

Electrochemical Technologies for Environmental Remediation

Nael G. Yasri and Sundaram Gunasekaran

Abstract Contamination of environmental compartments with a myriad of chemical pollutants is inevitable. Many physical, biological, photolytic, chemical, and electrochemical techniques are in use for the pollutant remediation. Notably, elegant solutions to remediating environmental pollutants have been provided by electrochemical methods. Literature supports the versatility, energy efficiency, environmental compatibility, and cost-effectiveness of electrochemical methods for pollutant remediation. This chapter aims to describe electrochemical methods for remediation of a variety of dilute pollutants, organic contaminants, organic complexes with metals, and recovery of heavy metals. Additionally, effort has also been made to discuss major bioelectrochemical methods for the generation of energy from waste stream as power source.

Keywords Environmental pollution • Remediation • Electrochemistry • Electrochemical technologies • Bioelectrochemistry

Introduction

Advances in technology and increased consumer demand for goods and services have resulted in increased amounts of pollutants present in the environment. The pollutants are usually categorized under different subtypes, and various regulatory bodies often refer to those that are most dangerous to the environment as belonging to a “Black List,” which includes persistent organic pollutants (POPs) such as organohalogen, organophosphorus, some metals, and their organometallic complexes. Many POPs

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are toxic and resistant to conventional biological and chemical wastewater treatments and bioaccumulate in the environment (Calow 2009).

Many problems associated with hazardous wastes, however, can be avoided if proper actions are taken in the early stages by either waste reduction (cutting down the amount of waste at the origin) or waste elimination (replacing hazardous materials with “green” chemicals or using treatment processes which reduce the amount of waste requiring ultimate disposal). This would necessitate ensuring that waste is recovered as much as possible and when necessary disposed off using methods that are benign to the health of humans and the environment. However, it is said that municipal wastewater may contain as much as 9.3 times the amount of energy required for its treatment (Fan et al. 2012). Waste streams, therefore, can be considered as a preliminary source of energy and technologies, which can generate energy from waste, and are considered as “green” or environmentally friendly (Harnisch et al. 2015; Liu et al. 2005). Consequently, it is important to consider the following hierarchy of priorities while dealing with wastes: prevention, reduction, reuse, recycle, and appropriate utilization of waste as a source of energy (Wang et al. 2010c).

The many techniques used in the remediation of wastes fall under the major categories of physical, biological, photolytic, chemical, and electrochemical. Of these, electrochemical methods often provide elegant solutions to remediating environmental pollutants (Janssen and Koene 2002; Ota et al. 2014); they offer several advantages over other methods such as versatility, energy efficiency, amenability to automation, environmental compatibility, and cost-effectiveness.

Generally, electrochemistry is considered a physicochemical discipline with wide-ranging applications that are directly or indirectly useful in our daily life. These include chemical conversion for energy generation, energy storage (battery charging/discharging), metal coating, surface technology, biological systems (nervous, cardiology, and cells), corrosion, electroanalysis, sensor, electrosynthesis, pollution control, recycling, treatment, remediation, and disinfection (Ota et al. 2014). Electrochemical techniques have been used since the early 1960s for the treatment of wastewater containing metallic, organic, and inorganic compounds (Chen and Hung 2007; Comninellis 2010; Rajkumar and Palanivelu 2004). The technique is known for its broad adaptability. For example, in an electrochemical cell various types of reactions such as oxidation, reduction, phase separation, dilution, concentration, and biological and photolytic reactions can be monitored directly or indirectly. Separation of the reaction products is feasible by implementing various established designs or controlling reactors and/or reaction conditions. Pollutants of different types or phases, i.e., solids, liquids, or gases, could be dealt with. Also, electrochemical reactors are scalable for treating solution volumes ranging from milliliters to barrels or more. Electrochemical treatment is usually performed at temperatures lower than non-electrochemical approaches, which leads to increased energy efficiency. Varying the applied potential, design of electrochemical cells, and choice of electrodes could help minimize power losses, voltage drops, and unwanted side reactions. Additionally, data collected in terms of current and voltage facilitate process automation and control. External control of the

electron transfer across the interfaces causes the electrons to obtain a specific energy, thus making electrons the main reagent for the interface reaction; this “clean reagent” promotes environmentally benign technology (Chen and Hung 2007; Comninellis 2010). For example, a prudent choice of electrode type (interface surface) enhances the selectivity of the electrode and hence prevents the production of unwanted side reactions. Overall, electrochemical processes are generally simple and, if properly designed, cost-effective.

Commonly, pollutant species which are targeted for electrochemical treatment are rather dilute, seldom exceeding in concentrations a few hundred or thousand parts per million (ppm). Therefore, electrochemical pollutant remediation falls under the electrochemistry of dilute solutions, which is completely different from that of treating concentrated media. For example, electrochemical properties of effluents contaminated with toxic heavy metals are different from those of electroplating or electrowinning media, which are very dilute. Accordingly, the design considerations of electrochemical cells for treating dilute streams are different than those for concentrated solutions.

The applications of electrochemical technologies for industrial recycling and effluent treatment include the removal, recovery, and separation of dissolved metals, destruction of dissolved organic materials, and treatment of waste gases. More recently, electrochemical technology is used to generate electric power or hydrogen from waste products in the so-called microbial fuel cells (MFCs) (Logan 2008) or microbial electrolysis cells (MECs) (Logan et al. 2008), respectively. Considering other applications, electrochemistry can be used to control electrode potentials for detoxification of specific biological inhibitor compounds, such as phenolic and furfural produced during various chemical and biological platform treatments (Lee et al. 2015).

Given the above, this chapter aimed to describe electrochemical methods for remediation of a variety of dilute pollutants, organic contaminants, organic complexes with metals, and recovery of heavy metals. In addition, electrochemical methods to generate energy from waste stream as power source are also included.

Electrochemistry: The Basics

Electrochemistry is the science that deals with the consequences of transferring electric charges from one phase to another; in particular, it deals with the electric properties at interfaces. For example, when two phases (a metal electrode and an electrolyte solution containing ions) are brought into contact, some ions in one phase tend to transfer to the other, carrying their electric charge. This creates a potential difference across the region between the two phases. This region is called an interface (or electrode interface), and the potential is called the interface potential (or electrode potential). Thereby, in an electrochemical cell, at one electrode-electrolyte interface, electrons leave the electrode (electron source, cathode), and the particles (cations) of the solution are reduced. At the other interface,

the electrode (electron sink, anode) takes electrons from the particles, and oxidation takes place. External control of electron transfer rates across the interface causes the electrons to obtain specific energy.

The definitions and sign conventions of anode and cathode used are conventional, with anode always being the site of oxidation and cathode, the site of reduction. The conventional signs of currents and potentials measured at the both sites (anode/cathode) depend on the type of electrochemical cell. For example, in a galvanic cell (e.g., batteries), where reactions are spontaneous, the cathode is assigned positive (electron sink, where reduction takes place). However, in the electrolysis cell where current or potential is applied to drive a chemical reaction, the anode is assigned positive. The control of the sign and the rate of electrons exchange at the interfaces in the electrochemical cell are additional advantages to possibly control the chemical reactions through an applied potential, which can help promote process automation.

Electrolysis can be used for wastewater treatment exploiting the oxidation/reduction reactions at the electrodes (Chen 2010). Reduction takes place at the cathode by the action of diffused cations toward the surface (e.g., deposition of metal ions on cathode) generating cathodic currents; while at the same time, anions diffuse toward the anode for oxidation to take place at the surface generating anodic currents.

General Aspect of Electrochemistry

Before describing the main electrochemical treatment technique and the mechanisms involved, it is helpful to review the basics of electrochemistry, which is necessary to understand the performance of various remediation processes. Efficiency calculation of the electrochemical remediation process are summarized in [Box 1].

Box 1 Calculation of Efficiency Parameters Current Efficiency and Energetic Parameters

Electrochemical remediation of pollutants is usually monitored on the basis of change in the pollutant concentration in the treated solution or by using collective parameters such as chemical oxygen demand (COD, in mg O₂ L⁻¹) and/or total organic carbon (TOC, in mg carbon L⁻¹). The effectiveness of the electrolysis process (α) to remediate substances is monitored by the percentage removal (%) calculated as:

$$\alpha (\%) = \frac{\text{actual decrease in concentration}}{\text{initial material concentration}} \times 100 \quad (1)$$

(continued)

Box 1 (continued)

The data of concentration variation also allow calculating efficiency parameters for determining the efficiency of electrochemical processes in terms of electrical charge consumed. To calculate the instantaneous current efficiency (ICE), which is defined as the ratio of current effectively used in the remediation process (I_{ef}) at a given time (t) to the applied current (I_{appl}),

$$\text{ICE}(\%) = I_{\text{ef}} / I_{\text{appl}} \quad (2)$$

For example, the ICE for COD removal during electrolysis in a batch operation at a constant current is calculated as (Brillas et al. 2009):

$$\text{ICE} (\%) = \frac{(\text{COD}_t - \text{COD}_{t+\Delta t}) F V_S}{8 I_{\text{appl}} \Delta t} \times 100 \quad (3)$$

where, COD_t and $\text{COD}_{t+\Delta t}$ are the COD values at times t and $t + \Delta t$ (s), F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), V_S is the solution volume (L), the constant 8 is the oxygen equivalent mass (g eq^{-1}), and I_{appl} is the applied current (A).

Similarly, the current efficiency is the ratio of theoretical to actual energy required for given electrochemical reaction. The theoretical energy requirement is usually calculated from the expected reaction product from Faraday's laws if there were no side reactions, and the actual energy required is calculated from the input energy to the system. For example, applying 2 Faradays ($2 \times 96,485 \text{ C}$) of electrical charge to Cu electroplating cell should theoretically deposit mole equivalent of copper metal on the cathode (where 2 is the number of electrons charge on the cathode to deposit one Cu atom). On the other hand, considering COD decay ($\text{mg O}_2 \text{ L}^{-1}$) for electrochemical organic remediation process, average current efficiency (ACE) at time t is given by Eq. 4.

$$\text{ACE} (\%) = \frac{\Delta \text{COD}_t F V_S}{8 I t} \times 100 \quad (4)$$

Other practical parameter is electrochemical energy consumption (EEC), defined as the energy (kWh) required to treat unit volume (m^3) of effluent or unit COD (mg COD^{-1}) or unit TOC (mg TOC^{-1}) (Brillas et al. 2009). EEC is considered an important parameter in comparing the efficiency of different electrochemical remediation methods in regard to energy-related calculations. The EEC (kWh) during operational time (t in h) at constant current (I in A) and voltage (E in V) can be estimated per unit volume (V_s in m^3), unit COD mass, or per unit TOC mass according to Eqs. 5, 6, and 7, respectively (Brillas et al. 2009).

(continued)

Box 1 (continued)

$$\text{EEC (kWh m}^{-3}\text{)} = \frac{E_{\text{cell}} I t}{V_s} \quad (5)$$

$$\text{EEC (kWh (g COD)}^{-1}\text{)} = \frac{E_{\text{cell}} I t}{(\Delta \text{COD})_t V_s} \quad (6)$$

$$\text{EEC (kWh (g TOC)}^{-1}\text{)} = \frac{E_{\text{cell}} I t}{(\Delta \text{TOC})_t V_s} \quad (7)$$

Usually electrochemical treatment like any other treatment can proceed in either batch or continuous operation. In a batch operation, the volume of effluent treated is constant during the treatment period (the solution can be stirred, circulated, or statically stable). In a continuous operation, wastewater is continuously allowed to flow through and treated. In the continuous system, an important parameter is hydraulic retention time (HRT), or the hydraulic residence time, defined as the average duration; the effluent remains in the reactor and calculated by dividing the volume of reactor by effluent flow rate (Eq. 8).

$$\text{HRT (min)} = \frac{\text{Volume of reactor (mL)}}{\text{Flow rate (mL/min)}} \quad (8)$$

Parameters, such as α , ICE, ACE, and EEC, can all be calculated for continuous operation to be compared with various electrochemical treatment approaches.

Faraday's Law

Faraday's law is the basic law that governs the theory of electrochemistry. It states that (a) amount of chemical change produced by an electric current is directly proportional to the quantity of electricity that passes during a certain time and (b) amounts of different substances liberated by a given quantity of electricity are proportional to their chemical equivalent weights. Faraday's law is expressed in terms of the weight (w in g) of metal deposited at the electrode as:

$$w = \frac{I t A}{z F} \quad (9)$$

where: I is applied current (A), t is duration (s), A is atomic weight of metal deposited (g), z is metal valence, and F is Faraday constant (96,487 C/mol).

The Faraday constant is the quantity of electricity required to deposit the equivalent weight in grams of a metal (atomic weight = equivalent

weight $\times$ valence). This means that (a) by measuring the quantity of electricity that passes, one has a measure of the chemical change that will be produced and (b) by knowing the chemical equivalent weight of a substance, one can predict the amount of substance that will be reacted by a given quantity of electricity.

Current Density and Limiting Current Density

The current density (J), defined as the current per unit area of electrode, is very important in electrochemical operations. The character of the reactants, the distribution, and the efficiency of the process all depend on J . Limiting current density (J_L) is defined as the current density at which ions deplete as rapidly as they can diffuse (reach and react) to the electrode surface. The J_L of any electrolyte increases with the concentration of ions. In this way the current efficiencies obtainable also increase. J_L is related to the thickness of the diffusion layer (region at the electrolyte-electrode interface where concentration gradient occurs compared to the bulk solution) by the following expression:

$$J_L = \frac{k}{d} \quad (10)$$

where d is thickness of the diffusion layer

$$k = \frac{D n F C}{1 - N} \quad (11)$$

where D is diffusion coefficient, n is ion valence, N is transport number, C is concentration of ionic species, and F is the Faraday constant.

Note that when C is low (low ion concentration), N is normally zero; thus:

$$k = \frac{D n F C}{d} \quad (12)$$

If d is constant, a decrease in ionic concentration will produce a proportional decrease in J_L . Similarly, by decreasing d it is possible to increase J_L and thereby increase reaction rates.

Overvoltage

The reaction potential for reversible and irreversible reactions at the electrode surface is known, by convention, as electrode potential. In some cases, high kinetic barrier has to be overcome for the interface reaction to occur, which is achieved by

applying an extra potential (extra energy) called overvoltage (η) (or over potential). The value of η is directly related to both voltage of the electrochemical cell and efficiency of the process. There are a number of types of η , whose source and how it influences the course of the electrochemical reactions are described below.

- (i) Concentration overvoltage: When current is passed through a cell, the activity of ions (concentration) near the electrode changes. Taking the deposition of metal ions on the cathode surface as an example, the replenishment of these ions from the bulk solution is not as fast as the deposition process. This delay in replenishment causes a difference in concentration, which lowers the equilibrium potential. This difference in the equilibrium potential is termed as concentration overvoltage (η_c).
- (ii) Activation overvoltage: The energy lost due to the slowness of electrochemical reactions and the dissociation of molecules at the electrode interface for an electrochemical reaction to take place is called activation overvoltage (η_{act}). This can simply be explained by the fact that most metal ions are hydrated in solution, and the coordination sphere of the ions must be distorted and the water molecules freed from their association with the metal ion for the process of deposition to take place. This portion of energy form an energy barrier consists of two components: the activation energy of the charge transfer reaction toward the electrode surface and the electric energy associated with the interaction between ions and the electrode. For most metals depositing on a cathode η_{act} is fairly small and can usually be neglected, unless i is very large. However, certain metals and all gases show evidence of considerable η_{act} .

