)$$

for old passivated electrodes,

$$U_0 = E + \frac{d}{\kappa}i + K_1 \ln i + \frac{K_2 i^n}{\kappa^m}. \quad (17)$$

On the right-hand side of Eqs. (16) and (17), both K_1 and K_2 are constants. Although E is related to the transport number of Al^{3+} and OH^- , it approaches constant when κ is large, the case for electrocoagulation. Eqs. (16) and (17) indicate that U_0 is independent on pH and it does not change significantly with flowrate. For new aluminum electrodes, $E = -0.76$, $K_1 = 0.20$. For passivated aluminum electrodes, $E = -0.43$, $K_1 = 0.20$, $K_2 = 0.016$ and $m = 0.47$, $n = 0.75$ [35].

With U_0 obtained, the total required electrolysis voltage U of an electrocoagulation process can be calculated easily. For the mono-polar mode, the total required electrolysis voltage is the same as the electrolysis voltage between electrodes, that is

$$U = U_0. \quad (18)$$

For the bi-polar mode, the total required electrolysis voltage is U_0 times the number of total cell which is the number of electrodes minus one. Thus:

$$U = (N - 1)U_0. \quad (19)$$

N is usually less than 8 in order to maintain high current efficiency for each electrode plate. Usually, DC power supply is employed. In order to minimize the electrode surface oxidation or passivation, the direction of power supply is changed at a certain time interval. Fifteen minutes were found to be optimal for water treatment using aluminum electrodes. A three phase AC power supply was also used with six aluminum electrodes (three pairs) in treating colloidal wastewaters from petrochemical industries. Alternating current was also explored [36].

3.2. Electrode materials

As stated earlier, the materials employed in electrocoagulation are usually aluminum or iron. The electrodes can be made of Al or Fe plates or from scraps such as Fe or Al millings, cuttings, etc. When the waste materials are used, supports for the electrode materials have to be made from insert materials. Care needs to be taken to make sure that there are no deposits of sludges in between the scraps. It is also necessary to rinse regularly of the surface of the electrode plates or the scraps.

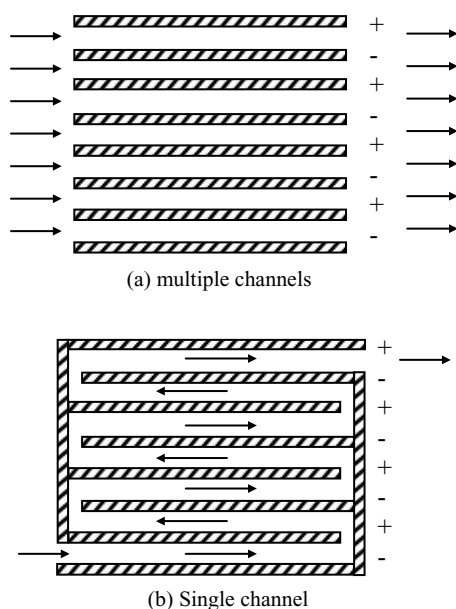


Fig. 11. Mode of water flow.

Because there are a definite amount of metal ions required to remove a given amount of pollutants, it is usually to use iron for wastewater treatment and aluminum for water treatment because iron is relatively cheaper. The aluminum plates are also finding applications in wastewater treatment either alone or in combination with iron plates due to the high coagulation efficiency of Al^{3+} [26]. When there are a significant amount of Ca^{2+} or Mg^{2+} ions in water, the cathode material is recommended to be stainless steel [28].

3.3. Typical design

Depending on the orientation of the electrode plates, the electrocoagulation cell can be horizontal or vertical, Fig. 10. To keep the electrocoagulation system simple, the electrode plates are usually connected in bi-polar mode. The water flow through the space between the plates can be multiple channels or a single channel, Fig. 11. Multiple channels are simple in the flow arrangement but the flowrate in each channel is also small. When the electrode surface passivation cannot be minimized otherwise, increasing the flowrate by using a single channel flow is recommended.

For water treatment, a cylindrical design can be used as shown in Fig. 12. It can be efficiently separate the

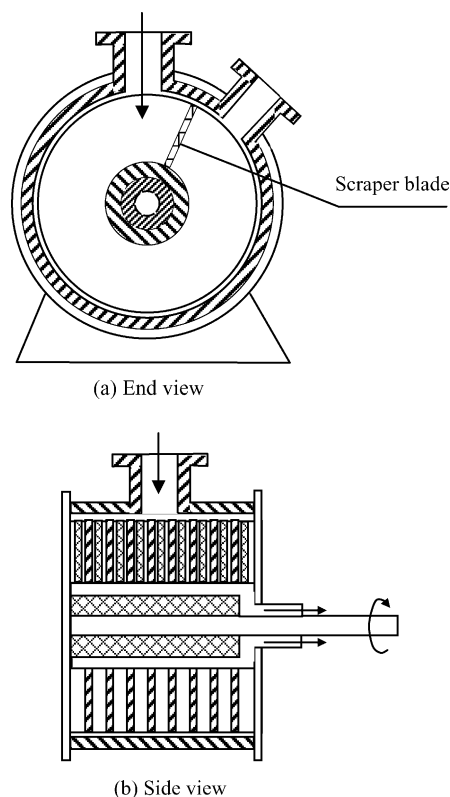


Fig. 12. Electrocoagulation unit with cylindrical electrodes.

suspended solids (SS) from water. In order to prevent any blockings, scraper blades are installed inside the cylinder. The electrodes are so fitted that they are at the open space of the teeth of the comb. An alternative of cylindrical design is given in Fig. 13 where a venturi is placed in the center of the cylinder with water and coagulants flowing inside it to give a good mixing. The electrocoagulation reactor can be operating in continuous as well as in batch operation. For batch operation such as the cases for treating small amount of laundry wastewater or for the water supply of construction site, the automation is an important issue. The electrocoagulation has to be followed by a sludge removal process. It is either a sedimentation unit or a flotation unit.

3.4. Effluents treated by electrocoagulation

Electrocoagulation is efficient in removing suspended solids as well as oil and greases. It has been

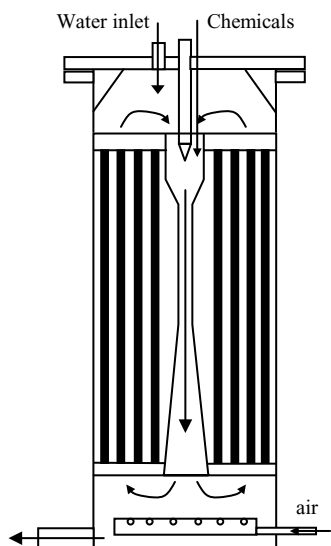


Fig. 13. Rod electrodes in a cylinder electrocoagulation unit.

proven to be effective in water treatment such as drinking water supply for small or medium sized community, for marine operation and even for boiler water supply for industrial processes where a large water treatment plant is not economical or necessary. It is very effective in coagulating the colloidal found in natural water so that reduces the turbidity and color. It is also used in the removal or destruction of algae or microorganisms. It can be used to remove irons, silicates, humus, dissolved oxygen, etc. [28].

Electrocoagulation was found particularly useful in wastewater treatment [37]. It has been employed in treating wastewaters from textile [38–41], catering [29,42], petroleum, tar sand and oil shale wastewater [43], carpet wastewater [44], municipal sewage [45], chemical fiber wastewater [46], oil–water emulsion [47,48], oily wastewater [34] clay suspension [49], nitrite [50], and dye stuff [51] from wastewater. Copper reduction, coagulation and separation was also found effective [52].