The relation between current and η_{act} is a logarithmic function given by the Tafel equation (Eq. 13) (Zoski 2006).

$$\eta_{act} = a + b \log J \quad (13)$$

where a and b are constants dependent on the reaction mechanism and J is current density.

- (iii) Resistance overvoltage: The most common form of resistance overvoltage (η_r) arises from the passage of electric current through an electrolyte solution surrounding the electrode. Such a solution shows resistance to current flow resulting to an ohmic (IR_{ex}) drop in potential between the electrodes. A less common form of η_r is caused by the formation of a surface-adherent film that itself possesses substantial resistance. In some cases, one or both electrodes are covered with a film of resistance different from that of the origin.

The evolution of hydrogen and oxygen at the electrode surfaces during the electrolysis of dilute aqueous solutions of acid or bases is well known and considered a prominent phenomenon in the electrolysis of dilute effluents. Hydrogen overvoltage (η_H) is of great importance in the electrolysis solutions containing metal ions. In fact, if there was no η_H , many metals could not be deposited from aqueous solution. η_H depends strictly on the cathode (material and surface).

Some cathodes cause a large η_H value, which will allow some metal ions to deposit on the surface without the evolution of hydrogen gas or allow metal deposition and hydrogen evolution to take place at the same time. η_H is higher on smooth surfaces than on rough ones and has a value that varies from negligible on platinum surface and quite low on graphite to perhaps as much as 1 volt on mercury.

Mechanism of Electrolysis and the Transport of Ions

The ability of a solvent, especially water, to ionize substances dissolved in it makes electrolysis possible. However, the demand for electric charge at the interface cannot be met by ions, which remain stationary in the solution, or just move about at random. Different ions move at different rates from the bulk solution to the interface between solution and electrode, and electron transfer processes at the interfaces accompany this. An example is the case of using metal salt as an electrolyte in normal electroplating solutions. As metal is deposited at cathode, the solution in its immediate vicinity is depleted of metal ions. If plating is to continue, these ions must be replenished. There are three possible ways in which ions reach the electrode surface, which may also occur simultaneously. These mass transfer methods are (Zoski 2006) (1) diffusion, (2) convection, and (3) migration and are detailed below:

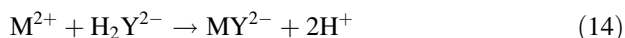
1. Diffusion occurs as a result of concentration gradient being set up at the electrode interface with electrolyte. A difference in concentration can arise when electrochemical reaction occurs at the electrode surface, converting ions, and consuming out of a solution by electron transfer, so reducing the concentration of ions near the electrode compared with the concentration a few thousand angstroms further into the liquid. This gives rise to the movement of species from higher to lower concentration. Hence, diffusion occurs for ionic or uncharged species through the solution as a result of concentration gradient.
2. Convection occurs as a result of hydrodynamic flow and can be characterized as either forced or natural. Forced convection occurs when the solution is stirred, and natural convection occurs when the solution is stirred or not. When differences in pressure, density, or temperature exist in various parts of the electrolyte, then the liquid begins to move as a whole or in parts. For example, when metal ions are deposited on the electrode, the density of the solution at the electrode-solution interface is reduced. This density change causes an influx of ions from the surrounding solution to move toward the electrode, independently of that caused by diffusion. Lower-density solution at the vicinity of the electrode surface flows upward, while the higher density solution flows down into the bulk solution creating a convection current. The difference between diffusion and convection, therefore, is that diffusion occurs because of change in concentration of ions and convection because of density variation.

3. Migration involves movement of cations and anions through a solution under the influence of an applied potential between electrodes placed in the solution. The movement is initiated due to the attraction of opposing charges, i.e., the potential gradient will act upon the ions to push the positive ions toward the negative electrode and the negative ions toward the positive electrode. If the moving species are neutralized (uncharged) or the concentration of ions reacting at the electrode is small compared to the concentration of other ions in the solution, the effect of ionic migration is negligible compared to that of diffusion.

Treating Methods for Metals and Inorganic and Organic Metal Complexes

Several methods are used for the removal and recovery of metal ions from industrial effluents including chemical precipitation (Özverdi and Erdem 2006; Pérez et al. 2010), adsorption (Babel and Kurniawan 2003; Guo et al. 2010; Li et al. 2003), biosorption (Sulaymon et al. 2014), solvent extraction (Kocaoba and Akcin 2005), cementation (Konsowa 2010), membrane filtration (Borbély and Nagy 2009; Landaburu-Aguirre et al. 2010), ion exchange (Alyüz and Veli 2009), coagulation (Charemtanyarak 1999), flocculation (Beltrán Heredia and Sánchez Martín 2009), flotation (Kurniawan et al. 2006), reverse osmosis (Dialynas and Diamadopoulos 2009), electrodialysis (Abou-Shady et al. 2012; Chaudhary et al. 2000), and electrochemical treatment (Tao et al. 2014). However, there are practical limitations to most of these methods arising mostly from the presence of organic, complexing, or chelating reagents present in streams.

Similarly, for effluents containing organic materials, there are many possible ways to remediate them. However, the efficiency of many of these methods is reduced in the presence of heavy metal ions, and this is particularly true if the organic species form strong complexes with the metal ions in solution (Quivet et al. 2006). The presence of organic and inorganic species with metal ions changes the chemical, physical, and toxicological properties of the metal ions (Bradl 2005). For example, the presence of ethylenediaminetetraacetic acid (EDTA) as a complexing agent in a metal-containing solution will result in the formation of anion charged complex (Eq. 14).



where EDTA is assigned the formula H_4Y ; disodium salt (Na_2H_2Y) supplies the complex-forming ion H_2Y^{2-} in aqueous solution. The ligand is normally hexadentate and reacts with heavy metals (M^{n+}) in 1:1 ratio. Thus divalent metal ions (M^{2+}), for example, react with disodium salt as shown in equation (Chaudhary et al. 2000).

These metals anions are stable and soluble at moderately high pH (>8), which prevent the process of metal hydroxide precipitation when attempt is made to remove heavy metals by precipitation at high pH. Additionally, the presence of metal ions can retard the destruction of organic contaminants with the efficiency of recovery of the metal being reduced by the complexing species (Carrier et al. 2006). The treatment approaches for these complexes include ion exchange (Nabi et al. 2006), reverse osmosis (Ujang et al. 2010), and nanofiltration (Gao et al. 2014). These methods generate concentrated solutions from which the metal must be removed/recovered prior to liquid disposal. The alternative treatment method includes breaking the metal-organic complex into free metal and free chelating agent, followed by separation of the metal in an insoluble form with the organic agent discharged for subsequent treatment. Breaking the metal-reagent bonds requires chemical or other form of energy input into the system. For example, catalytic decomposition applying catalytic advance oxidation (CAO) such as photolytic treatment is applied to degrade organics incorporated with metals using photoactive species such as titanium dioxide (TiO_2) or hydrogen peroxide (H_2O_2) at a certain pH (Soderquist et al. 2012). The combination of two techniques such as catalytic decomposition by applying advance oxidation, say by ultraviolet (UV) irradiation, followed by electrochemical removal of freed heavy metals ions (Chaudhary et al. 2009) is a promising method to remove heavy metals over relatively long decomposition periods.

Processes other than CAO require the use of chemicals as oxidants which is disadvantageous due to the addition of more chemicals to the waste streams that may complicate the treatment process (Prairie et al. 1993). For example, Katoh (1986) patented a process to treat liquid wastes containing chelated heavy metal compounds, which involves pH adjustment, iron polysulfate addition to form an iron chelate compound, then removal of the formed product via flocculation, and precipitation of the flocs at high pH. Other researchers applied similar approaches but attempted to reduce the use of aggressive and hazardous chemicals such as acids and bases. Al-Zoubi et al. (2015) proposed a method to treat industrial effluents containing heavy metals employing the coagulation/flocculation principles. They used various types of polymers to reduce the use of iron (Fe) or aluminum (Al) ions as flocculants to remove heavy metals and can be discharged into designated receptacles for further treatment.

Considering both their value and adverse impact on the environment, heavy metals should be reclaimed from industrial effluents. Generally, the coagulation/flocculation system creates sludge, which will contain the removed pollutants that require further treatment or disposal (discussed in detail later). This is also true for electrocoagulation or electroflocculation systems, where sacrificial Fe or Al electrodes are employed to generate coagulants. Kaspar et al. (Morkovsky et al. 1999) patented a process and apparatus for electrocoagulation treatment of industrial wastewater employing sacrificial electrodes conjugated with foaming system to flocculate pollutants. Some advance research has been performed to improve the performance of electrochemical coagulation/flocculation system by adding steps such as disinfection/oxidation with ozone, UV, and ultrasonic treatment, as well as

recirculation in the electromagnetic field to reduce or to treat the sludge (Visnja et al. 2013).

Overall, the aforementioned treatment methods simultaneously remove, to a certain extent, mixed heavy metals from solution. However, considering the value of heavy metals, for the treatment process to be effective, their separation and recovery from waste streams have to be taken into account.

Electrochemical Approaches for Separation, Removal, and Recovery of Metals

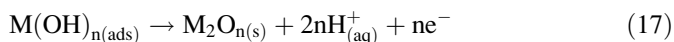
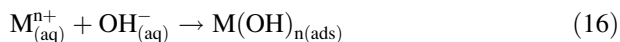
Electrochemical methods to remove heavy metals involve the deposition of metal ions from effluents on cathode surface and have the advantages of recovery as well as removal. The electrodeposition (ED) process can be performed by imposing either fixed current or fixed potential. Essentially, in an electrochemical cell containing mixed metal ions, the deposition reaction at the cathode, which requires the least negative potential, will initially take place, especially if the deposition potential of any alternative process is much more negative and almost exclusively if the alternative potential is only slightly more negative. If the potential is made sufficiently negative to produce a second reaction, that reaction may occur simultaneously, and if potential is made enough for the electrolysis of water to occur, hydrogen will start to produce at cathode surface. There are exceptions for some metals that cannot be deposited from aqueous solutions such as titanium (Ti) and Fe, which are very active metals and cannot be electroplated on electrode. The metal ions with associate ligands (water or complex anion) attach themselves at certain preferred sites (irregular surfaces); at the same time, metal ions bound to the electrode surface and partially neutralize their charge, and the associated ligands dissociate to diffuse back into the solution. Monoatomic growth layers are produced until several neighboring lattices meet to form a coating on the electrode. The nucleation energy, energy required for the formation of nuclei on the cathode surface, can be calculated from Eq. 15.

$$\Delta G = -N^* z_i e_0 |\eta| + \varphi(N) \quad (15)$$

where N^* is number of atoms per nucleus growth (cluster), z_i is charge of the metal ion, e_0 is elementary charge of the electron, $|\eta|$ is absolute value of the applied overvoltage, and $\varphi(N)$ represents the increased surface tension caused by the addition of new atoms.

Applying the same principle at the anode side, the reaction, which requires the least positive potential, occurs at the anode, unless the potential becomes so positive that a second reaction is possible. In aqueous electrolyte solution, if applied potential is sufficient to produce oxygen, the electrolysis of water will take place. Under some electrochemical conditions, metals may react at the anode surface to form metal oxides. This phenomenon is well established going back to the early

nineteenth century, when electrochemists used galvanic cells as power source to produce metal oxide-coated anode (Schlesinger and Paunovic 2014). The formation of metal oxide on anode depends on the metal ion present and pH of the electrolyte. For example, during the electrolysis of lead ions, deposition of lead on the cathode and lead oxide on the anode will occur simultaneously over a wide pH range. However, with most transition metals a film of metallic hydroxide may form on the anode in alkaline media (according to Eqs. 16 and 17), which is converted subsequently as a result of applied potential to metal oxide. The electrochemical formation of metal oxide film on anode is widely utilized in the modern development of solar cells. However, in some cases the presence of such films reduces the current flowing through the electrochemical cell, and hence the film acts as an insulator.



In developing potential methods for recovering metal ions from secondary sources, often the solution to be treated will contain more than one metal ion in dilute concentrations, for example, in effluents originating from metal-coating baths, dissolution of spent solder, wire scrap in mining, and hydrometallurgical leaching solutions. In these cases, we need to reclaim individual metals separately for the process to be efficient and economical. Generally, a multistep chemical process is employed including acid/alkali leaching, followed by extraction, cementation, precipitation, or electrowinning (Clancy et al. 2013; Crundwell et al. 2011). Applying electrochemical separation is also possible. Hence, a selective ED of individual metal can be achieved theoretically by careful control of electrode potential and solution media (Grimshaw et al. 2011). There have been several attempts on separate ED from mixed metal ion solutions, e.g., Cu/Cd, Zn/Cu, and Pb/Cu (Doulakas et al. 2000). In many cases, especially those involving Cu, the difference in standard electrode potential ensures that selective ED is effective. A selective ED process can be performed by stabilizing the cathode voltage at the metal potential (referenced to a standard calomel electrode), which allows the selected metal at the selected potential to deposit on the cathode surface. However, the selectivity can be disturbed if impurities or complexing agents of inorganic/organic species are presented. For example, from standard reduction potentials of Sn, Pb, and In (−0.1364, −0.1263, and −0.338 V, respectively), we presume that selective separation of Sn/In and Pb/In is possible. However, in an acidic leaching solution, Pb was electrodeposited on cathode and removed from solution but not indium (Yasri 2001), thus separate ED of In, Sn, and Pb would require careful control of the acidity of the solution and in the presence of complexing agent (Grimes et al. 2017).

Electrochemical methods employing membrane technology (i.e., electrodialysis) are effective for scale-up and metal ion separation. The process of metal separation can be performed by adding chemicals that selectively complex (mask) one group of elements and prevent transportation across the cation exchange membrane (CEM)

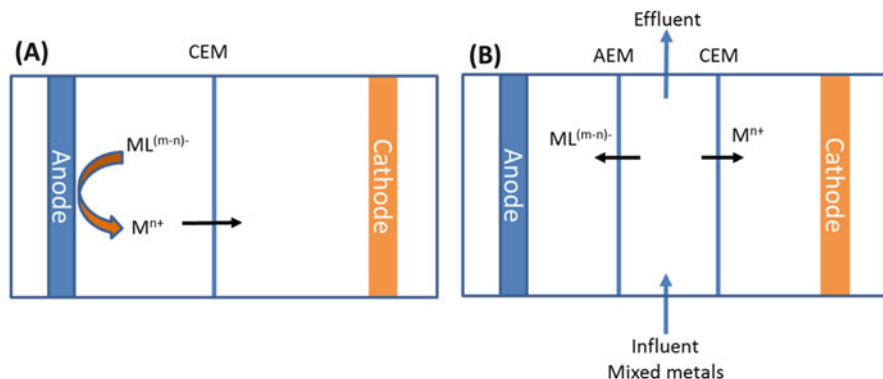


Fig. 1 Two-compartment (a) and three-compartment (b) electrodialysis cell (Adapted from Chaudhary et al. (2000) and Yasri (2001))

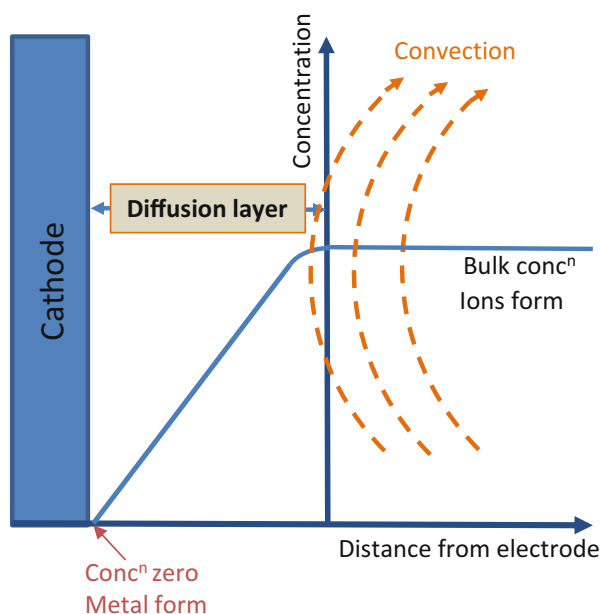
while allowing transportation of unmasked hydrated cations (Allen and Chen 1993; Da browski et al. 2004; Pedersen et al. 2005; Sadrzadeh et al. 2008). The basic concept of the separation process using electro dialysis with enhanced cation and anion exchange is demonstrated in Fig. 1 (Chaudhary et al. 2000; Yasri 2001). Briefly, in a three-compartment electro dialysis cell (Fig. 1b), the separation is achieved by exploiting the greater stability of the complexing agent such as EDTA with one of the metal mixtures. For example, in a three-compartment electro dialysis cell, $Ni-(EDTA)^{2-}$ complex and hydrated Co^{2+} ions are separated by electro-transferring from the feed solution to the electro dialysis anolyte and catholyte chambers, respectively (Chaudhary et al. 2000; Yasri 2001). Applying the same principle, various metal ions are separated, e.g., Cu and Pd from Co (Yasri 2001).