4. Electroflotation

Electroflotation is a simple process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water

Table 2

The range of gas bubbles at different pH and electrode materials

pH	Hydrogen (μm)			Oxygen (μm)
	Pt	Fe	C	Pt
2	45–90	20–80	18–60	15–30
7	5–30	5–45	5–80	17–50
12	17–45	17–60	17–60	30–70

electrolysis [53]. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively. EF was first proposed by Elmore in 1904 for flotation of valuable minerals from ores [2].

4.1. Factors affecting electroflotation

The performance of an electroflotation system is reflected by the pollutant removal efficiency and the power and/or chemical consumptions. The pollutant removal efficiency is largely dependent on the size of the bubbles formed. For the power consumption, it relates to the cell design, electrode materials as well as the operating conditions such as current density, water conductivity, etc. If the solid particles are charged, the opposite zeta-potential for the bubbles are recommended [54].

4.1.1. pH effect

The size variation of the bubbles depends on water pH as well as the electrode material as shown in Table 2 [55]. The hydrogen bubbles are smallest at neutral pH. For oxygen bubbles, their sizes increase with pH. It should be noted, however, the cathode materials affect the size of the hydrogen bubbles, so do the anode materials. The bubble sizes obey a log-normal distribution [54].

Using buffer solution, Llerena et al. [56] found that the recovery of sphalerite is optimal at pH between 3 and 4. They also documented that during this pH range, the hydrogen bubbles are the smallest, about $16 \pm 2 \mu\text{m}$. Decrease or increase pH from 3 to 4 results in the increase of hydrogen bubbles. At pH of 6, the mean hydrogen bubbles is $27 \mu\text{m}$. At pH of 2, the hydrogen bubbles are about $23 \mu\text{m}$ when the current density was all fixed at 500 A/m^2 using a 304 SS wire. Oxygen and hydrogen were separated in their research

Table 3

The mean gas bubble size at different current density and electrode materials, pH 9

Electrode	Current density (A/m ²)				
	125	200	250	300	375
Hydrogen gas bubbles diameter (μm)					
SS plate	34	32	29	26	22
200 mesh	39	35	32	31	28
100 mesh	45	40	38	30	32
60 mesh	49	45	42	40	37
Oxygen gas bubbles diameter (μm)					
Pt plate	48		46		42
200 mesh	50		45		38

and it was found that the increase of pH in the cathode chamber and pH decrease in the anode chamber are very quick when no buffer solutions were used. The recovery efficiency of oxygen is about half of that of hydrogen proportional to the amount of gas generated at a given current. This was also confirmed by O₂ and H₂ gas sparging.

4.1.2. Current density

The gas bubbles depends also on the current density [57,58]. The surface condition affects the particle size, too. The polished mirror surface of the stainless steel plate gives the finest bubbles, Table 3. Besides size of bubble, the bubble flux, defined as the number of gas bubbles available per second per unit cross-section area of the flotation cell, also plays a role in mineral flotation, recovery of different sized particles [58]. A decrease of gas bubble sizes was found with the increase of current intensity, Table 3. Burns et al. [59] found that such a decrease of bubble size with increase in current density was true only at the low end of current densities. When the current density is higher than 200 A/m², no clear trend can be observed with gas bubbles ranging from 20 to 38 μm, Table 4.

4.1.3. Arrangement of the electrodes

Usually, an anode is installed at the bottom, while a stainless steel screen cathode is fixed at 10–50 mm above the anode [56,60,61], Fig. 14. Such an electrode arrangement cannot ensure quick dispersion of the oxygen bubbles generated at the bottom anode into wastewater flow, affecting flotation efficiency. Moreover, if the conductivity of wastewater is low,

Table 4

The mean gas bubble size at different conditions (polished graphite electrodes, DI water, Na₂SO₄)

Ionic strength	Current density (A/m ²)	Gas	Mean size (μm)
0.1	52.3	O ₂	18.6
	98.5		21.2
	129.2		23.3
	196.7		17.1
	212.3		37.9
	295.4	H ₂	20.0
	393.8		20.7
	492.3		28.7
	590.8		26.2
	689.2		20.7
	787.7		25.3
	886.1		31.5
	55.4		29.7
	98.5		37.7
	196.9		19.3
0.01	33.8	O ₂	27.0
	46.2		24.7
	58.5		22.0
	36.9	H ₂ s	37.6
	43.1		37.3
	55.4		22.0

energy consumption will be unacceptably high due to the large inter-electrode spacing required for preventing the short-circuit between the upper flexible screen cathode and the bottom anode.

Chen et al. [62] proposed and tested the novel arrangement of electrodes with anode and cathode placed on the same plane as shown in Fig. 15. Effective flotation was obtained because of quick dispersion of the small bubbles generated into the wastewater flow. Quick bubble dispersion is essentially as important as the generation of tiny bubbles. For a conventional electrode system, only the upper screen cathode faces the wastewater flow, while the bottom anode does not

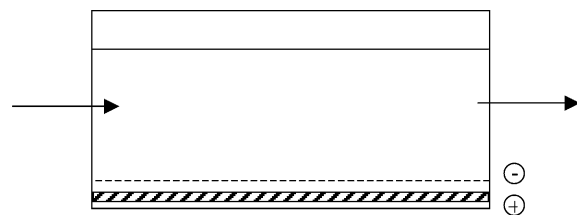


Fig. 14. Conventional electrodes arrangement for electroflotation.

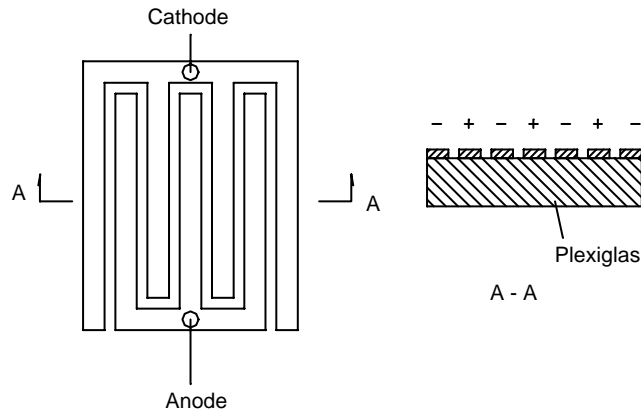


Fig. 15. Novel electrodes arrangement for electroflotation.

interact with the flow directly. Therefore, the oxygen bubbles generated at the bottom anode cannot be dispersed immediately into the wastewater being treated. Consequently, some oxygen bubbles may coalesce to form useless large bubbles. This not only decreases the availability of the effective small bubbles, but also increases the possibility of breaking the flocs formed previously, affecting the flotation efficiency. When the anode and the cathode are leveled, such an open configuration allows both the cathode and the anode to contact the wastewater flow directly. Therefore, the bubbles generated at both electrodes can be dispersed into wastewater rapidly and attach onto the flocs effectively, ensuring high flotation efficiency. Another arrangement of the electrodes is shown in Fig. 16. It has the advantage of the uniform property of the surface of an electrode. It is also very much efficient [26].

Meanwhile, the open configuration has been proven quite effective in the flotation of oil and suspended solids. Significant electrolysis energy saving has also been obtained due to the small inter-electrode gap used in the novel electrode system. It is useful to point out that the electrolysis voltage required in an EF process is mainly from the ohmic potential drop of the solution resistance, especially when the conductivity is low and the current density is high. Since the ohmic potential drop is proportional to the inter-electrode distance, reducing this distance is of great importance for reducing the electrolysis energy consumption. For a conventional electrode system, due to the easy short-circuit between the upper flexible screen electrode and the bottom electrode, use of a very small spacing is technically difficult. But for the electrode system shown in Figs. 15 and 16, the inter-electrode gap can be as small as 2 mm.