In an electro dialysis system, problems may arise when using a system with a two-compartment cell, i.e., anolyte and catholyte chambers without a middle chamber (see Fig. 1a). The masked metal-EDTA complex will be in immediate contact with the anode surface, which may oxidize due to the anodic oxidation process that causes dissociation of the metal complex, freeing the associated metal and permitting the movement of metal toward the catholyte chamber, which reduces efficiency of the separation process. Here, it is important to use a three-compartment electro dialysis cell (Fig. 1b), in which the metal-EDTA is transferred to the anolyte chamber. Although this complex can be destroyed at the anode surface to release the hydrated metal ions, due to the natural properties of the anion exchange membrane (AEM), these ions cannot cross the membrane to return to the feed or catholyte compartments. Moreover, during the separation process, in the catholyte chamber the hydrated metal ions will either remain in solution or deposit on the cathode depending on the electrolysis condition (e.g., pH, cathode material, type of hydrated metal ions, and concentration).

Electrolysis of Dilute Metal Solutions

Generally, as consequences of industrial processing, toxic metal species, which are to be treated, are found in dilute concentrations, rarely in excess of a few hundred or thousand ppm. During electrolysis, however, the transport of ions in dilute solutions (<1000 ppm) is completely different from that in concentrated solutions. This presents problems for ED and removal of the metals from dilute solutions. Electrolyzing solution containing dilute metal ions, the concentration of these ions will form a gradient from the bulk of the electrolyte to the surface of the electrode where the value at the electrode is zero (that metal ions deposit in metallic structure) at limiting current density creating a diffusion layer (or boundary layer) of thickness ~ 0.5 mm (in unstirred solution). Figure 2 illustrates the boundary layer established between the electrode surface and the bulk of the electrolyte. It can be distinguished that in addition to the concentration gradient, ions are forced to move by convection and migration. But, due to the low concentration of ions in dilute solutions, the most effective way to transport the ion across the boundary layer up to the electrodes is by diffusion. For metal ions to be deposited on the electrode and removed from dilute solutions, the ions must cross the diffusion layer, and for this to occur, the effective thickness of this layer must be small. If the boundary layer thickness is not reduced and the current density is increased beyond that which brings the ion concentration to zero at the electrode surface, then other competing reactions such as the evolution of hydrogen will take place and lower the efficiency of the metal deposition process.

Fig. 2 Diffusion layer is established between a cathode surface and the solution. The concentration gradient of metal ions varies from zero at the cathode surface to the bulk concentration



Fick's laws (Zoski 2006) govern the diffusion of ions in the electrolysis processes. In Fick's first law, the steady-state diffusion flux is theoretically shown to be proportional to the gradient of concentration. Fick's second law is the basis for the treatment of most time-dependent diffusion problems in electrochemistry. In Fick's first law (Eq. 18), the rate of diffusion is directly proportional to the concentration of the dissolved substances, and the rate of diffusion in any given direction is directly proportional to the rate at which the concentration diminishes in that direction.

$$\frac{dQ}{dt} = -D(C_b - C_e)/dx \quad (18)$$

where dQ/dt = flux of the material per second per unit area, D = diffusion coefficient, C_b = concentration of ion studied in the bulk, C_e = concentration of ion studied at the electrode, dx = distance over which the concentration change occurs, and $(C_b - C_e)/dx$ = concentration gradient.

When the ionic concentration is reduced, the forces diffusing the ions to the electrode become progressively less effective, and the diffusion layer becomes more and more depleted of ions. Therefore, the maximum rate at which deposition can occur progressively decreases along with the upper limit of current density, which can be used.

Electrochemical Removal and Recovery of Metals

Electrochemical technologies widely used for toxic metal removal are electrocoagulation (EC), electroflotation (EF), and electrodeposition (ED) (Fu and Wang 2011). Electrochemical treatment is preferred if valuable metals are to be recovered and returned to the production cycle. However, due to the low metal concentration and the presence of various complexing materials in industrial wastes, the task is not as easy as theoretically predicted.

EC and EF are utilized to remediate effluents containing both organic pollutants and heavy metals; thus the principles of both methods are discussed in detail later in sections below. Basically, EC involves the generation of coagulants in situ by electrochemically dissociating Fe or Al anodes into electrolyte solution to coagulate with pollutants at appropriate conditions. EF is a solid/liquid separation process that floats pollutants to the surface by bubbles of hydrogen and oxygen gases generated from water electrolysis. Both techniques can help remove a number of toxic heavy metals from effluents, e.g., Zn (II), Cu (II), Co (II), Ni (II), Ag (I), Cr (III), and Cr (VI). Although heavy metals are removed, huge volumes of sludge generated during the process require further chemical or physicochemical treatments if metals are to be reclaimed. Valuable heavy metals, therefore, are potentially lost in the process. Thus processes such as ED in which metals are reclaimed on the electrode surface are more advantageous.

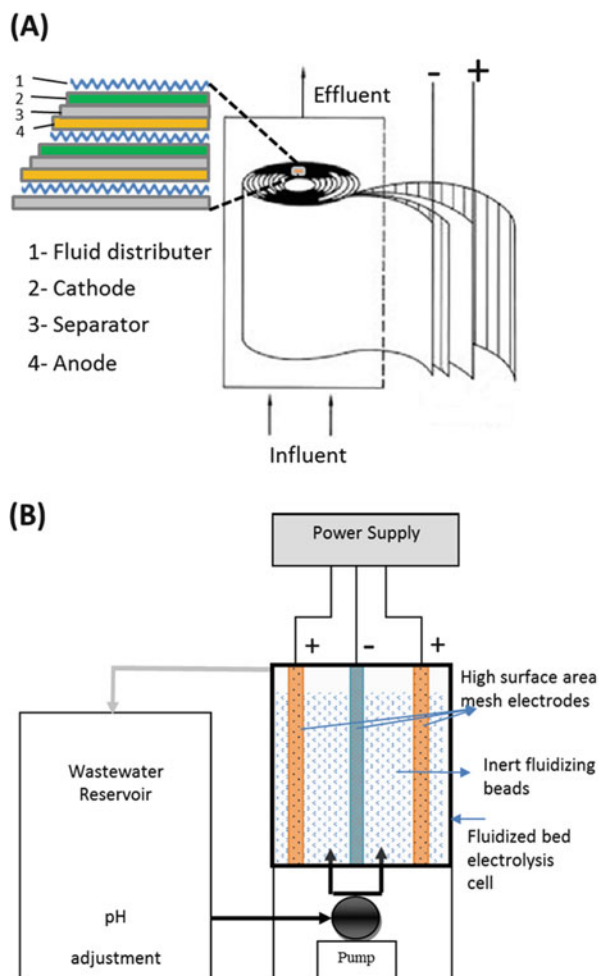
ED is a clean and effective method usually applied to recover metals from wastewater. It can be appropriately engineered and designed to suit different end-of-industrial operations. Metals can be recovered on the cathode and directly reused or returned to the commercial cycle by melting or dissolving as an anode in electroplating (Issabayeva et al. 2006). Nevertheless, ED of metals from a dilute stream (<1000 ppm), as mentioned previously, poses several major problems due to low mass transfer. To improve the efficiency of ED of metals from low concentration solutions, the required condition is $J < J_L$. Depleting all metal ions in the bulk solution is a time-consuming process. The alternative approach is to increase J_L by reducing the thickness of diffusion layer. This can be achieved by increasing the mass transfer of ions either by increasing the movement of the metal ions through agitation of the solution or by concentrating the ions in the vicinity of the electrode surface. A number of electrolytic cell designs have been proposed to enhance mass transfer within the cell, which involve agitation in combination with a moderately high electrode surface area per unit electrode volume (Kammel 1984). The agitation methods have involved rotating electrodes, mechanical stirring of solution, air agitation, turbulence promoters, slurry, or fluidized bed agitation (Grimm et al. 1998; Houghton and Kuhn 1974; Janssen and Koene 2002; Kammel 1984; Kim et al. 1998; Thilakavathi et al. 2012).

An extended surface electrolysis cell was developed by Robertson, with helix sandwich electrode configuration named “Swiss roll” cell (Robertson and Ibl 1977; Fig. 3a). Though good removal of heavy metals ions is achieved from dilute solutions using this cell, claiming the recovered metals was a problem, which required periodic stripping either by leaching the deposited metal in a proper acidic solution or anode dissolution in electrochemical cell.

Agitation of electrolyte between the cathode surface and the solution was employed in various cell designs, e.g., circulating the electrolyte using pumps or by air injection, ultrasound, electrode rotation, or hydraulic agitation of nonconductive particles in the space between the electrodes (Ota et al. 2014; Zoski 2006). Promising metal recovery of various types was achieved by using *Chemilec* cell, which is a fluidized bed cell with inert beads as the fluidizing medium. In *Chemilec* cell (Fig. 3b), the concentration of metal ions increases in the vicinity of the high surface area electrode due to the motion of the fluidized beads and hence increases the recovery rate (Segundo et al. 2012). While some of these cells can be effective in solutions of metal ion concentrations of ~ 50 – 150 mg/L (Ferreira 2008; Robertson and Ibl 1977), the performance is limited at the low end and thus does not meet the discharge level, which is typically less than 5.0 ppm and often below 1.0 ppm (Segundo et al. 2012).

The use of concentrator material is a useful in dealing with dilute solutions, which has been described in our recent patent disclosure (Gunasekaran and Yasri 2016). Concentrator electrochemical technique (CET) is used to improve deposition by concentrating metal ions in the electrolyte in an area close to cathode surface. This can be performed by housing a concentrator medium in close vicinity of the cathode surface. Concentrator material (CM) should have a good affinity to metal ions which effectively collects them from the bulk solution at active sites and

Fig. 3 (a) Swiss roll cell (Adapted from Robertson and Ibl 1977), (b) *Chemilec* cell consisting of an electrolysis chamber containing inert beads “fluidized” by fluid pressure (Adapted from Yasri 2001)



then releases these ions near the cathode surface improving the condition of ion transfer and ultimately increasing the deposition rate (Gunasekaran and Yasri 2016).

Figure 4a illustrates that the presence of CM reduces the effective distance of ion transfer from “a” to “b,” creating a new cell with metal ions concentrated near the electrode surface to increase the metal deposition efficiency (Gunasekaran and Yasri 2016). Very rapid removal of toxic metals (i.e., Cd^{2+} , Cu^{2+} , and Pb^{2+}) from dilute solutions has been achieved using CM compared to that obtained without CM (Yasri 2001).

CET can improve the process of removal and recovery of metals that can be electrochemically deposited on cathode. However, there are exceptions. Some metals such as Ti and Fe, which are very active metals, cannot be electroplated on cathode from aqueous solutions. Smara et al. (Smara et al. 2007) described a

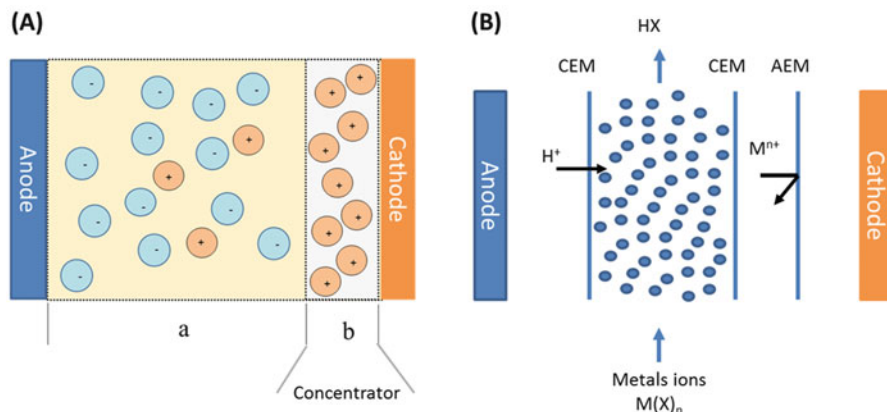


Fig. 4 (a) Concentrator material placed near a cathode in an electrochemical cell acts as a concentrating cathode and reduces the effective distance of ion transport from “a” to “b.” (b) Schematic of a hybrid ion-exchange/electrodialysis cell (Adapted from Smara et al. 2007)

different CET, in which heavy metals are removed from dilute mixtures by a hybrid ion-exchange/electrodialysis process. Toxic heavy metals such as Pb^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} were removed from dilute solutions to meet the discharge limit by continuous electro-permutation combining ion-exchange resins and membranes. Various types of CM such as activated carbon granules, activated carbon cloth, modified graphite, or functionalized copolymers surface can be used, where the choice depends mainly on the affinity of heavy metals to be treated toward the CM and the presence of various organic complexes in the effluent (Yasri 2001). The presence of organic species or complexes with metal ions may result in the alteration of metal ion charge and formation of complexes or chelate, which have low or no affinity to react or adsorb on the CM. Thus the presence of organic species may retard the removal rate of metallic ions.

The most important advantage of using CET is that the process of metal removal accompanies in situ regeneration of the CM within the system. Thus, during electrolysis, reduction of metal ions and water occurs on the cathode surface along with the oxidation of water and other anions at the anode. The electrolysis of water releases H^+ ions and hydronium ions (H_3O^+) on the anode, which move toward the cathode and bring about in situ regeneration of the CM. Thus the in situ regeneration allows prolonged use of CM without the need for external chemical or physical regeneration.