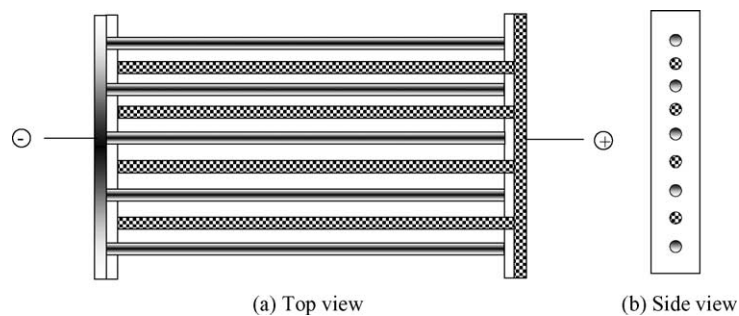


Fig. 16. Alternative electrode arrangement for electroflotation.

4.2. Comparison with other flotation technologies

The effective electroflotation obtained is primarily attributed to the generation of uniform and tiny bubbles. It is well known that the separation efficiency of a flotation process depends strongly on bubble sizes. This is because smaller bubbles provide larger surface area for particle attachment. The sizes of the bubbles generated by electroflotation were found to be log-normally distributed with over 90% of the bubbles in the range of 15–45 μm for titanium-based DSA[®] anode [62]. In contrast, typical bubble sizes range from 50 to 70 μm for DAF [63]. Burns et al. [59] reported that values of gas bubble size vary from 46.4 to 57.5 μm with the pressure decrease from 635 to 414 kPa for DAF. The electrostatic spraying of air [64] gives gas bubbles range from 10 to 180 μm with mean diameter being 33–41 μm [59]. Impeller flotation (IF) produces much smaller gas bubbles but its pollutant removal efficiency is not good probably due to the quick coalesce of the tiny bubbles to form larger ones soon after they are generated. Table 5 summarizes the comparison of different flotation processes for treating oily wastewater [65]. IC, OC and F in the table denote inorganic coagulants, organic coagulants and flocculants, respectively. Electroflotation clearly shows advantages over either DAF, settling or IF. When the conductivity is low, direct application of EF consumes large amount of electricity. For this case, addition of table salt (NaCl) is helpful [66].

4.3. Oxygen evolution electrodes

The electrode system is the most important part and thus considered as the heart of an EF unit. Although iron, aluminum and stainless steel are cheap, readily

available, and able to fulfill the simultaneous EC and EF, they are anodically soluble [29,56,59,67]. To make matters worse, the bubbles generated at partially dissolved electrodes usually have large sizes due to the coarse electrodes surfaces [42]. Graphite and lead oxide are among the most common insoluble anodes used in EF [59,68]. They are also cheap and easily available, but both show high O_2 evolution overpotential and low durability. In addition, for the PbO_2 anodes, there exists a possibility to generate highly toxic Pb^{2+} , leading to severe secondary pollution. A few researchers reported use of Pt or Pt-plated meshes as anodes [58,60]. They are much more stable than graphite and lead oxide. However, the known high cost makes large-scale industrial applications impracticable.

The well-known TiO_2 – RuO_2 types of dimensionally stable anodes (DSA[®]) discovered by Beer [25] possess high quality for chlorine evolution but their service lives are short for oxygen evolution [69]. In the last decade, IrO_x -based DSA[®] have received much attention. IrO_x presents a service life about 20 times longer than that of the equivalent RuO_2 [70]. In general, Ta_2O_5 , TiO_2 , and ZrO_2 are used as stabilizing or dispersing agents to save cost and/or to improve the coating property [71–75]. Occasionally, a third component such as CeO_2 is also added [70,75]. It should be noted that although incorporation of Ta_2O_5 , TiO_2 and ZrO_2 can save IrO_x loading, the requirement of molar percentage of the precious Ir component is still very high. The optimal IrO_x contents are 80 mol% for IrO_x – ZrO_2 , 70 mol% for IrO_x – Ta_2O_5 , and 40 mol% for IrO_x – TiO_2 , below which electrode service lives decrease sharply [73]. The IrO_x – Ta_2O_5 -coated titanium electrodes have been successfully used as anodes of EF [42,76]. Nevertheless, due to the consumption of

Table 5
Economic parameters in treating oily effluents

Treatment type	EF	DAF	IF	Settling
Bubble size (μm)	1–30	50–100	0.5–2	
Specific electricity consumption (W/m^3)	30–50	50–60	100–150	50–100
Air consumption (m^3/m^3 water)		0.02–0.06	1	
Chemical conditioning	IC	OC + F	OC	IC + F
Treatment time (min)	10–20	30–40	30–40	100–120
Sludge volume as percent of treated water	0.05–0.1	0.3–0.4	3–5	7–10
Oil removal efficiency (%)	99–99.5	85–95	60–80	50–70
Suspended solids removal efficiency (%)	99–99.5	90–95	85–90	90–95

large amounts of the IrO_x , $\text{Ti/IrO}_x\text{-Ta}_2\text{O}_5$ electrodes are very expensive, limiting their wide application.

The recently discovered $\text{Ti/IrO}_x\text{-Sb}_2\text{O}_5\text{-SnO}_2$ anodes have extremely high electrochemical stability and good electrocatalytic activity for oxygen evolution [77,78]. A $\text{Ti/IrO}_x\text{-Sb}_2\text{O}_5\text{-SnO}_2$ electrode containing only 10 mol% of IrO_x nominally in the oxide coating could be used for 1600 h in an accelerated life test and was predicted to have a service life over 9 years in strong acidic solution at a current density of 1000 A/m^2 . Considering the much lower current density used and nearly neutral operating environments in EF, the IrO_x content in the coating layer can be reduced to 2.5 mol% with sufficient electrochemical stability and good activity retained [62].

The electrode service life is strongly dependent on the current density used. A simple model relating the service life (SL) to the current density (i) has been obtained [35]:

$$\text{SL} \propto \frac{1}{i^\alpha}, \quad (20)$$

where α ranges from 1.4 to 2.0.

4.4. Typical designs

The electroflotation system consists of two electrodes, a power supply and a sludge handling unit. The electrodes are usually placed at the bottom or close to the bottom of the cell. Depending on the geometry of the EF cell, the electrodes can be placed vertically or horizontally. The horizontal placement is the most popular choice [60,79,80]. Electroflotation is usually combined with electrocoagulation or chemical flocculation, Fig. 17. In order for the chemical reagents to mix well with the pollutants before flotation, fluidized

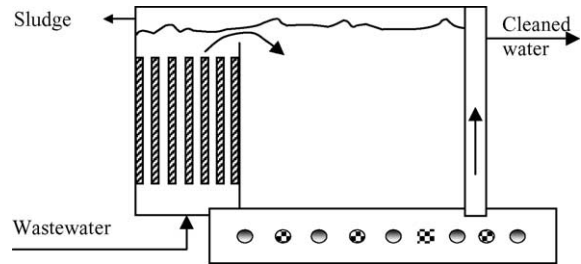


Fig. 17. Combined electrocoagulation and electroflotation.

media have been used [81], Fig. 18. This design allows an intensive contact of the solid phase in the mixing chamber with coagulants to form suspension particle agglomerates and at the same time not to break up the floculates formed. The two stages of electroflotation ensures the removal of finely dispersed particles. The installation of an ion exchange membrane between the electrodes in the fine electroflotation unit serves the purpose of controlling the pH of the treated water. The addition of partitions in an electroflotation unit helps to better utilize the gas generated and the flotation volume if non-rectangular flotation unit is employed [82], Fig. 19. Co-current and counter-current electroflotation systems, Fig. 20, were also investigated in industrial scale [83]. Frequently, it may be necessary to separate the cathode and anode chambers in order to avoid the atomic hydrogen or oxygen to react with the solid particles in mining system, the automatic pH adjustment in each chamber has to be provided [84]. Although there are equations available for the design of electroflotation unit [85], the actual design of an industrial operation has to base on careful laboratory study.