Electrochemical Approaches for Remediation of Organics

Biological treatment is the most popular and highly economical option for treating effluents containing dissolved organics. However, bioremediation is mainly effective for organic molecules, which are biodegradable or biodegradable. When organic

compounds are resistant to biological treatment, however, they will persist in the environment, and in some cases the pollutants adversely affect the traditional biological treatment by inhibiting the biological species. In such cases, effective pretreatment should be considered prior to discharging off to the biological treatment plant. For example, traditional biological inhibitors such as aromatic phenolic compounds or basic heterocyclic aldehyde compounds (e.g., furfural, hydroxymethylfurfural, etc.) are produced during natural hydrolysis of a wide variety of plant materials containing polysaccharide or from industries, which could find their way into the biological treatment plant. Although these compounds are considered toxic to bacteria, they are very soluble and can form highly stable soluble complexes with toxic heavy metals that make the solubilization and hence mobilization of the metal pollutants possible. Evidence shows that underestimating the aggregation of such materials in aqueous systems can adversely affect the health of humans and the environment (Suanon et al. 2016).

A possible strategy to treat such pollutants is by detoxifying the unwanted inhibitor products via a pretreatment, e.g., reduction with chemicals, photolytic treatment, electrochemical treatment, etc. This will render the effluent bioavailable for the subsequent traditional biological treatments. However, selectively remediating one compound in a mixture is not an easy task, and other unwanted by-products could be produced. Thus, a careful thought, analysis, and optimization of the detoxification process coupled with subsequent biological treatment is necessary to eliminate the adverse effects of by-products or to entirely remediate the inhibitors.

Electrochemical treatment is often thought of as an elegant solution to remediation problems due to the ability to control the level of electron transfer of both oxidation and reduction processes. Accordingly, various cell designs have been used to remediate many toxic, biologically resistant, and inhibitor materials (Lee et al. 2015). Thus electrochemistry could be considered in some cases as complete treatment step and in others as a complement to other remediation processes (e.g., biological). For example, selective detoxification of organic compounds that act as bio-inhibitors could be achieved in situ with biological treatment by either oxidation or reduction in electrochemical cell (Cha and Choi 2015). During oxidation, either the generated oxygen at the electrode interface or the electrode itself will accept electrons from organic pollutants using electric energy, break gradually of organic bonding, and form intermediates which differ in molecular shape from the original (that are not recognizable by microorganism as the original inhibitor) (Panizza and Cerisola 2009). During reduction, molecules, for example, microbiological inhibitor “furfural” or “hydroxymethylfurfural,” gain electrons from the electrode surface and reduce to the corresponding alcohol or other reduced molecules that are not inhibitors. The process of electrochemical remediation is highly dependent on the effluent conditions, concentration, and the presence of other pollutants and the fate of end-of-pipe effluent for posttreatment. The electrochemical treatments suitable for organic remediation are (a) electrocoagulation, (b) electro-oxidation, (c) electro-Fenton’s oxidation, (d) electroadsorption, and (e) electro-biological oxidation.

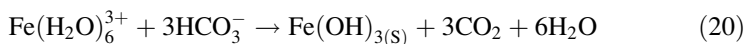
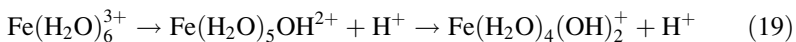
Electrocoagulation

Electrocoagulation (EC) is a technique rapidly growing area of wastewater treatment that uses both principles of electrochemistry and coagulation. Coagulation or flocculation is the process by which particles aggregate and precipitate from colloidal suspension. These aggregation processes are alternative to chemical precipitation for the removal of dissolved and suspended pollutants such as organics or metals from aqueous solutions. Coagulation involves the reduction of electrostatic repulsive forces between the colloidal particles in the solution. It is different from flocculation, which depends on the presence of bridging compounds to form chemical bonding links between the colloidal particles and enmesh the particles in relatively large masses called floc networks (Sahu et al. 2014).

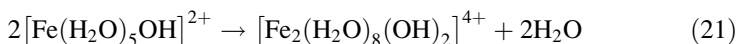
In EC although both agglomeration processes of coagulation and flocculation occur simultaneously, the process is named after coagulation. Generally, the process of coagulation is enhanced by adding certain ions to solution to reduce the electrostatic repulsion between particles to aggregate. Similarly, in EC the electric current helps to reduce electrostatic repulsion, agglomerate organic constituents, and other suspended solids in water. The agglomerated organics have the ability to adsorb certain ionic constituents, making it possible to separate and remove flocculent with a majority of suspended organics and some ionic constituents. A broader approach of electrocoagulation refers to an applied sufficient voltage to sacrificial anodes, such as Fe or Al, allowing the oxidation of anode materials and forming Fe or Al hydroxide flocculent (gelatinous metal hydroxides) within the electrolyte, which can help settle colloidal particles or unwanted pollutant species from the electrolyte (Khandegar and Saroha 2013; Mollah et al. 2001).

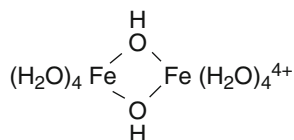
Principle

The hydrated metal ions at the anode, particularly those with a charge of +3 or more, tend to act as Brönsted acids (lose H^+ ions from the water molecules bound to them in aqueous solution, Eqs. 19 and 20). The acidity of a metal ion increases with charge and decreases with increasing radius.



The tendency of hydrated metal ions to behave as acids may have a profound effect on the coagulation chemistry. Hydroxide, OH^- , bonded to a metal ion, may function as a bridging group to join two or more metal hydroxides together allowing a dehydration-dimerization process (Eq. 21).





Additional hydrogen ions may detach from water molecules in the dimers, providing OH^- anion for further bonding and leading to the formation of polymeric hydrolytic species. These types of polymers will continue to grow, forming colloidal hydroxyl polymers that eventually precipitate due to gravity, which collectively remove pollutants along within their pores. At the same time, during electrolysis, water is also electrolyzed, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attach to flocculated particles and make them lighter and float them to the surface. Besides the coagulation and flocculation processes, synthetic polyelectrolytes such as starch and cellulose derivatives, proteinaceous materials, and gums composed of polysaccharides may be added to stimulate coagulant aggregation. More recently, selected synthetic polymers, including neutral polymers and anionic and cationic polyelectrolytes, that enhance agglomeration have come into use (Sahu et al. 2014).

In the EC cell, as in any electrochemical cell, other reactions occur simultaneously with the aforementioned coagulation reactions, including cathodic reduction of reducible particles, anodic oxidation, and mass transfer of ions in solution, which complicate the process and prevent the prediction of final products. These make EC a complex synergistic process with several reactions and mechanisms occurring simultaneously to remove pollutants.

Metals other than Fe and Al have a similar tendency to form polymeric species with OH^- as a bridging group. These are Be(II), Bi(III), Ce(IV), Co(III), Cu(II), Ga(III), Mo(V), Pb(II), Sc(II), Sn(IV), and U(VI). In commercial and practical EC processes, however, anode materials preferably used are Fe and Al; this is due to the wider pH range (~4 to 11) useful with these ions, reduced cost, and avoidance of introducing environmentally unfriendly metal species into the end of the treatment residues.

Apparatus

The basic EC apparatus consists of electrolysis chamber containing one or more pairs of anode and cathode connected to an external power source (Fig. 5). The design of the electrolysis chamber should expose the contaminated water to electrolysis in batch or continuous system. The electrodes can be designed as plates, perforated plates, or tubes to maximize the efficiency. The electrodes as mentioned earlier could be composed of different materials; however, the most often used are

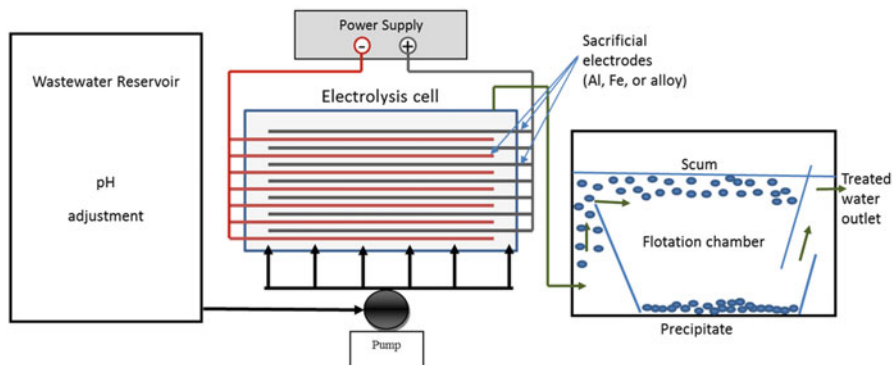


Fig. 5 Schematic presentation of the electrocoagulation reactor. Gravity and floatation are the driving forces for dewatering of the treated effluent

Al, Fe, or stainless steel. A series of electrolysis reaction chambers can be used each with different electrode materials. The electric system, composed of control power supply with typical direct current, is required, although using alternating current technology may prevent the formation of an oxide layer on the anode. The effluent then has to pass to a system to dewater the precipitated/coagulated solids. The principle of dewatering system is to stimulate precipitation of floc/coagulant similar to the settling tank used in conventional treatment plants.

The process optimization of the EC treatment typically includes the type of sacrificial electrode material, distance between the electrodes, electrolyte pH, applied current density, retention time (or reaction time) of the electrolyte, and possible additives to stimulate coagulation or flocculation of particles.

The EC devices are engineered and marketed in various designs that range from electrochemical cells containing simple set of anodes and cathodes to very complex electrochemical assemblies. EC can be attached to an acquisition system to control both the electrode potential and the process of anode scarification. Additionally, EC can also be put in situ with decantation units for precipitate accumulation and integrated with other utilities such as ultrasonic probe, ultraviolet light, or ozone generator, thus achieving in situ so-called advance oxidation.

The EC technique has been extended using bipolar packed beds with metal rings (Ögütveren and Koparal 1992), beads (Jeong et al. 2012), or flat surface (Hu et al. 2008) as bipolar electrodes isolated from each other by electrolyte. The metal bipolar electrodes have to be made of sacrificial metals applying the same principle of the EC, e.g., steel, Fe, or Al can be used. A bipolar packed bed reactor is particularly convenient in achieving high mass transfer because of the large electrode surface area. This arrangement will greatly increase the rate of sacrificial bipolar material to produce coagulant.

Applicability

The EC technology may be effective in the near-neutral water, where coprecipitation with Fe (or Al) hydroxide could remediate relatively clean water. Potential applications of EC system may include pretreatment, or final stage for effluent containing mainly colloidal particles, dissolved organic, suspended solids, and heavy metals, e.g., a high-density sludge in domestic water treatment plant, neutral tailing water in mining industries, and wastewater from food processing, petroleum, oil-sands, and pulp and paper mill industries. However, posttreatment is still required in some cases to final remediation and removal of coagulants formed.

Advantages and Limitations

The main advantage of using EC is its low capital cost, low energy consumption, and minimum requirement of added chemicals, which lower the contamination of the aggregate residues (except for coagulant materials used). The removed pollutants, total dissolved solids, and suspended solids aggregate after treatment (or concentrated) within the coagulants with no major alteration of their chemical structure (except the partial oxidation of some organics due to reaction at the anode surface). Thus, making the recovery of chemicals added from the precipitate after treatment is possible. This is especially important when dealing with high-value chemicals and critical metals or even to reuse the treated effluent.

One of the major limitations of EC, however, is that it can be barely selective for removing a group of pollutants, e.g., heavy metal mixture could be removed simultaneously with organic presences in solution. Other limitations include the need for regularly replacing sacrificial anodes when used, limited efficiency of the process for certain pollutants, and the need for additional control steps to enhance conductivity and pH adjustment (Do and Chen 1994). For example, when the Fe/Al anode of the EC system is oxidized in acidic conditions, no flocculent is formed because Fe and Al are soluble below pH 3. Additionally, the main drawback of EC system is the volume of accumulated precipitates that requires additional treatment units to isolate and dewater the residues.

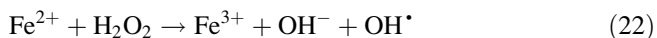
Electro-Fenton's Oxidation

The Fenton's process, originated by Henry John Horstman Fenton in the late nineteenth century, indicates that highly reactive hydroxyl radicals are formed during the reaction of hydrogen peroxide (H_2O_2) and ferrous (II) ions. Since this finding, reagents involving both H_2O_2 and Fe^{2+} are named Fenton's reagent; however, the application of this as an oxidizing reagent was only realized in the

late 1960s (Huang et al. 1993). During the process H_2O_2 is dissociated and consumed, whereas organic-enriched electrons are oxidized and ferrous ions catalyze the process.

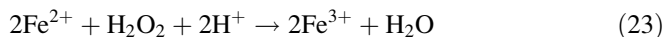
Principle of Fenton's Reaction

The main principles of the Fenton's reaction are the dissociation of the reagent H_2O_2 during the oxidation of Fe^{2+} to Fe^{3+} , the formation of hydroxide anion (OH^-), and the highly reactive hydroxyl radical ($\text{OH}^\bullet$) (reaction 22), which attacks and destroys organic pollutants.



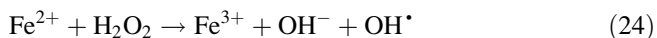
The ferrous ions (Fe^{2+}) in Fenton's reagent act as catalyst to initiate the decomposition of H_2O_2 in chain reactions to generate hydroxyl radicals.

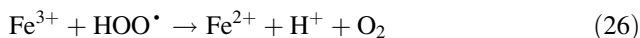
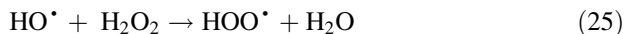
Similar to the coagulation process, Fenton's reagent can be generated chemically or electrochemically. Chemically, H_2O_2 is spiked into a solution containing ferrous ions, whereas, electrochemically, the hydroxide radicals are generated in situ within the electrochemical cell. A simplified overall Fenton reaction (Eq. 23) suggests that H^+ (acid environment) is needed for the decomposition of H_2O_2 and to produce the maximum amount of hydroxyl radicals (Walling 1975).



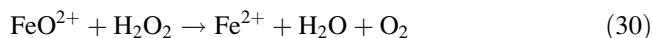
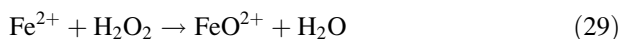
Fenton reaction is categorized as one of the advanced oxidation processes (AOPs) (Oturán et al. 2011). The main function of AOPs is the generation of highly reactive free radicals to break the backbone structure of organic pollutants. In Fenton reaction, Fe^{2+} act as redox catalyst for $\text{OH}^\bullet$ to break carbon-hydrogen bond in organic molecules and initiate radical chain reactions. Although hydroxyl radicals ($\text{HO}^\bullet$) are unstable electrophiles that are effective in destroying organic bonding, the process is very slow in the absence of Fe^{2+} ; whereas, the reagent reacts rapidly and non-selectively with nearly all electron-rich organic compounds in the present of Fe^{2+} as catalyst (Wang and Xu 2011). Metal ions other than Fe, for example, cobalt, manganese, and copper, have been used as catalyst to improve the efficiency in Fenton reaction (Pimentel et al. 2008); however Fe^{2+} is the most effective when used at an optimal concentration of 0.1 M soluble FeSO_4 .