The following example can provide some guidelines in the design of an electroflotation system. This

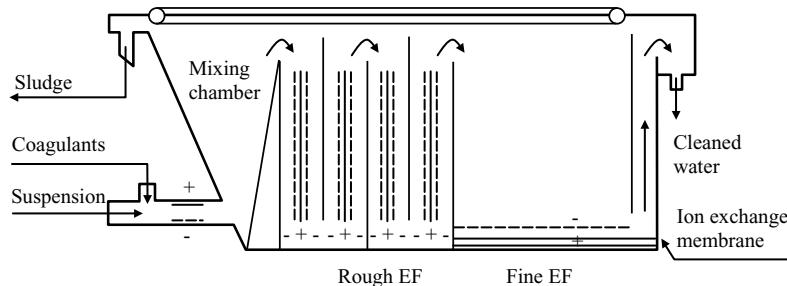


Fig. 18. Electroflotation with a fluidized media.

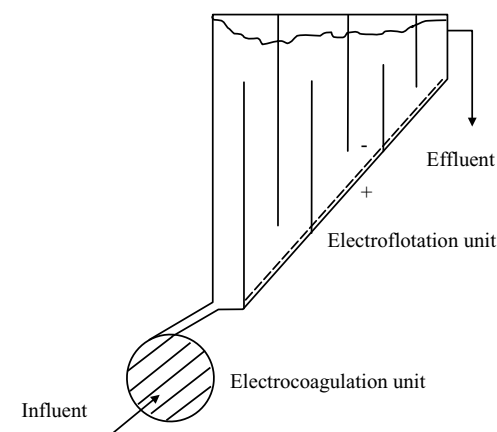


Fig. 19. Electroflotation with built-in partitions.

design was made and tested for highly concentrated industrial sewage from porcelain and faience industry [80]. The schematic diagram is shown in Fig. 21. The system consists of a case, a sludge collector, and an electrode pile. The body is made of polypropylene and is of rectangular shape. The unit is divided by a partition to have two sections. Each section is further partitioned into two chambers. Electrode piles

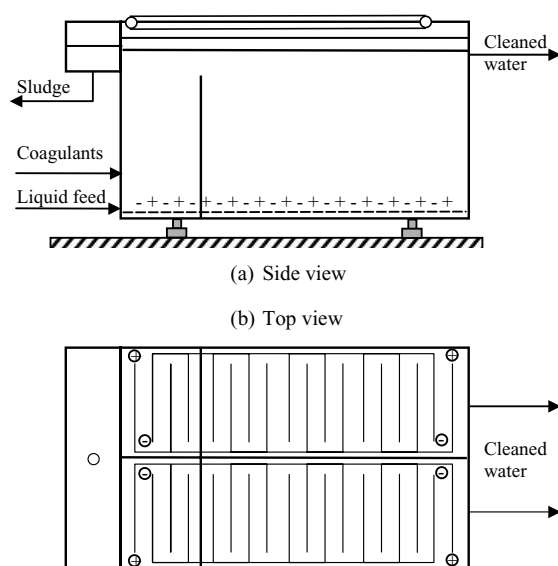


Fig. 21. A typical electroflotation unit design.

are placed vertically in each chamber. The body is equipped with inlet and outlet pipes with flanges connected with pipelines and sludge collectors consisting of a scrubbing devices and a geared motor.

The electrode pile consists of a set of rectangular plates 1 mm thick. The cathodes are made of a stainless steel and the anodes are made of titanium-based DSA[®]-type materials (Ti/Ru–TiO₂). The spacing between the electrodes is 3 mm. To prevent the formation of sediment, crest shaped electrodes are used which are arranged within the same plane to avoid short-circuit. DC power supply was employed. The overall dimensions are 2100 mm × 1115 mm × 1500 mm with the optimum height of the work zone being 0.8 m. The output of the system is up to 10 m³/h. The specific power consumption is 0.2–0.4 kW h/m³.

The equipment operates as follows. The liquid is fed into the first two chambers and then spills over the partitions into the second two chambers before flowing into a water header via an opening in the bottom part. The scrubbing device shifts the sludge from the surface in a direction opposite to the liquid flow and into a collecting pocket with a conic bottom located at the end of the floater on the side of the liquid inlet. The sludge is removed from the system via a branch pipe. Chemical coagulants and flocculants may be injected into the feeding line to intensify the purification. For

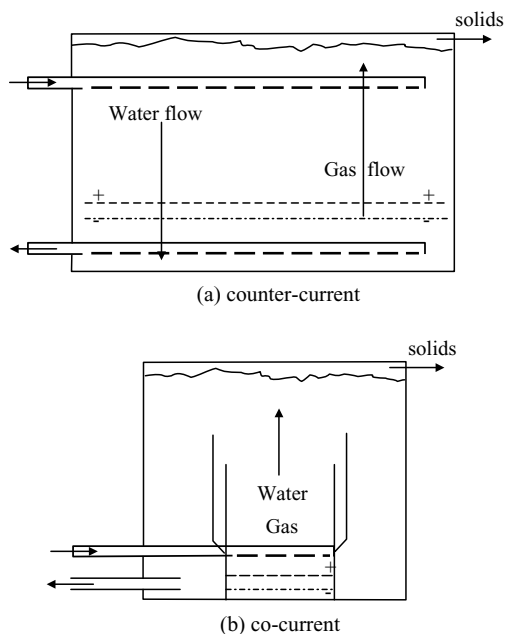


Fig. 20. Water-gas flow in an electroflotation unit.

Table 6
Electroflotation of industrial sewage in comparison with sedimentation

Parameter	Purification method	
	Sedimentation	Electroflotation
Duration (h)	2.0–7.0	0.2–0.4
Coagulant consumption (g/l)	0.20–0.40	0.02–0.04
Efficiency (%)	70–80	95–99
Moisture of sediment (%)	98.5–99.8	92.0–95.0
Volume of sediment (%)	17.0–20.0	0.1–0.2

Initial conditions: pH 7, BOD₅ = 50–100 mg/l, SS = 1700–28,900 mg/l, milky color.

this type of wastewater, the established chemicals to use are aluminosilicon flocculant-coagulant (AKFK). Introduction of 15 mg/l AKFK into water containing 300 mg/l suspended particles removes 92–95% impurities whereas the same amount of aluminum sulfate removes only 15% impurities. AKFK is made of SiO₂, Al₂O₃ and Fe₂O₃ with their respective concentrations being 25, 17 and 0.9 g/l. Table 6 lists the results of the electroflotation process in comparison with sedimentation method.

4.5. Wastewaters treated by electroflotation

Mineral recovery remains the major user of electroflotation [86]. In water and wastewater treatment, flotation is the most effective process for the separation of oil and low-density suspended solids [87–91]. Electroflotation is found effective in treating palm oil mill effluent [68], oily wastewater or oil–water emulsion [61,65,66,92,93], spent cooling lubricant [94], wastewater from coke-production [95], mining wastewater [67], groundwater [60], food processing wastewater [96], fat-containing solutions [97], restaurant wastewater [42] or food industry effluents [98], dairy wastewater [99], urban sewage [80], pit waters [100], colloidal particles [54], heavy metal containing effluents [84,101–103], gold and silver recover from cyanide solution [104], and many other water and wastewaters [56,65,83].

5. Electrooxidation (EO)

Study on electrooxidation for wastewater treatment goes back to the 19th century, when electrochemical

decomposition of cyanide was investigated [105]. Extensive investigation of this technology commenced since the late 1970s. During the last two decades, research works have been focused on the efficiency in oxidizing various pollutants on different electrodes, improvement of the electrocatalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation. Experimental investigations focus mostly on the behaviors of anodic materials, the effect of cathodic materials was not investigated extensively although Azzam et al. [106] have found a considerable influence of the counter electrode material in the anodic destruction of 4-Cl phenol.