The process of generating radicals in Fenton reaction involves a complex sequence of chain reactions in an aqueous solution. Investigation performed by Barb et al. (1951) on the reactions of ferrous and ferric ions with H_2O_2 suggested that the free radical formation consists of the following chain reactions steps:



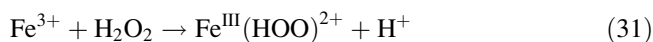


Equation 24 serves as a chain initiation step and Eqs. 27 and 28 as termination steps, and the cycle in Eqs. 24, 25, and 26 forms the oxidation and regeneration of reagents steps (Neyens and Baeyens 2003). Although many evidences suggest the involvement of hydroxyl radicals in the oxidation of various organic compounds (Walling 1975), others claimed that the reaction between H_2O_2 and Fe(II) produces ferryl ion (FeO^{2+} ; an oxidizing Fe(IV) species) as an active intermediate species in the Fenton chemistry (see Eqs. 29 and 30 (Deguillaume et al. 2005)). The presence of ferryl ions suggests a non-radical oxidation reaction pathway of organic substances.

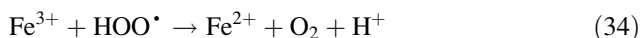


However, two reaction pathways for the first step in Fenton chemistry are a radical pathway, which considers the production of $\text{OH}^\bullet$ as a main radical and a non-radical pathway to produce ferryl ions (Deguillaume et al. 2005).

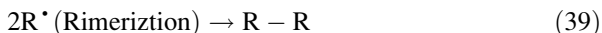
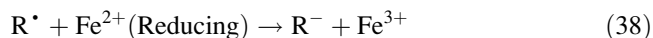
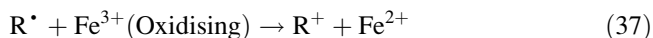
Moreover, Fe(II) acts as catalyst, which means regeneration of ions should take place during the process. Studies have shown that the reaction of H_2O_2 with Fe^{2+} primarily leads to oxidation of Fe^{2+} to ferric ions (Fe^{3+}), which immediately forms an Fe(III) -hydroperoxy complex formulated as $\text{Fe}^{\text{III}}(\text{HO}_2)^{2+}$ (Neyens and Baeyens 2003). A spectrophotometric study has confirmed that the formation of these complexes is very fast that equilibria are attained within a few seconds after mixing of Fe(III) and H_2O_2 solutions (De Laat and Gallard 1999). Once formed, the Fe(III) -hydroperoxy complexes are assumed to decompose to yield Fe^{2+} and $\text{HOO}^\bullet$:



The presence of both $\text{HOO}^\bullet$ and Fe^{2+} in solution leads to a series of chain reactions involving various highly oxidizing free radicals and ions as noted in reactions below:



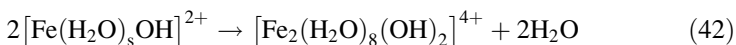
Oxidation of organic molecules (RH) coexist in solution with Fenton reagent will be initiated by attacking both $\text{OH}^\bullet$ radicals and Fe ions to produce active organic radicals ($\text{R}^\bullet$), charged organic species, and dimer species, those react to cause further chemical decomposition of the organic compounds (Neyens and Baeyens 2003).



Organic radicals ($\text{R}^\bullet$) are very reactive species that simultaneously react in chain reactions to produce spectra of various radical products that may be of higher oxygen content of alkoxy ($\text{RO}^\bullet$), alkylperoxy ($\text{ROO}^\bullet$), or higher oxidation state. The formed radicals react further causing chemical decomposition of organic contaminant.



A mixture of original organic contaminant, free radicals, and ions will continue to react in chain reactions. However, if the pH of the solution reaches a value from 3 to 7, Fe(III) ions generated in the above redox reactions react with hydroxide ions in a similar manner to those found in coagulation process, to form ferric-hydroxo complexes according to Eq. 42.



These complexes can be observed as small flocs during the Fenton oxidation step that takes relatively a long time to complete (overnight). This observation may account as a termination step and also for the coagulation capability of Fenton's reagent. Thus organic molecules may be captured within the flocs and account for some chemical oxygen demand (COD) removal during the process.

Principle of Electro-Fenton Oxidation

The application of electrochemical field to Fenton process is more efficient than that of Fenton's reagent operated at the same conditions (Zhang et al. 2006). This was attributed to the efficient cathodic regeneration of Fe^{2+} (Brillas et al. 2009). Figure 6 depicts the typical interface reactions occurring at the electrode surfaces during electro-Fenton oxidation (EFO). In EFO, however, highly reactive $\text{OH}^\bullet$ are generated in situ within the electrochemical cell, which helps the process

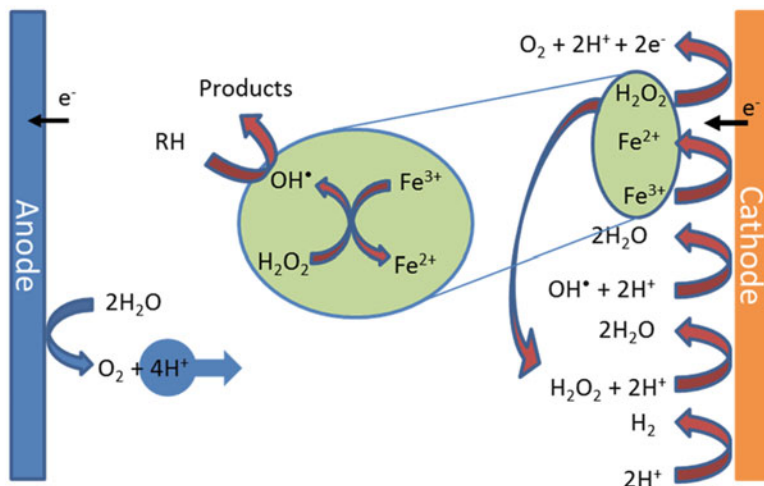
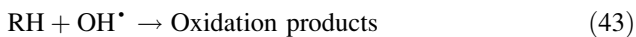


Fig. 6 Schematic illustration of the major reactions occurring during the electro-Fenton process. RH represents the organic pollutants, which undergo oxidation

in many ways, e.g., avoiding the transportation of H_2O_2 reagent, controlling the process of $\text{OH}^\bullet$ production, and avoiding the storage of H_2O_2 that leads to partial loss of reagent activity. Moreover, in the EFO, Fe sulfate is added as a source of Fe^{2+} catalyst; however, to maintain the catalyst property of Fe^{2+} , the oxidized form (Fe^{3+}) will be reduced at the cathode surface at relatively low reduction potential ($E = 0.77$ V vs. standard hydrogen electrode, SHE) (Brillas et al. 2009). Thus, the electrode surface will serve to add an extra step to accelerate the production of $\text{OH}^\bullet$ by increasing the speed of Fe^{2+} production (see Eq. 24).

Categories of electro-Fenton process can be divided based on the process operation and method of introducing the reagent into the reactor; i.e., reagent Fe^{2+} and H_2O_2 are either added externally or generated in the electrochemical reactor (Zhang et al. 2006). In the first case, Fe^{2+} (or Fe^{3+}) are externally added whereas H_2O_2 is internally generated at the electrodes (see electrochemical production of H_2O_2 in the next section). In the second case both H_2O_2 and Fe^{2+} are generated within the cell using a sacrificial Fe or steel anode. The third case involves external simultaneous addition of both reagents (Fe ions either Fe^{2+} or Fe^{3+} and H_2O_2) and is known as Fere-Fenton method (Chou et al. 1999).

The kinetics of electro-Fenton oxidation process is presented in Eq. 43, and the kinetics of organic decomposition is determined using Eq. 44:



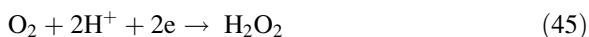
$$\frac{d[\text{RH}]}{dt} = K_{\text{abs}} [\text{RH}][\text{OH}^\bullet] \quad (44)$$

where K_{abs} is the absolute rate constant of the reaction and $[\text{RH}]$ and $[\text{OH}^\bullet]$ the concentration of organic and hydroxyl radicals, respectively.

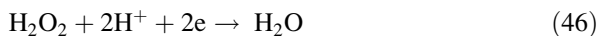
Considering, however, $\text{OH}^\bullet$ are reactive species and their concentration never accumulates in solution, they could be considered constant, and the kinetic rate of reaction, therefore, is considered first order.

Electrochemical Production of H_2O_2

As mentioned previously, H_2O_2 could be produced as a result of electrolysis at certain conditions in aqueous media. We present a brief description of the possible mechanism of H_2O_2 production to give an overview of the electro-Fenton process. For more details on the conditions required to produce stable H_2O_2 with higher yield, readers are referred to various articles in the literature (Brillas et al. 2009). Basically, H_2O_2 could be electrogenerated using parallel plates in an electrochemical cell to reduce dissolved oxygen (DO) or sparged O_2 (or air) in acidic solutions containing dilute supporting electrolyte (Qiang et al. 2002). DO is reduced in acidic medium at the cathode surface to H_2O_2 according to Eq. 45.



In electro-Fenton, the in situ production of H_2O_2 is a value-added process that reduces the hazardous transportation of the material itself and avoids dissociation of H_2O_2 during storage. Electrochemical production of H_2O_2 occurs at low potential ($E^\circ = 0.44$ V vs. SCE), in homogeneous environment, with divided or undivided cells. In undivided electrochemical cell, the main competing reaction is the decomposition of H_2O_2 itself at the cathode surface to produce water molecules (Eq. 46). Thus, the cathode material has a significant impact on the decomposition of H_2O_2 , which is attributed to the hydrogen overpotential of the cathode material. Reports show that the decomposition rate of H_2O_2 on graphite cathode in alkaline solutions is less than on metal cathodes such as copper, stainless steel, lead, and nickel (Sudoh et al. 1985). Graphite exhibits a high overpotential for H_2 evolution and low catalytic activity for H_2O_2 decomposition, along with relatively good stability, conductivity, and chemical resistance.



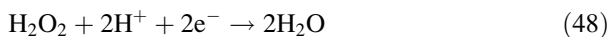
Though, the use of flow-type electrochemical cell system helps to avoid accumulation of H_2O_2 at the cathode surface (Eloy Isarain-Chávez et al. 2013). Thus H_2O_2 production from DO in flow-type system will serve the purpose for Fenton process and can be carried out selectively in acidic medium.

Advantages and Limitations of the Electro-Fenton Process

Unlike the Fenton, the electro-Fenton process is less expensive and less risky in handling chemicals, especially for H_2O_2 production, which could be generated in situ. Additionally, the main advantage is the extra control parameter of the electrode potential that allows controlling anode scarification, overall process degradation, and continuous regeneration of ferrous (II) catalyst at the cathode, which advance the degradation rate of organic pollutants and minimize sludge production (Nidheesh and Gandhimathi 2012). As compared with the Fenton process, the electro-Fenton is highly efficient, with less sludge production; however, sludge is still produced and dewatering of the end product precipitate is one of the drawbacks.

Parameters limiting the operation of electro-Fenton process include the pH of the effluent treated, rate of DO (or O_2 sparging), applied current, Fe^{2+} concentration, H_2O_2 concentration, electrode type, and cell design. Most of these parameters are optimizable for the best efficiency and least cost.

The pH of the electrolyte solution is considered the most important factor for the electro-Fenton process. Many interference reactions may occur due to variations in the pH. For example, Fe species begin to precipitate as $\text{Fe}(\text{OH})_3$ at $\text{pH} > 3$ that reduce the electro-Fenton and enhance removing pollutants via electrostatic attraction and coagulation (Mollah et al. 2001). However, researchers have reported that at lower pH values, Fe ions form stable complex species with H_2O_2 , which also participates and inhibits the Fenton process (Wang et al. 2010c). However, pH 3 is considered optimal for the Fenton (and electro-Fenton) process, which helps the stability of oxonium ions (H_3O_2^+) according to Eq. 47; at this low pH decomposition reaction may also take place according to Eq. 48.



At higher pH ($7.0 <$), however, H_2O_2 rapidly decomposes to oxygen and water (Wang and Lemley 2001). Though, according to many reports pH ~ 3.0 is the most efficient for the electro-Fenton process (Brillas et al. 2009). But, considering the fact that pH of treated wastewater is usually higher than 3.0, adjusting the optimal pH to 3.0 is problematic and disadvantageous to the electro-Fenton process because of the additional step of pH adjustment as well as the chemicals needed.

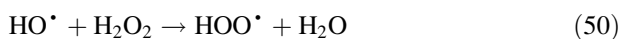
In contrast, during the in situ production of H_2O_2 , oxygen is sparged into the system (see electrochemical production of H_2O_2). Meaning that increasing the oxygen sparging rate can increase the DO concentration and the mass transfer rate of DO, hence increasing the production of H_2O_2 (Wang et al. 2010c). Therefore, the rate of DO or external O_2 supply to the system will have a profound effect on the process (considering that there is no other external H_2O_2 source to the system). One of the important factors affecting the DO rate is temperature, i.e., the DO rate decreases with increasing temperature. Although some reports showed

that increasing the temperature of operation will increase the generation rate of oxidizing species (such as $\text{HO}^\bullet$ or high-valence Fe species) (Sun et al. 2007), higher temperature will also increase self-decomposition of H_2O_2 (Özcan et al. 2008), and the optimum operating temperature is about 30 °C (Umar et al. 2010).

Moreover, the applied current can limit the electro-Fenton process, which even provokes reverse reactions or competitive reactions such as hydrogen production at the cathode and oxygen discharge at the anode. Accordingly, some studies have indicated that the upper limit of current density in the electro-Fenton process is about 6.4 A/m² and not exceeding 10 A/m² (Jiang and Zhang 2007).

Similarly, increasing the concentration of Fe^{2+} in the electro-Fenton process will enhance the consumption of $\text{HO}^\bullet$ radicals according to termination reaction (Eq. 28). Thus, increasing the Fe^{2+} concentration may adversely affect the process. Hence, the effects of both components of Fenton's reagent (Fe^{2+} and H_2O_2) are closely linked, and the optimization experiments are usually performed on the basis of their ratio ($[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$) (Brillas et al. 2009; Ting et al. 2009). Depending on the persistence of the effluent to be treated, however, the level of $[\text{Fe}^{2+}]$ in the electro-Fenton process can range from 0.2 mM (Liu et al. 2007a) up to 2.0 mM (Wang et al. 2010c) and not exceeding 15 mM (Wang et al. 2008). Whereas for H_2O_2 the initial concentration should range from 25 mM (Ting et al. 2009) up to about 60 mM (Anotai et al. 2010).

Additionally, the feeding mode of H_2O_2 has a profound effect on the treatment process (Ting et al. 2009). H_2O_2 could be fed to electro-Fenton cell in single addition and in a timed sequence or, as discussed previously, produced in situ electrochemically. When H_2O_2 is added in one step or fed in quick sequence, its initial concentration will be the highest during the reaction, which will unfavorably affect the lifetime and the level of the produced hydroxyl radicals in the medium that to be scavenged by the H_2O_2 itself according to Eq. 50 (Zhang et al. 2007).



Considering the weaker oxidizing power of hydroperoxyl radical ($\text{HOO}^\bullet$) and to avoid the scavenging effect, sequential addition of H_2O_2 or in situ production is preferred.