5.1. Indirect electrooxidation processes

Electrooxidation of pollutants can be fulfilled through different ways. Use of the chlorine and hypochlorite generated anodically to destroy pollutants is well known. This technique can effectively oxidize many inorganic and organic pollutants at high chloride concentration, typically larger than 3 g/l [50,107–113]. The possible formation of chlorinated organic compounds intermediates or final products hinders the wide application of this technique [109]. Moreover, if the chloride content in the raw wastewater is low, a large amount of salt must be added to increase the process efficiency [113–116].

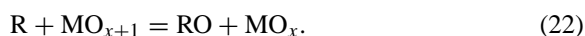
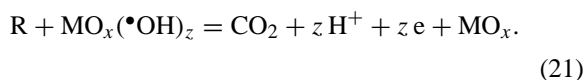
Pollutants can also be degraded by the electrochemically generated hydrogen peroxide [117–122]. In this system, the cathode is made of porous carbon-polytetrafluorethylene (PTFE) with oxygen feeding and the anode is either Pb/PbO₂, Ti/Pt/PbO₂, or Pt. Fe²⁺ salts can be added into the wastewater or formed in-situ from a dissolving iron anode [120] to make an electro-Fenton reaction. The degradation of aniline was found to be about 95% when UV irradiation is employed also. Simply sparging oxygen into the solution also helps the removal of aniline when electricity is on [119]. The electrically generated ozone is also reported for wastewater treatment [123,124].

Farmer et al. [125] proposed another kind of electrooxidation, mediated electrooxidation, in treating mixed and hazardous wastes. In this process, metal ions, usually called mediators, are oxidized on an anode from a stable, low valence state to a reactive,

high valence state, which in turn attack organic pollutants directly, and may also produce hydroxyl free radicals that promote destruction of the organic pollutants. Subsequently, the mediators are regenerated on the anode, forming a closed cycle. The typical mediators include Ag^{2+} , Co^{3+} , Fe^{3+} , Ce^{4+} and Ni^{2+} [125–130]. Mediated electrooxidation usually needs to operate in highly acidic media. In addition, there exists the secondary pollution from the heavy metals added. These disadvantages limit its application.

5.2. Direct anodic oxidation

Electrooxidation of pollutants can also occur directly on anodes by generating physically adsorbed “active oxygen” (adsorbed hydroxyl radicals, $\bullet\text{OH}$) or chemisorbed “active oxygen” (oxygen in the oxide lattice, MO_{x+1}) [131]. This process is usually called anodic oxidation or direct oxidation. The physically adsorbed “active oxygen” causes the complete combustion of organic compounds (R), and the chemisorbed “active oxygen” (MO_{x+1}) participates in the formation of selective oxidation products:



In general, $\bullet\text{OH}$ is more effective for pollutant oxidation than O in MO_{x+1} . Because oxygen evolution, reaction (9), can also take place at the anode, high overpotentials for O_2 evolution is required in order for reactions (21) and (22) to proceed with high current efficiency. Otherwise, most of the current supplied will be wasted to split water.

The anodic oxidation does not need to add a large amount of chemicals to wastewater or to feed O_2 to cathodes, with no tendency of producing secondary pollution and fewer accessories required. These advantages make anodic oxidation more attractive than other electrooxidation processes. The important part of an anodic oxidation process is obviously the anode material. Anode materials investigated include glassy carbon [132], Ti/RuO₂, Ti/Pt–Ir [109,133], fiber carbon [107], MnO₂ [134,135], Pt–carbon black [136,137], porous carbon felt [138], stainless steel

Table 7

Potential of oxygen evolution of different anodes, V vs. NHE

Anode	Value (V)	Conditions	Reference
Pt	1.3	0.5 M H ₂ SO ₄	[142]
Pt	1.6	0.5 M H ₂ SO ₄	[219]
IrO ₂	1.6	0.5 M H ₂ SO ₄	[76,142]
Graphite	1.7	0.5 M H ₂ SO ₄	[219]
PbO ₂	1.9	1 M HClO ₄	[155]
SnO ₂	1.9	0.5 M H ₂ SO ₄	[167]
Pb–Sn (93:7)	2.5	0.5 M H ₂ SO ₄	[142]
Ebonex® (titanium oxides)	2.2	1 M H ₂ SO ₄	[178]
Si/BDD	2.3	0.5 M H ₂ SO ₄	[200,197]
Ti/BDD	2.7	0.5 M H ₂ SO ₄	[203]
DiaChem	2.8	0.5 M H ₂ SO ₄	[142]

[50], and reticulated vitreous carbon [139,140]. However, none of them have sufficient activity and at the same time stability. The anodes that were studied extensively are graphite, Pt, PbO₂, IrO₂, TiO₂, SnO₂, and diamond film. We will discuss them in more details subsequently.

5.2.1. Overpotential of oxygen evolution

As discussed previously the anodic activity depends on the value of overpotential of oxygen evolution. Table 7 gives a comparison of most extensively investigated anode materials. For a better understanding of the performance of the anodes, the formation potentials of typical oxidants are listed in Table 8. It is clear that IrO₂, Pt, and graphite show much smaller values of overpotential of oxygen evolution. This indicates that effective oxidation of pollutants on these anodes occurs only at very low current densities or in the

Table 8

Formation potential of typical chemical reactants [142,220]

Oxidants	Formation potential
H ₂ O/ $\bullet\text{OH}$ (hydroxyl radical)	2.80
O ₂ /O ₃ (ozone)	2.07
SO ₄ ²⁻ /S ₂ O ₈ ²⁻ (peroxodisulfate)	2.01
MnO ₂ /MnO ₄ ²⁻ (permanganate ion)	1.77
H ₂ O/H ₂ O ₂ (hydrogen peroxide)	1.77
Cl ⁻ /ClO ₂ ⁻ (chlorine dioxide)	1.57
Ag ⁺ /Ag ²⁺ (silver(II) ion)	1.5
Cl ⁻ /Cl ₂ (chlorine)	1.36
Cr ³⁺ /Cr ₂ O ₇ ²⁻ (dichromate)	1.23
H ₂ O/O ₂ (oxygen)	1.23

presence of high concentrations of chlorides or metallic mediators. When the current density is high, significant decrease of the current efficiency is expected from the production of oxygen. The boron-doped diamond (BDD) film on titanium substrate [141] or other valve metals as in DiaChem electrodes [142] gives the highest value of oxygen evolution overpotential. Thus, anodic oxidation can take place on its surface at significantly high current density with minimal amount of

oxygen evolution side reaction. This leads to an effective and efficient process. It is indeed the most active anode for oxidation of various pollutants as discussed in the following sections.