Apparatus

The essential part of electro-Fenton reactors and the design of the apparatus are mostly depending on the design of the electrolytic chamber and the type of the electrodes housed in it. Several types of reactors have been utilized with various designs to optimize the efficiency of the process and to assist the method of

introducing the reagents into the reactor. Typical electrolytic reactors and electrodes used for the process and found in the literature have been reviewed and summarized by Brillas et al. (2009) and Nidheesh and Gandhimathi (2012). Briefly, reactors used for electro-Fenton's process are oxygen or air bubbling reactor (Brillas and Casado 2002; Rosales et al. 2012; Rosales et al. 2009), divided electrolytic chambers, or undivided electrolytic cell. On laboratory scale, air bubbling reactor with moderate volume (not exceeding 1.0 L) has been successfully used to decolor dye and textile wastewater (Rosales et al. 2012; Rosales et al. 2009). The reactor is usually designed to produce H_2O_2 electrochemically via oxygen reduction on the cathode. Therefore, continuous saturation of air at atmospheric pressure is made by bubbling air near the cathode to insure a constant O_2 level in the chamber. Similarly, diaphragm-divided or undivided electrolytic cells could be utilized as an electro-Fenton reactor with in situ H_2O_2 electrogenerated at the cathode (or fed from external sources to catholyte chamber). Divided apparatus usually consist of two half-cells (a cathodic compartment and an anodic compartment), which are connected by a salt bridge or brought together with diaphragm or membrane separator. The effluent is treated in the cathodic chamber in batches or as continues flow. Electrolysis occurs under constant current conditions using a direct current power supply between the cathode and the anode. Since the cathode material highly influences process efficiency, it should be chosen to have low interface oxygen overpotential to facilitate rapid production of hydroxyl radicals simultaneously with the reduction of Fe (III) ions. Reaction at the cathode surface is the key to the process that cathode is denoted, in some cases, as the working electrode whereas the anode is denoted as a counter electrode. Various materials or chemically modified surface of graphite, carbon, activated carbon, carbon cloth, boron-doped diamond (BDD), Pt, or stainless steel are used as cathodes for wastewater treatment (Nidheesh and Gandhimathi 2012). The use of different composite cathode materials or surface-modified nanoparticles is emerging as cathode materials for lower interface overpotential and enhances more uniform current distribution at the electrode surface. These include chitosan (Li et al. 2009), carbon nanotubes decorated nanoparticles (Ai et al. 2008), and graphene-based nanocomposite (Le et al. 2015). On the other side, anodes are placed at an appropriate distance away from the cathode, considering that the higher distance between the electrodes leads to an increase in ohmic drop through the electrolyte and then an equivalent increase in cell voltage and energy consumption. Additionally, selection of unstable anode will cause deterioration of electrode in electrolytic cells. Therefore, dissolution-resistant anode that is highly stable and unable to electrolyze into solution is ideal for the process. The most stable anode for electro-Fenton conditions is Pt; however, due to its high cost, materials such as BDD, titanium coated with TiO_2 , $\text{IrO}_2/\text{RuO}_2$, $\text{IrO}_2/\text{SnO}_2/\text{Sb}_2\text{O}_5$, etc. are used.

Electro-Oxidation

Electrochemical oxidation or “anodic oxidation” was introduced in the early 1970s to destroy organic molecules and has been applied widely for the treatment of wastewater from the textile and related industries. The technique is very effective in color removal by breaking the conjugated bonds in dye molecules; during the process colorless compounds are formed upon rupturing the dye molecule. It means that the conjugated chromophore systems which give color to dye molecules in some cases are easy to rupture, which points to the fact that the molecule is only partially decomposed to colorless compounds. This was satisfactory to the textile industries to meet with the public demands to reduce dye and color leached into the wastewater system. Although this satisfies the requirement of decolorization, it is unlikely that the method will lead to complete mineralization without going through a series of organic intermediates. The degradation of dye molecules can result in the formation of noncolored dye fragments and can result in the formation of environmentally unfriendly degradation products such as aromatic amines and chloro-organic compounds (Donaldson et al. 2002).

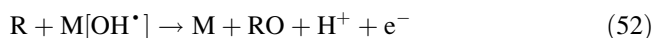
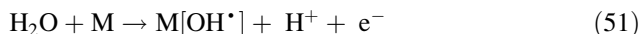
For anodic oxidation, an electrochemical cell requires a two-electrode system of cathode and anode (mesh or plate). Multiple electrodes could be used; however, the types of anode material and electrolyte have a great impact on the oxidation mechanism, on the end products and the efficiency of the oxidation process. High oxygen evolution, stable, non-sacrificial anodes are required for prolonged operation and to avoid electrode dissolution during electrolysis. On the other side of the cell, depending on the application, cathode consisting of mild steel, titanium, or graphite is widely used.

Generally, electrochemical oxidation takes place in an electrolyte that facilitates transfer of ions between two electrodes. When conductivity of the effluent is low, electrolyte should be added to increase the conductivity and to help generate free radicals for the oxidation process to take place. In this process organic compounds are oxidized effectively with little consumption of chemicals and with little or no sludge production. Previous investigations have shown that salt (NaCl) is an effective electrolyte for the electro-oxidation (EO) of organics from wastewater.

In EO, two mechanisms can be distinguished for remediation of organic pollutants: (1) direct anodic oxidation that occurs at the electrode-solution interface and (2) indirect anodic oxidation that occurs via surface active species generated continuously at the electrode surface and reacts within the electrolyte to convert the carbon backbone structures of pollutant molecules to smaller fractions or theoretically to carbon dioxide and water. Spontaneous direct and indirect mechanisms could also occur during remediation.

Direct Anodic Oxidation

In direct electrolysis, generally, at a specific electrode potential, the pollutants are oxidized after adsorption at the electrode surface. The mechanism generally involves the formation and adsorption of hydroxyl radicals at the anode surface (M) (Eq. 51) (Güven et al. 2008), which enhances the participation of organic pollutants (R) in direct electron transfer at the electrode surface and hence the process of oxidation (Eq. 52).



The process is known as catalytic electrode oxidation, and a specific potential is required to allow oxidation to occur that is called “catalytic oxidation potential”. Depending on the anode surface material and its electrocatalytic activity, oxidation is theoretically possible at a potential lower than the oxygen overpotential (no oxygen evolution). Oxygen is transferred from water to the organic pollutant with the aid of electric energy at the anode surface interface. In this reaction, water is the source of oxygen atoms for the oxidation of organic molecules to form ideally an oxidized form of the molecules at the anode.

Traditionally, noble metals such as Pt and palladium, as well as metal oxide-coated anodes, e.g., iridium dioxide, ruthenium-titanium dioxide, iridium-titanium dioxide, and lead dioxide, possess high oxygen overpotential and are good catalysts to use as anode for direct anodic oxidation. Recently, metal nanoparticles (MNP) and their derivatives have emerged as promising electrode materials for direct electrochemical oxidation at fixed anodic potential due to their large surface-to-volume ratio, biocompatibility, and low price. Popular MNP candidates for electrode modification are cobalt (Co) (Yin et al. 2009), nickel (Ni) (Chauke et al. 2010), iron (Fe(II,III)) (Yin et al. 2011), zinc (Zn) (Najafi et al. 2014), ruthenium (Ru) (Li et al. 2010), and tungsten (W) (Peng et al. 2014). However, the main problem of EO using MNP-modified electrodes is the inherent structure of these materials and oxidation susceptibility of pollutant, leading to deactivation of MNP and their derivatives, commonly called electrode poisoning effect, due to the high affinity of MNP to adsorb pollutants forming of a polymer layer on the anode surface (Jiao et al. 2014). Thus deactivation is less pronounced with weaker adsorption properties or inert surface such as BDD (Panizza and Cerisola 2009).

A promising new generation of electrodes modified with nanoparticles of non-metallic, carbon-based backbone structure is under investigation for various electrocatalytic oxidation purposes. Materials such as carbon nanotubes (Ruoff and Lorents 1995), graphene (Geim and Novoselov 2007), graphene oxide (Dreyer et al. 2010), and modified structure of these materials are widely investigated. Typically, chemical reactions performed on organic molecules and surfaces have been used as starting points for chemical functionalization of these carbon-based nanomaterial structures. Specifically, changing the doping level with foreign atoms

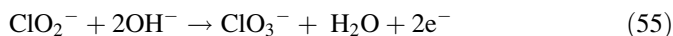
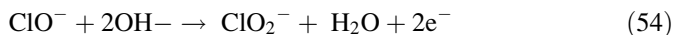
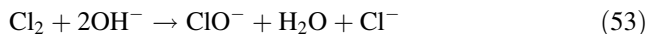
is an effective method to intrinsically modify the properties of pristine host materials (Lim et al. 2010). Among them, nitrogen doping plays a critical role in regulating the electronic (Wang et al. 2010e) and the catalytic properties of the modified electrode (Yasri et al. 2014, Yasri et al. 2015a). The heteroatoms present in the graphitic framework make these catalysts nonelectron neutral, favor the molecular adsorption and consequently enhance specific redox reactions at the electrode interface (Liang et al. 2012). Doped carbon-based backbone structures find wide applications as metal-free, cost-effective electrodes for highly efficient electrochemical catalytic oxidation.

Indirect Electro-Oxidation

Indirect EO involves attacking the pollutant molecules within the bulk solution by several oxidizing species formed under the electrolysis conditions at sufficient applied potential (Israilides et al. 1997; Kim et al. 2002b). It can be performed at overpotential exceeding the value of oxygen evolution, so that water discharges at the electrode, forming free radicals during the process of oxygen evolution that ideally oxidizes organic pollutants to release CO₂ at the anode and discharge protons. However, when no electrolyte is present, current efficiency is reduced due to oxygen evolution at the electrode surface. On the other hand, the idea of indirect EO is to oxidize pollutants in a sustainable manner; thus avoiding high overpotential is preferred to prevent electrode fouling. Attempt is usually made to facilitate indirect electron transfer between anode surface and pollutants by electrochemically generating redox reagents at low potential; these materials act as electron shuttle or mediator between the electrode and the organic pollutants.

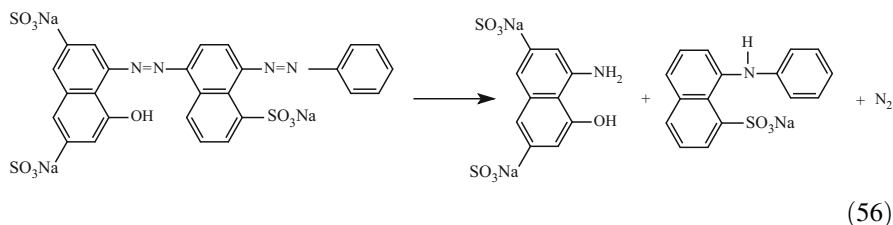
Generally, electrolytes act as mediators or redox catalyst in the reaction media enhancing the destruction efficiency of pollutants (Panizza and Cerisola 2009). In this case, if electrolyte is present, various species and radicals may be formed to attack organics spontaneously. Hence the type of oxidation products and intermediates would highly depend on the type of electrolyte present. For example, oxidizing species could be formed upon anodic reaction, e.g., active chlorine, ozone, and persulfates, or at cathodic reaction, e.g., hydrogen peroxide. If chlorine is in the solution, species such as Cl₂, Cl[•], ClO[•], ClO₂, Cl₂^{•-}, O₃, OH[•], O[•], H₂O₂, O₂, H₂, and CO₂ can be formed in the electrolyte (Donaldson et al. 2002; Israilides et al. 1997; Park et al. 2009). In these cases, highly tolerant electrode should be used, to prevent fouling of the electrode or polymer formation at the electrode surface. Though, active radicals and ions present within the medium may integrate into the system to react with organic pollutants. For instance, considering a basic scenario when electrolyzing solution containing chloride ions (Cl⁻), this will result in the formation of Cl₂ as well as hydronium ions (H₃O⁺) at the anode surface, and at the same time water molecules are hydrolyzed at the cathode surface to form hydroxyl ions (OH⁻). Chlorine will participate indirectly in anodic oxidation by

forming hypochlorite ions (ClO^-) in alkaline medium (Eq. 53) and chlorite (ClO_2^-) and chlorate (ClO_3^-) ions (Eqs. 54 and 55) in stronger alkaline medium (Fernandes et al. 2004).

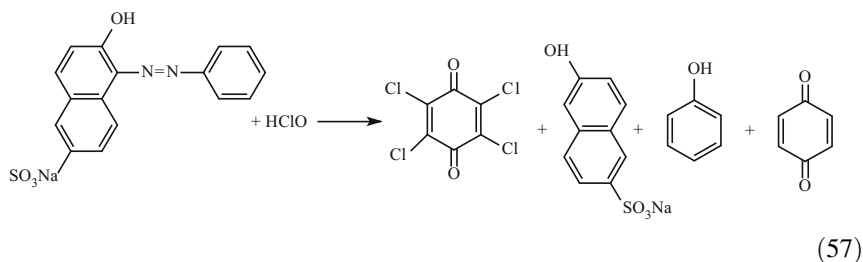


Ions and radicals formed at the electrode surfaces are free to move within the electrolyte and react with organics to produce intermediates during the process. The potentials of various species to react with pollutants and to form intermediates are strongly dependent on the pH, the initial electrolyte concentration, the pollutant, the electrode type and the solution medium (Al-Haq and Gómez-López 2012; Panizza and Cerisola 2009).

Numerous researchers have studied the mechanism of anodic oxidation and the possible intermediate products. For instance, dyes such as blue 2 K decolorized during anodic oxidation due to the breakdown of diazo conjugated bonding according to Eq. 56 (Naumczyk et al. 1996).



It has been also reported that in the presence of salt NaCl as electrolyte, there is evidence for the formation of chlorinated organic products (Naumczyk et al. 1996). For example, dyes such as light orange 6 and methylene blue are oxidized in the presence of hypochlorite or in electrochemical reactor to form various fragments containing chlorine in their structure (see Eq. 57 (Naumczyk et al. 1996) and scheme in Fig. 7 (Donaldson et al. 2002; Yasri 2001)):



Since these intermediates, and particularly the chlorinated compounds, may be more harmful to the aqueous environment than the organic molecules from which

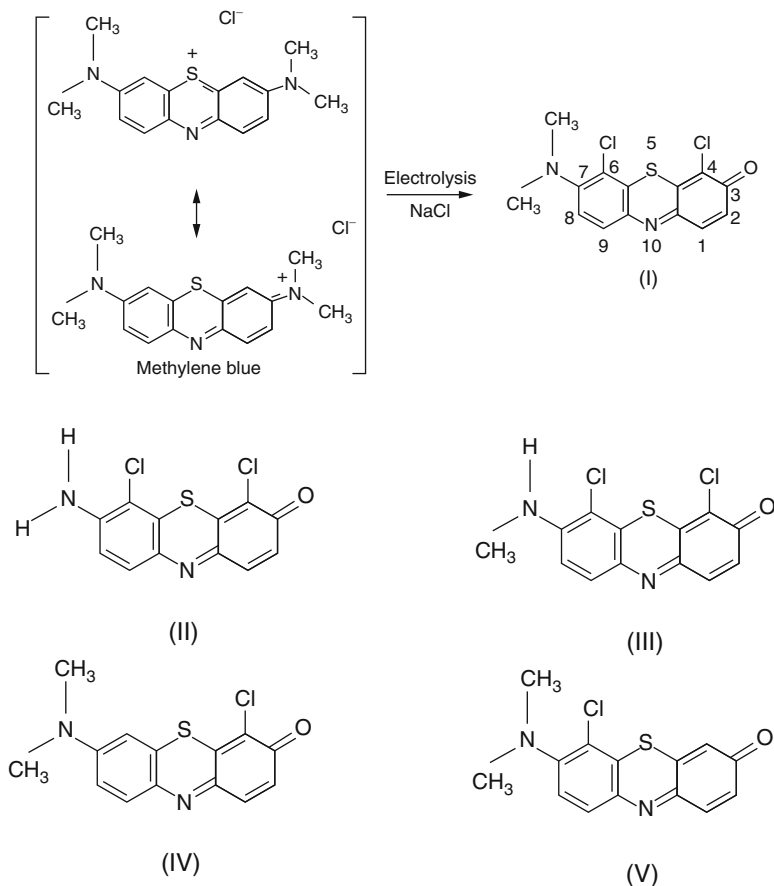


Fig. 7 Intermediate (I–V) formed during the electrochemical oxidation of methylene blue in chlorinated medium (From Donaldson et al. (2002) and Yasri (2001))

they are formed, it is necessary to set additional process to eliminate the discharge of hazardous products to waste stream. In this aspect we and others have shown such chlorinated intermediates can be effectively eliminated (Cong and Wu 2007; Yasri 2001) if subjected to further activated carbon polishing (Rajkumar and Palanivelu 2004) or electroadsorption treatment (Yasri et al. 2015b).