5.2.2. Performance of anodic oxidation

Table 9 compares the performance of different anodes in the degradation of various pollutants under different conditions. Two parameters are of particular

Table 9
Comparison of the performance of different anodes

Anode	Pollutant	Current density (A/m ²)	CE (%)	Removal efficiency	Comment	Reference
Granular graphite	Phenol	0.03–0.32	70	70, 50% mineralization	5-month stable operation	[144]
Planar graphite	Phenol	10–100	24.6–63.5	6–17%, COD	NaOH as electrolyte	[145]
Pt or Ti/Pt	Phenol	300		30%, TOC	pH 12, initial concentration 1000 mg/l, in 0.25 M Na ₂ SO ₄	[165]
	Ammonia	8.5	53	95%	pH 8.2 using phosphate buffer, poor performance for organics	[146]
	Glucose 15 organics	100–900	15–20 5	30%	1 M H ₂ SO ₄	[221] [148]
PbO ₂	Aniline	$I = 2$ A	15–40	>90% in 1 h	Initial concentration 2.7 mM, pH 2, packed bed of PbO ₂	[153]
	Phenol	$I = 1, 2, 3$ A		46–80%	Anodic cell: initial concentration 14–56 mM, in 1.0 sulfuric acid, packed bed of PbO ₂	[211]
Ti/PbO ₂	Phenol	300		40%, TOC	pH 12, initial concentration 1000 mg/l, in 0.25 M Na ₂ SO ₄	[165]
	Landfill leachate	50–150	30% for COD 10% for NH ₄ ⁺ –N	90% for COD 100% for NH ₄ ⁺ –N		[172]
	Glucose	100–900	30–40	100%	1 M H ₂ SO ₄	[221]
	2-Chlorophenol	80–160	35–40	80–95%, COD	Pb ²⁺ formation, initial COD = 1000 mg/l, 25 °C	[157]
IrO ₂	Organic	Low	17			[149]
	1,4-Benzoquinone				Rupture of rings only	[151]
	Chlorinated phenols	0.6 50	54 1.8		Na ₂ SO ₄	[150]
Ti/SnO ₂ –Sb ₂ O ₅	2-Chlorophenol	80–160	35–40	80–95%, COD	Oxalic acid as intermediates	[157]
	Glucose	100–900	<20	30%	1 M H ₂ SO ₄	[221]
	Phenol	300		100%	pH 12, initial concentration 1000 mg/l, in 0.25 M Na ₂ SO ₄	[165]
		500	58		70 °C, 10 mM	[149]
	Landfill leachate				CV method, similar to PbO ₂ Similar to PbO ₂	[171] [172]
Ebonex [®]	Trichloroethylene	Fixed potential 2.5–4.3 V	<32	10–70%	Stable in aqueous media, Ti ₄ O ₇ to TiO ₂	[179]

concern, one is the current density, and the other is the current efficiency. Comninellis and Plattner [143] proposed to use electrochemical oxidability index (EOI) to differentiate the performances of different electrodes. EOI is the mean current efficiency from the initial concentration of pollutant to the time when the pollutant is nearly zero, τ [143]. To calculate EOI, one needs to know the instantaneous current efficiency, ICE, defined as the current efficiency at a given time of electrooxidation. Thus,

$$\text{EOI} = \frac{\int_0^\tau \text{ICE} \, dt}{\tau}. \quad (22)$$

Because EOI calculation so defined include significantly the contribution of ICE at long reaction time when the pollutant concentration is very low and mass transfer rather than electrochemical kinetics controls the process. Hence, the EOI so calculated is very low, ranging from less than 0.05 to 0.58 for electrochemically degrading various benzene derivatives on Pt anode [143]. If EOI is to be used, I believe the value of τ should be so selected that it equals to the time when mass transfer control just starts. Since we do not have the values of ICE where mass transfer control just begins, the average current efficiencies from initial to final values of a process are used for comparison instead.

For graphite electrodes the maximum CE obtained was as high as 70% at very low current densities ranging from 0.03 to 0.32 A/m² [144]. When current densities increased to 10–100 A/m², the CE values were only 6–17% [145]. Despite the satisfactory results obtained in oxidizing simple inorganic pollutants at very low current densities [146], Pt electrodes show poor efficiencies in anodic oxidation of organic compounds [147,148]. The carbon black addition was found to enhance the performance of Ti/Pt anodic oxidation of aqueous phenol significantly [136]. As mentioned before, IrO₂ has been widely investigated as an electrocatalyst for O₂ evolution. The low current efficiency is expected [149,150]. The low activity of this anode in oxidizing 1,4-benzoquinone may be related to the low current value has to be employed [151].

PbO₂ is the most widely investigated anode material for electrooxidation. Usually, PbO₂ electrodes are prepared either by anodically polarizing metal lead in H₂SO₄ solutions [152,153] or by electrochemically coating PbO₂ films on Ti substrates [149]. In order

to increase the activity, PbO₂ is sometimes doped by Bi, Fe, Ag [154–156]. For oxidation of organic pollutants like aniline, PbO₂ anode is very efficient with reasonable value of current efficiency [153]. The operating current density is also of reasonable value, 80–160 A/m² [157]. PbO₂ electrodes are relatively cheap and effective in oxidizing pollutants. The only concern for this electrode is the formation of Pb²⁺ ions from the electrochemical corrosion.

Pure SnO₂ is an n-type semiconductor with a band gap of about 3.5 eV. The valence band arises due to the overlap of filled oxygen 2p levels. The tin 5s states are at the bottom of the conduction band [158]. This kind of oxide exhibits a very high resistivity at room temperature and thus cannot be used as an electrode material directly. However, its conductivity can be improved significantly by doping Ar, B, Bi, F, P and Sb [159–165]. In electrochemical application, Sb is the most common dopant of SnO₂. Doped SnO₂ films are usually used as transparent electrodes in high-efficiency solar cells, gas detectors, far IR detectors and transparent heating elements [158]. The conductive SnO₂ films can be prepared by vapor deposition [160], sputtering [166], spray pyrolysis [165,167], sol-gel [168], and brush-dry-bake technique [169]. The onset potential for O₂ evolution on Sb-doped SnO₂ is about 1.9 V versus NHE in 0.5 M H₂SO₄ solution [170], similar to that on PbO₂.

Kotz et al. [165] first reported anodic oxidation of pollutants on Sb-doped SnO₂-coated titanium electrodes (Ti/SnO₂-Sb₂O₅). The CE obtained on Ti/SnO₂-Sb₂O₅ was about five times higher than that on Pt [148]. Comninellis [149] measured the CE of SnO₂-Sb₂O₅ to be 0.58 for 71% degradation of phenol while the values for PbO₂, IrO₂, RuO₂ and Pt are, respectively, 0.18, 0.17, 0.14 and 0.13 at $i = 500 \text{ A/m}^2$, pH 12.5, initial concentration of 10 mm, reaction temperature of 70 °C. Grimm et al. [171] investigated phenol oxidation on SnO₂-Sb₂O₅ and PbO₂ using a cyclic voltammetric method and also found that the former was more active. Nevertheless, Cossu et al. [172] reported that there was no substantial difference in activity between SnO₂-Sb₂O₅ and PbO₂ in treating landfill leachate. This might be associated with the presence of high concentrations of chlorides in this type of waste.

Despite the high efficiency for pollutant oxidation, Sb₂O₅-SnO₂ electrodes lack sufficient

electrochemical stability just like PbO_2 . Lipp and Pletcher [169] conducted a long term test of $\text{SnO}_2\text{--Sb}_2\text{O}_5$ in 0.1 M H_2SO_4 solution at a constant potential of 2.44 V versus NHE and found that the current dropped from initial 0.2 to about 0.1 A within a few hours and to 0.06 A after 700 h. Correa-Lozano et al. [173] also investigated the stability of $\text{Sb}_2\text{O}_5\text{--SnO}_2$ electrodes and found that the service life of $\text{Ti/Sb}_2\text{O}_5\text{--SnO}_2$ was only 12 h under an accelerated life test performed at a current density of 1000 A/m² in 1 M H_2SO_4 solution. At 10,000 A/m² and 3 M H_2SO_4 , this electrode can only last a few seconds [174]. Although addition of IrO_2 into the $\text{SnO}_2\text{--Sb}_2\text{O}_5$ mixture increased the service life significantly [77,78], the resulting electrodes have an overpotential of O_2 evolution of 1.5 V versus NHE in 0.5 M H_2SO_4 electrolyte.

Pure TiO_2 has a band gap of 3.05 eV [175] and thus shows poor conductivity at room temperature. TiO_2 is usually used as a photocatalyst in wastewater treatment. By doping with Nb and/or Ta, TiO_2 conductivity was successfully improved [176,177] to be used as an electrocatalyst for pollutant oxidation. This type of electrodes is usually made by baking the Ti substrates coated with Nb and/or Ta-doped TiO_2 films at 450 °C, followed by annealing the films at 650–800 °C in the presence of H_2 and a small amount of water vapor to reduce the Nb(V) to Nb(IV). The preferred molar concentration of (Nb + Ta) in the oxide coating is 2–6% [176]. TiO_2 electrodes are stable at low current densities (below 30 A/m²), but their lifetimes are significantly shortened when operated at high current densities [177]. Another conductive titanium oxide is Ebonex[®] that is also able to serve as an anode material. Ebonex[®] is a non-stoichiometric titanium oxide mixture comprised of Magneli phase titanium oxides Ti_4O_7 and Ti_5O_9 , and made by heating TiO_2 to 1000 °C in the presence of H_2 [178]. Although Ebonex[®] is stable in aqueous media throughout the practical pH range, anodic oxidation in 1 M sulfuric acid results in partial oxidation of Ti_4O_7 to TiO_2 , and surface passivation under extreme conditions may be an issue [179].

5.2.3. Boron-doped diamond electrode

Diamond is a fascinating material. Diamond is known for its high strength, extreme hardness, high resistance to thermal shock, and infrared transmissivity

[180]. It exhibits many unique technologically important properties, including high thermal conductivity, wide band gap, high electron and hole mobilities, high breakdown electric field, hardness, optical transparency, and chemical inertness [181]. Structurally, diamond has a cubic lattice constructed from sp^3 -hybridized tetrahedrally arranged carbon atoms with each carbon atom bonded to four neighbors [182]. The stacking sequence is ABCABC with every third layer plane identical. This structure is fundamentally different from that of graphite which consists of layers of condensed polyaromatic sp^2 -hybridized rings with each carbon atom bonded to three neighbors. Impurities in diamond can make it an insulator with a resistivity of $>10^6 \Omega \text{ m}$ and a band gap energy of 5.5 eV [181]. A recent finding from Sweden shows that pure diamond can be a very good conductor of electrons [183].

Diamond films are usually synthesized by chemical vapor deposition (CVD) [184]. Early CVD of diamond was carried out by thermal decomposition of carbon-containing gases such as CH_4 and CO [185,186] at gas temperatures between 600 and 1200 °C. The gas temperatures were about the same as the surface temperature of the diamond seeds that were exclusively used as substrates. The diamond growth rates were only about 0.01 $\mu\text{m/h}$, too low to be of commercial significance. In addition, the material was often contaminated with non-diamond carbon and required frequent interruptions to remove the accumulated graphite by hydrogen etching at a temperature $>1000^\circ\text{C}$ and a pressure $>50 \text{ atm}$, or by oxidizing in air at the atmospheric pressure [187].

In the mid-1970s, Derjaguin and Fedoseev [188] recognized the crucial role of atomic hydrogen in etching graphite deposits preferentially and successfully synthesized diamond on non-diamond substrates at a commercially practical deposition rate ($>1 \mu\text{m/h}$). This was a historic milestone in the development of diamond CVD techniques. However, intensive interests in diamond CVD did not arise until the early 1980s when Matsumoto et al. [189,190] revealed the details of synthesizing high-quality diamond films on Si and Mo substrates using hot-filament CVD (HFCVD). The typical deposition conditions were: methane concentration 1% in hydrogen, substrate temperature 700–1000 °C, filament temperature $\sim 2000^\circ\text{C}$, total gas pressure 13–133 mbar, and reaction time 3 h. Since then, new techniques such as microwave

Table 10

Treatment of different wastewaters and solutions using Si/BDD electrodes [199]

Wastewater/solution	Oxidation conditions	COD reduction (%)
Kodak E6 first developer	Initial COD 32,500 mg/l; solution volume 30 ml; current 0.31 A; current density 1000 A/m ² ; electrolysis time 6.25 h	73
Kodak E6 color developer	Initial COD 19,050 mg/l; solution volume 30 ml; current 0.31 A; current density 1000 A/m ² ; electrolysis time 4.75 h	80
Phenol solution	Initial COD 3,570 mg/l; solution volume 60 ml; current 0.31 A; current density 1000 A/m ² ; electrolysis time 18 h	94
Hydroquinone solution	Initial COD 23,530 mg/l; solution volume 60 ml; current 0.15 A; current density 500 A/m ² ; electrolysis time 38 h	97

plasma-assisted CVD [191] and DC discharge CVD [192] were developed rapidly. The diamond growth rates are in the order of 0.1 to near 1000 $\mu\text{m/h}$ [193], demonstrating the good prospect of diamond films for industrial applications.

The conductivity of diamond can be improved significantly by doping boron. Boron doping is usually achieved by adding B_2H_6 [194,195], or $\text{B}(\text{OCH}_3)_3$ [196,197] to the gas stream, or placing boron powder near the edges of the substrate prior to insertion into the CVD chamber [198]. A general useful range of the boron/carbon weight ratio in the boron-doped diamond is from ca. 0.02 to ca. 10^{-6} [199]. The onset potential for O_2 evolution on boron-doped diamond film on silicone substrate (Si/BDD) electrodes in 0.5 M H_2SO_4 solution is about 2.3 V versus NHE [197,200], 0.4 V higher than that on PbO_2 and SnO_2 . This indicates that diamond electrodes have higher CE for pollutant oxidation. Besides the increase in oxygen overpotential, the increase in hydrogen overpotential was also found by doping nitrogen leading to the widest window for water split reaction [142]. This conductive BDD film opened new frontiers of the diamond application in electrochemical synthesis and analysis, sensor development for in vitro or in vivo biomedical application, for long-term environmental

studies. Particularly, BDD film was found to be the most active anodic material for degradation of refractory or priority pollutants such as ammonia, cyanide, phenol, chlorophenols, aniline, TCE, various dyes, surfactants, landfill leachate [141,201–204].

Unlike PbO_2 , SnO_2 and TiO_2 , the BDD thin films deposited on Si, Ta, Nb, and W by CVD have shown excellent electrochemical stability [197]. The lifetime of Nb/BDD, for example, is over 850 h in the accelerated life test performed at 100,000 A/m² in 0.5 M H_2SO_4 solution. Even after several weeks of oxidation, the properties of these electrodes were not affected and poisoning of the surface was not detectable. However, Si/BDD electrodes are not suitable for industrial applications because Si substrates are very brittle and their conductivity is poor. Yet, large-scale usage of Nb/BDD, Ta/BDD, and W/BDD electrodes is impossible due to the unacceptably high costs of Nb, Ta and W substrates.

Basically, the function of a substrate is to provide a facile pathway for the flow of current through the electrode assembly and a mechanical support for the thin diamond film. The materials that can probably be used as substrates must simultaneously have three important attributes: good electrical conductivity, sufficient mechanical strength, and electrochemical inertness or

Table 11

Oxidation of various organic compounds on Si/BDD electrodes [197,206,207]

Compound	Oxidation conditions	CE (%)
Phenol	Initial concentration 0.002 M; current density 300 A/m ² ; pH 2; charge loading 4.5 Ah/l; final phenol concentration <3 mg/l	33.4 ^a
CN^-	Initial concentration 1 M; current density 360 A/m ² ; 95% CN^- elimination; 1 M KOH	41
Isopropanol	Initial concentration 0.17 M; current density 300 A/m ² ; <90% conversion	>95
Acetic acid	Initial concentration 0.17 M; current density 300 A/m ² ; 90% conversion; 1 M H_2SO_4	85

^a Calculated value based on charge loading.