Electrochemical System for Electro-Oxidation

Due to the wide range and diverse features of industrial wastes and conditions that usually contain a mixture of organic and inorganic compounds, no common EO reactor is in use. Process optimization is achieved by the nature and structure of the

electrode material, experimental conditions, and electrolyte composition. Hence, no single end-of-pipe reactor design is suitable for all EO applications. The most important part in EO apparatus are the electrodes that serve as catalyst for the oxidation reaction. To high destruction efficiency, many different electrodes (especially anodes) have been investigated for their direct and/or indirect EO ability. In practice, however, most anodes are capable of both direct and indirect EO, i.e., by applying high overvoltage; both reactions could occur simultaneously to participate in organic oxidation and oxygen evolution reactions.

There are numerous electrode types for remediating various pollutants (Martinez-Huitle and Ferro 2006; Panizza and Cerisola 2009; Wu et al. 2014). Among these Pt is considered as ideal anode for EO of various pollutants, e.g., phenol, chlorophenols, glucose, benzene, hydroxybenzoic acid, methanol and formic acid, synthetic dyes, herbicides, and naphthalene-sulfonic acids (Panizza and Cerisola 2009). Pt electrodes are commonly known as dimensionally stable anodes (DSA) as they are highly stable under relatively high applied voltage, inert to many chemical reactions, and have low hydrogen and oxygen overpotentials, i.e., hydrogen is oxidized and protons are reduced readily at the Pt surface in aqueous solution. In practice, however, since the cost of Pt electrodes is high, industries prefer to replace it with other type of DSAs.

Electrodes of pristine metal (M) coated with metal oxide (MO) such as ruthenium oxide (RuO_2), iridium oxide (IrO_2), tin oxide (SnO_2), antimony pentoxide (Sb_2O_5), lead dioxide (PbO_2), or mixed metal oxides (that contain more than one metal oxide) find their application as DSAs with practical oxidation efficiency. The pristine electrodes usually are of nontoxic, rigid, easy to fabricate metals such as titanium (Ti) or tin (Sn) and Ti being the most popular due to its physical properties, e.g., low density, easy machinability, high anticorrosion, and relatively low cost. Pristine Pb electrode coated with PbO_2 (Pb/PbO_2) has been tested for EO of organics and considered as a stable anode material, relatively inexpensive and effective in oxidizing pollutants. However, the high toxicity of Pb, its propensity for electrochemical corrosion, and the need to avoid Pb contamination due to the release of Pb^{2+} prevent the use of Pb/PbO_2 as a stable anode (Martinez-Huitle and Ferro 2006).

Generally, metal oxides represent one of the most important categories of solid catalysts due to their acid-base and redox properties, which are widely used as active phases in either chemical or electrochemical reactions (Wu et al. 2014). The use of metal oxide (or mixed metal oxide)-coated electrode (M/MO) enhances the oxygen evolution reaction, allows the use of anode at fairly high potential, and due to their surface properties increases the catalytic oxidation of organics (Wu et al. 2014). Moreover, mixed metal oxides may exhibit, in some cases, a significant improvement in catalytic activity than their respective single-component metal oxides, perhaps due to the increase in active acidic or basic sites or change in the chemical states of the metal ions (Alaya and Rabah 2013). Electrodes coated with metal oxides may be prepared by electrodeposition at the anode surface (anodization) by applying electric potential to solution containing the desired metal ions after adjusting pH suitably. Other appropriate surface-spreading methods,

e.g., sol-gel, spin coating, chemical vapor deposition, or thermochemical decomposition (Wu et al. 2014), are also used to prepare such electrodes.

The important fact in M/MO anode is that during the synthesis, metal oxides are formed at the anode surface at applied potential by oxidizing the metal species present in solution, so that increasing the applied potential to value exceeding the synthesis potential will stabilize the MO on anode. This explains the stability (un-deterioration) of metal oxide-coated anode when operating at high cell voltage and can be categorized as DSA.

Titanium base metal coated with RuO_2 is usually a good catalyst when dealing with solution containing chlorine and hence is utilized for chloralkali processing (Panizza and Cerisola 2009). On the other hand, IrO_2 -coated Ti is a good electrode for oxygen evolution and used for water electrolysis and metal electrowinning (Kulandaisamy et al. 1997). Considering other types of coating, SnO_2 doped with Sb or other entities such as Ar, B, Bi, F, Cl, P, etc. finds wide applications in electrochemical oxidation. Chemically, SnO_2 is a semiconductor (n-type) with low conductivity (Donaldson 2007); however, when SnO_2 is doped with an electron donor or acceptor, the conductivity is highly improved. For example, electrode coated with Sb-doped SnO_2 exhibits a good conductivity with oxygen overpotential (1.9 V vs. SHE) that is slightly higher than that of Pt electrode (i.e., 1.6 V vs. SHE in 0.5 M H_2SO_4). This property makes Sb-doped SnO_2 attractive for anodic oxidation of organics. Indeed, SnO_2 - Sb_2O_5 -coated Ti electrode advanced Pt anode with nearly fivefold higher in efficiency and completes remediation of a wide range of organic compounds from wastewater (Ding et al. 2007; Stucki et al. 1991). Although laboratory research documents the high advantage of Ti/ SnO_2 - Sb_2O_5 electrode, commercially it is unavailable due to the short service life (maximum of 15 h) (Ding et al. 2007).

There is a growing interest in BDD as a new electrode material that has high conductivity, which is commercially feasible at fairly reasonable cost (Panizza and Cerisola 2009). The electrode is usually prepared from pristine conductive or nonconductive materials such as Si, Ta, Nb, W, Mo, and glassy carbon (Martinez-Huitle and Ferro 2006; Panizza and Cerisola 2009). The pristine material is coated with diamond by energy-assisted (plasma or hot filament) chemical vapor deposition; it is made conductive by doping with various levels of boron atoms (Scarsbrook et al. 2007). These types of electrodes possess (Fuchigami et al. 2014) a wide potential window (~ 3.0 V between oxygen and hydrogen evolution), stability in very aggressive media, and inert surface with low adsorption properties of organic pollutants. Thus, BDD are widely used for near-complete remediation of a wide range of organic pollutants in wastewater, e.g., textile dyes (Faouzi et al. 2007), bisphenol (Murugananthan et al. 2008), phenolic compounds (Iniesta et al. 2001; Morão et al. 2004), endocrine disruptor compounds (Yoshihara and Murugananthan 2009), carboxylic acids (Gandini et al. 2000), benzoic acid (Montilla et al. 2002), organic acids (Chailapakul et al. 2000), pharmaceutical waste (Brillas et al. 2005; Murugananthan et al. 2010), surfactants (Panizza et al. 2005), and real wastewater (Zhu et al. 2009).

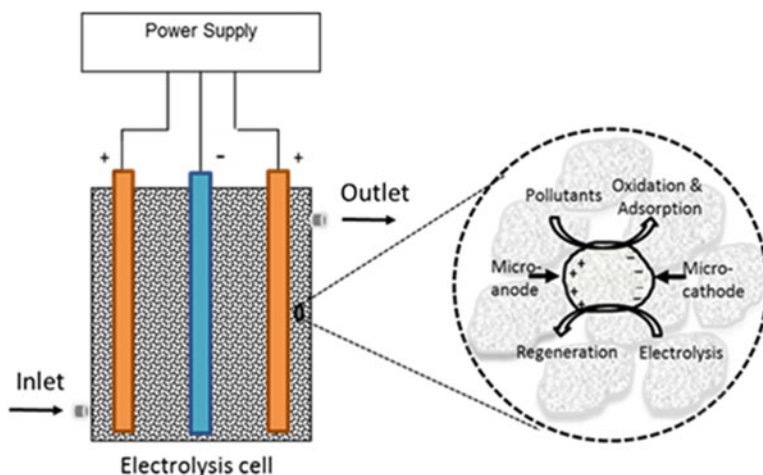


Fig. 8 Schematic representation of electroadsorption (EA) unit. Under the applied electric field, micro-anodes and micro-cathodes are established on adsorbent particles. The formation of numerous microelectrolytic cells enhances simultaneous oxidation, adsorption, and regeneration processes

Other anode materials widely employed for EO are carbon-based and graphite electrodes, such as graphite rod, graphite felt, carbon cloth, carbon paper, granules, and brushes. For graphite electrodes (sheets or rod), the current efficiency of anodic oxidation is low (Martinez-Huitle and Ferro 2006). Increasing the applied potential is accompanied by surface deterioration due to exfoliation of the surface particles (to form partially oxidized graphene nanoparticles (Yasri et al. 2014)), which reduces the lifetime and limits their application for anodic oxidation (Martinez-Huitle and Ferro 2006). However, the use of these types of electrodes is preferred as they are very cheap and possible to be fabricated with high porosity and large surface area and can combine adsorption and electrochemical degradation of pollutants. Indeed, the possible use of graphite material, especially of granule activated carbon as adsorbents and at the same time in applied field as electrode oxidizers has widened the scope of their applications in the so-called three-dimensional (3-D) electrode systems (Yasri et al. 2015b). In 3-D electrode system, the graphite particles are filled in the electrochemical system as in packed bed (see Fig. 8) or as fluidized bed to act as electroadsorption (EA) cell.

Adsorption is commonly used to remove dilute toxicants from effluents. This is done in an EA cell by means of adsorbent particles of activated carbon under an applied electric field. This system is not only helpful in enhancing the adsorption property of the adsorbent but also in increasing oxidation via a mechanism that involves creation of bipolar field on the adsorbent particles. Thus, the adsorbent particles placed within the electric field form micro-anodes and micro-cathodes at their two extremities. This essentially leads to the formation of a large number of microelectrolytic cells. For example, when using activated carbon granules as adsorbents, the graphite particles become such microelectrodes. The effective

number of cells created will enhance the adsorption properties and at the same time destroy pollutants (Zhang et al. 2013; Ding et al. 1987).

The use of such an EA system has been very effective in remediating organic pollutants such as dyes (Yasri 2001). However, if the adsorption capacity of pollutants on the activated carbon is already low because of the nature or the lack of active sites on both of adsorbents and the adsorbed materials, the presence of electric field will not enhance greatly the capacity of adsorption. Thus treatment of effluents using EA unit alone is likely not suitable for effective remediation. Therefore, it is important to look for methods that can create active sites (Yasri et al. 2015).

Bioelectrochemical Approaches for Organic Remediation

Energy generation from waste is one of the key sustainable technologies. Municipal wastewaters may contain as much as tenfold the energy required for its treatment (Fan et al. 2012). Energy from waste can be generated in various forms during primary treatment, e.g., electricity, heat, or production of fuel. In biological treatment, biotic entities digest soluble organic or inorganic entities from waste streams to produce metabolism products such as alcohol, methane, or hydrogen. Electrochemical applications have utilized some of the natural bacterial processes for energy conservation at electrodes in either or both anode and cathode compartments for electron donors and acceptors, respectively (Rittmann 2008). Thus, these devices transform chemical energy into electric energy via electrochemical reactions involving microbes or enzymes. For example, dissimilatory Fe-reducing bacteria (DMRB) (e.g., *Shewanella* and *Geobacter*) oxidize organics and transfer electrons to anodes. The energy in the electrons can be utilized for electricity generation in a microbial fuel cell (MFC) (Kato et al. 2012; Kim et al. 2002a) or for hydrogen gas production in a microbial electrolysis cell (MEC) (Cheng and Logan 2011). These systems contain an anode, a cathode, an electrolyte, and an electric circuit; microbial growth at one or both electrodes is either separated into two chambers or located in one (Fig. 9). The main difference between MFC and MEC is a stand for adding a small amount of voltage (>0.2 V) in MEC to that produced by bacteria at the anode to allow for the production of H_2 at cathode surface. Also, the operational conditions at the cathode are different for MFC and MEC. MFC is usually operated with an excess of dissolved O_2 , whereas for MEC the condition should be optimized for cathode system to allow the promotion of H_2 production. Both systems hold the same anodic principles, i.e., the microbes grow at the anode surface, degrade organic and/or inorganic substrates via their metabolisms, to produce electric power in MFCs (Fig. 9a) or as electron source to produce hydrogen in MECs (Fig. 9b).