Table 12
Comparison of Ti/BDD with Ti/Sb₂O₅–SnO₂ for pollutant oxidation [203]

Pollutant	Current density (A/m ²)	Charge (Ah/l)	Initial COD (mg/l)	Ti/BDD		Ti/Sb ₂ O ₅ –SnO ₂	
				Final COD (mg/l)	CE (%)	Final COD (mg/l)	CE (%)
Acetic acid	200	5.53	1090	33	64.0	756	20.2
Maleic acid	200	6.43	1230	46	61.7	557	35.0
Phenol	100	4.85	1175	39	78.5	450	50.1
orange II	200	6.25	1120	95	54.9	814	16.4
Reactive red HE-3B	200	6.25	920	45	46.9	714	11.0

easy formation of a protective film on its surface by passivation [199]. In addition, the costs of the materials should be acceptable. Titanium possesses all these features and is therefore considered to be a good substrate material. Actually, this metal has been widely used in DSA[®] for over 30 years. The deposition of stable BDD films on Ti substrates with CVD from the standard gas mixture of H₂ + CH₄ is very difficult up to date. Cracks may appear leading to the delamination of the diamond films under electrochemical attack at high loads [197]. By adding CH₂(OCH₃)₂ in the precursor gas, Chen et al. [141,203] have managed to deposit a BDD film on Ti substrate with satisfactory stability. Nowadays, diamond films can be deposited on the substrates with various geometries up to 0.5 m² using HFCVD method [205].

Carey et al. [199] patented the use of diamond films as anodes for organic pollutant oxidation. The Si/BDD electrodes they used were commercially obtained from Advanced Technology Materials Inc. The boron concentrations in the diamond films were 1000–10,000 ppm. Different wastewaters and solutions were investigated. Some results are summarized in Table 10. A Switzerland research group [197,206,207] also investigated anodic oxidation of various pollutants on Si/BDD electrodes. The results are summarized in Table 11. The CE obtained is very high, ranging from 33.4 to over 95%, depending on pollutant properties and oxidation conditions.

Beck et al. [208] compared Si/BDD with Ti/SnO₂, Ta/PbO₂ and Pt for oxidation of phenol. At a charge loading of 20 Ah/l, the total organic carbon (TOC) was reduced from initial 1500 to about 50 mg/l on Si/BDD, and to about 300, 650, and 950 mg/l on Ti/SnO₂, Ta/PbO₂ and Pt, respectively. Obviously, Si/BDD electrodes have much higher activity than

other electrodes. The performance of Ti/BDD anode is given in Table 12 [203].

5.3. Typical designs

The electrooxidation reactors are similar to those seen in Section 2.1 for metal recoveries. The concerns are also the current efficiency and also the space–time

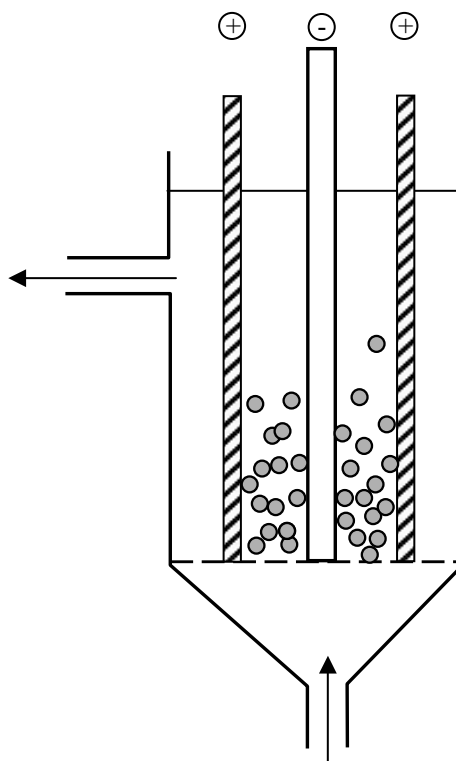


Fig. 22. Reactor with cylindrical electrodes.

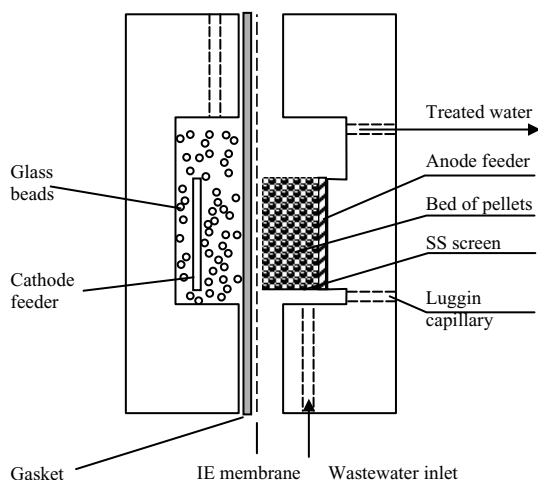


Fig. 23. Packed bed electrochemical reactor.

yield. The simplest electrooxidation reactor design is the bi-polar cell. Besides plane electrodes, the cylindrical electrodes can also be employed [137,209,210], Fig. 22. Inside the cylindrical anode, there are spherical particles with BDD coating serving as the bi-polar electrodes. Packed bed of about 1 mm pellets of proper anode materials can also be used [211,212], Fig. 23. Fig. 24 shows the bi-polar trickle tower that can be

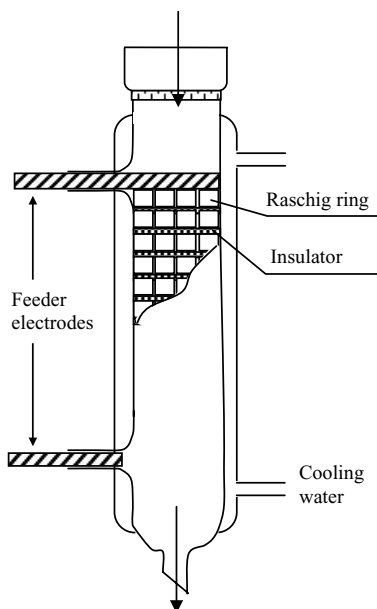


Fig. 24. Bi-polar trickle tower electrochemical reactor.

employed with insulating net separating adjacent layers of bi-polarized packing [213,214]. Filter press reactor is another design [215]. In order to improve mass transfer to the surface of the electrode, sonoelectrochemical process has been tested and proven enhancement was achieved [216,217]. A thin layer of biofilm can be immobilized on the surface of electrodes to have a bio-electro reactor. It was found to be capable of oxidation and reduction simultaneous in nitrification and denitrification when respective microorganisms are immobilized on the anode [218].

6. Summary

Electrochemical technologies have been investigated as the effluent treatment processes for over a century. Fundamental as well as engineering researches have established the electrochemical deposition technology in metal recovery or heavy metal-effluent treatment. Electrocoagulation has been used industrially and demonstrated its superior performances in treating effluents containing suspended solids, oil and grease, and even organic or inorganic pollutants that can be flocculated. Electroflotation is widely used in the mining industries and is finding increasing applications in wastewater treatment. The uniform and tiny sized bubbles-generated electrically give much better performance than either dissolved air flotation, sedimentation or even impeller flotation. This process is compact and easy to facilitate with automatic control. With the invention of stable, active and cheap materials for oxygen evolution, this technology will gradually replace the conventional flotation techniques. Indirect oxidation is still a viable technology for treating toxic or biorefractory pollutants although there are concerns about the formation of chlorinated intermediates in the case of using chlorine ions or about the complicated facilities in the case of using electrically formed hydrogen peroxide or ozone. Direct anodic oxidation represents one of the simplest technologies in the pollutant mineralization provided the anode materials are stable and have high overpotential of oxygen evolution. The investigation of various materials so far shows that titanium or other noble metal-based boron-doped diamond film is the candidate for industrial application. It has the widest window for water split and is inert in

tough situations. Further improvement in its stability in electrochemical application is required before its industrial acceptance.

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