Hydrogen is widely considered as imperative in building a sustainable energy future as it does not release any greenhouse gases upon combustion (Edwards et al. 2007). Thus, MEC is considered a new sustainable development for hydrogen

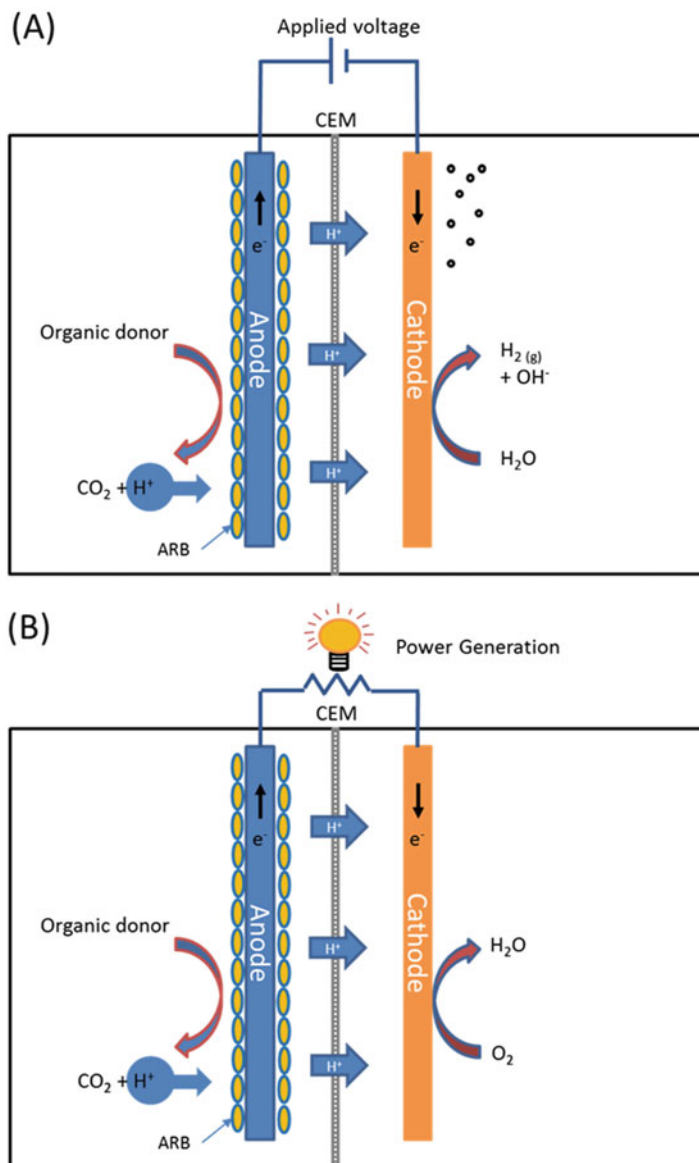
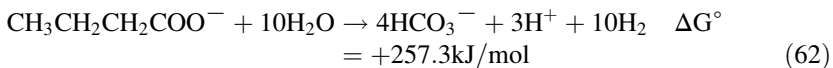
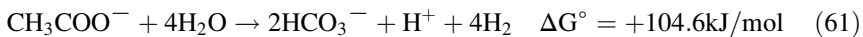
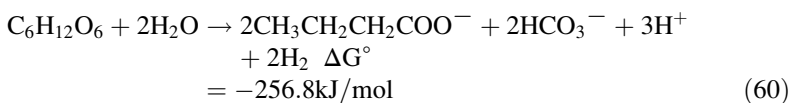
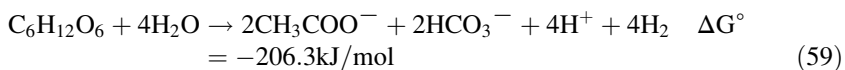
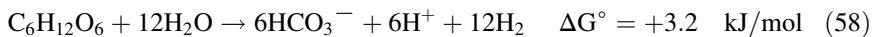


Fig. 9 Schematic diagrams of (a) MEC and (b) MFC systems consisting of two-compartment cells of anolyte and catholyte separated by cation exchange membrane (CEM). MEC produces H_2 by combining substrate utilization reaction at the anode by anodic respiring bacteria under small applied potential, and MFC produces electric current by combining two half-cell reactions of substrate utilization on the anode and oxygen reduction at the cathode

production (Cheng and Logan 2007a) that utilizes waste as a source of feed to various types of biomass (Wang and Ren 2013). The growth of anodic respiring bacteria (ARB) forming an exoelectrogen biofilm on anode as the main part of MEC to remediate organic waste releases protons to the anolyte medium and donates electrons to anode (Fig. 9a). The electrons flow toward the cathode, combine with protons, and release H_2 if only enough energy is provided to overcome the endothermic energy barrier of hydrogen overvoltage.

Theoretically, the maximum yield for complete oxidation of 1 mole glucose is 12 moles of H_2 (Eq. 58). For comparison, in the fermentation process, however, a 1 mole of glucose will produce maximum 4 moles H_2 if acetate is formed (Eq. 59) or 2 moles H_2 if butyrate is formed (Eq. 60). Moreover, the oxidation of glucose and its fermentation products of acetate and butyrate (Eqs. 58, 61, and 62) are not directly converted to H_2 without an external energy input (note that the free energy values of reactions are not spontaneous under standard conditions). Therefore, the use of MEC to oxidize these chemicals will theoretically provide the extra energy to remediate waste and produce additional H_2 .



In MECs, although bacteria are the cornerstone entities to metabolize substrates and provide energy, the system design, electrolyte properties, and anode and cathode materials also influence the performance of the reactor. Thus, it is necessary to optimize the MEC design and operating conditions to maximize H_2 production and minimize cost. Various parameters affecting H_2 production rate and bacteria enrichment for the better biofilm performance are briefly discussed herein. Methods of various parameters calculation are also presented in [Box 2].

Box 2 Calculation of Yield and Efficiency of MEC System

For simplicity, the following calculations are based on acetate as substrate (not complex) in the MEC system. A typical batch MEC system is shown in Fig. 9a. The electrodes are powered at a specified voltage (not exceeding 1.0 V) using a direct current power supply, connecting in series through a known resistor (R_Ω) with a data acquisition system to record the voltage drop

(continued)

Box 2 (continued)

across the resistor. The outcome current is calculated applying Ohm's law ($I = V/R_{\Omega}$), where V is the measured voltage drop across the resistor. The generated biogases from MECs are usually collected using the water displacement method, measuring the volume and determining the composition by using a proper gas chromatograph analysis for hydrogen, methane, and nitrogen (Yang et al. 2015). The H_2 yield is calculated based on molar ratio of the actual hydrogen production to substrate utilized,

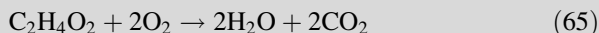
$$Y_{H_2} = \frac{n_{H_2 \text{ mol}} (\text{hydrogen produced})}{n_{S \text{ mol}} (\text{substrate consumed})} \quad (63)$$

The moles of H_2 produced are given from the volume (mL) of actual hydrogen production by applying ideal gas law;

$$n_{H_2} = \frac{V_{H_2} P}{R T} \quad (64)$$

where p (atm), T (K), and R the ideal gas constant (0.08206 L atm/K mol).

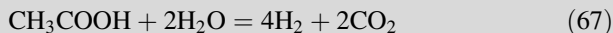
The number of moles of the substrate utilized (n_s) is usually calculated based on the soluble chemical oxygen demand (SCOD) consumed during the cycle; e.g., in the following oxidation reaction of acetate substrate:



$$n_s (\text{mol}) = \frac{\Delta \text{SCOD} (\text{mg})}{2 \times 32 (\text{O}_2)} \times \frac{\text{g}}{1000} \quad (66)$$

where ΔSCOD (mg) is SCOD consumed during the cycle; 32 is the molecular weight of oxygen.

Considering that the theoretical maximal production of H_2 from acetate is 4 moles,



The overall H_2 recovery (R_{H_2} , %) is calculated as a ratio of actual amount of hydrogen produced to the theoretical amount of hydrogen that should be produced by the same amount of substrate:

$$R_{H_2} (\%) = \frac{n_{H_2} (\text{mol})}{n_{th} (\text{mol})} \quad (68)$$

(continued)

Box 2 (continued)

$$n_{th} = 4n_s = \frac{2\Delta\text{SCOD (mg)}}{32 (\text{O}_2)} \times \frac{\text{g}}{1000} \quad (69)$$

On the other hand, ideally the fraction of electrons recovered as current is released at the cathode surface as hydrogen. Thus, identifying the coulombic efficiency (CE) would represent fraction of electrons, which is recovered as current versus that in the starting organic matter. Accordingly, CE is calculated from the theoretical maximal production of H_2 (n_{th}) and the current recovery over time using Eqs. 70 and 71.

$$CE = \frac{n_{CE}}{n_{th}} \quad (70)$$

$$n_{CE} = \frac{\int_{t=0}^t I_{90} dt}{2F} \quad (71)$$

where n_{CE} (mol) is the number of moles of hydrogen that could be recovered based on measured current and found by calculating the area under the curve of current density versus time throughout the reaction period, n_{th} (mol) is the number of moles of hydrogen theoretically produced from ΔSCOD consumed, dt is time interval (s), 2 in the Eq. 71 is the number of electrons used to convert hydrogen charge ($2\text{H}^+ = 2\text{e}^- \rightarrow \text{H}_2$), and I_{90} is the average current (A) recorded over time (t) and converted to cover the 90% of the charge accumulation. The use of I_{90} is more accurate when analyzing MEC performance in a batch process because it eliminates small current densities at the end of the cycle and focuses on the most useful part of the current generation cycle (Ivanov et al. 2013).

The cathodic hydrogen recovery (r_{cat}) is indicative of the number of moles of hydrogen recovered at the cathode compared to the moles that theoretically could have been produced from the current and is calculated using Eq. 72.

$$r_{cat} = \frac{n_{\text{H}_2}}{n_{CE}} \quad (72)$$

Volumetric hydrogen production rate (HPR) ($\text{m}^3 \text{H}_2/\text{m}^3/\text{d}$) should be normalized to the cathode liquid volume.

Calculation of Energy Recovery

The energy content of the amount of hydrogen recovered is compared with energy input. The source of energy input to the system is based on (i) the external electric energy input (η_E), (ii) energy input from the substrate (η_S), and (iii) energy input in both electricity and substrate ($\eta_E + S$).

(continued)

Box 2 (continued)

The energy recovery based on external electric energy input is calculated from Eq. 73:

$$\eta_E = \frac{-W_{H_2}}{W_{in}} \quad (73)$$

where W_{H_2} (J) is the energy content of the hydrogen and W_{in} (J) is the energy input to the system. Whereas, the energy content of hydrogen is calculated from heat of enthalpy (ΔH_{H_2}) (Eq. 74):

$$W_{H_2} = n_{H_2} \cdot \Delta H_{H_2} \quad (74)$$

where n_{H_2} (mol) is the number of moles of H_2 produced and $\Delta H_{H_2} = -285$ kJ/mol is heat of enthalpy of H_2 .

The energy input to the system (W_{in} , J) is equal to the total energy input (W_{ps} , J) subtracted from the energy loss on the external resistor (W_R , J) (see Eqs. 75 and 76).

$$W_{in} = W_{ps} - W_R \quad (75)$$

$$W_{in} = \int_{t=0}^t (IE_{PS} - I^2 R_{ex}) dt \quad (76)$$

where R_{ex} the external resistor (Ω), I (A) the current based on voltage drop measured across the external resistor, E_{PS} (V) the applied voltage of the power source, and dt (s) the time interval.

Energy recovery based on both the energy input and the energy in the substrate is calculated from Eq. 77.

$$\eta_{E+S} = \frac{-W_{H_2}}{W_{in} - W_S} \quad (77)$$

where W_S (J) is the amount of energy added by substrate, and given in Eq. 78;

$$W_S = n_S \Delta H_S \quad (78)$$

where n_S (mol) is the number of moles of substrate consumed during a batch cycle and ΔH_S the heat of enthalpy of the substrate ($\Delta H_{Acetate} = -874.3$ kJ/mol).

(continued)

Box 2 (continued)**Biomass Distribution Analysis**

To estimate the COD distribution in MEC systems, we assume that the only COD sinks are the production of gases and biomass (suspended, attached, and produced). Thus, the following overall mass balance equation should be established:

$$\text{COD}_{\text{initial}} = \text{COD}_{\text{H}_2} + \text{COD}_{\text{biomass, sus}} + \text{COD}_{\text{biomass, att}} + \text{COD}_{\text{final}} \quad (79)$$

where $\text{COD}_{\text{initial}}$ is the initial COD in the anode chamber, COD_{H_2} is the COD equivalent of hydrogen gas production during the studied cycle, $\text{COD}_{\text{biomass, sus}}$ is the COD for suspended biomass net accumulation over the incubation time in the anode chamber, $\text{COD}_{\text{biomass, att}}$ is the COD for attached biomass accumulated on the anode material over the cycle period, and $\text{COD}_{\text{final}}$ is the SCOD in the anode chamber at the end of the studied cycle.

According to the mass balance (Eq. 79), the only unknown COD sink is the attached biomass ($\text{COD}_{\text{biomass, att}}$), whereas $\text{COD}_{\text{biomass, sus}}$ can be determined according to Eq. 80, and the COD_{H_2} is calculated via Eq. 81 (Lee et al. 2008), i.e., each 1 mL of H_2 produced is equivalent to 0.654 mg COD (at 25 °C), and considering the fact that gas produced out of the cathode chamber is almost pure H_2 without any methane,

$$\text{COD}_{\text{biomass, sus}} = (\text{TCOD} - \text{SCOD})_{\text{final}} - (\text{TCOD} - \text{SCOD})_{\text{initial}} \quad (80)$$

$$\begin{aligned} 1 \text{ mL H}_2 &= \frac{1 \text{ mmol H}_2}{22.4 \text{ mL}} \frac{273.15 \text{ K}}{298.15 \text{ K}} \frac{2 \text{ meq e}^-}{\text{mmol H}_2} \frac{8 \text{ mg COD}}{\text{meq e}^-} \\ &= 0.654 \text{ mg COD} \end{aligned} \quad (81)$$

Exoelectrogenic Microorganisms

Microorganisms that can directly transfer electrons outside the cell to the electron acceptor (anode) without the need for exogenous mediators are known as exoelectrogens. These microorganisms are usually grown in anaerobic condition on anode surface as electron acceptor and utilize organics present in the effluent as electron donor. Electrochemical gradients are the backbone of basic cellular functions, including chemosmotic transport and ATP synthesis (Amit Kumar et al. 2012). The mechanisms of extracellular electron transfer have been proposed in three pathways: (i) through direct electron transfer through microbial outer membrane cytochromes; (ii) by electron shuttle molecules, mediated by the grown biofilm; and (iii) via a solid conductive protein produced by bacteria and shaped like nanowires or pili (Amit Kumar et al. 2012; Logan 2009a; Lovley 2008; Torres et al. 2010). Extracellular electron transfer mechanisms are not mutually exclusive within a species nor in one pathway. For example, *Shewanella oneidensis* can

transfer electrons via methods producing riboflavins that can function as electron shuttle. *Geobacter sulfurreducens* also has an outer membrane cytochrome and can produce nanowires that can conduct electrons through a 50- μm thick anodic biofilm (Nevin et al. 2008) but does not produce flavins or other mediators (i.e., pyocyanin, melanin, or quinones).

The analyte chamber in MEC operates in anoxic environment, which promotes the growth of anaerobic bacteria; however, the type of dominant entities enriched from activated sludge from wastewater treatment plant contains mixed culture inocula, which are strongly affected by the feeding substrate present in the electrolyte solution (effluent type). For example, *Pelobacter propionicus* and *Geobacter* are dominant in MECs fed with phosphate buffer solution and acetate as the substrate (Chae et al. 2008). *Shewanella* and *Pseudomonas* were the dominant bacteria in the two-chamber MEC with acetate as the substrate and carbonate buffer and sewage sludge as the inoculum (Liu et al. 2007b). *Pelobacter* is the dominant bacteria in the suspension and anodic fractions of an ethanol-fed MEC inoculated with sludge (Parameswaran et al. 2010).

Anode System

Continuous development of anodes for beneficial microbial attachment and substrate utilization in MEC system is critical for better performance of MECs (Baudler et al. 2015; Wagner et al. 2012). Important factors affecting the immobilization of biological entities in MECs are the type of anode materials and their configuration (He et al. 2015). Immobilization in biological system is generally defined as the physical confinement or localization of viable cells including enzymes, cellular organelles, animal and plant cells to a certain supporting region for biocatalytic purposes. Immobilization is performed to limit free transportation of biota while retaining their catalytic activities, which differ from those of the surrounding environment.

Generally, microbial cell immobilization (MCI) on supporting region is categorized as (i) passive, using the natural tendency of microorganisms to attach and grow on natural or synthetic surfaces, and (ii) active, with the help of flocculating agents, chemical attachment, and gel encapsulation. In both the selection of the support material is crucial. For wastewater treatment, support materials should meet the criteria of insolubility, nonbiodegradability, nontoxicity, simplicity of immobilization procedure with high retention to specific organisms, and preferably low cost. Other physical characteristics such as material high porosity, non-swelling, and compressible are also of concern.

Conductive carbonaceous materials are favored for anodic MCI (Logan 2010; Logan et al. 2008), and the choice of these materials for cultivating ARB is always related to their conductivity, chemical stability, adsorptive capacity, porosity, and high surface area (Logan 2010; Logan et al. 2008). Carbonaceous fabric anodes that

are usually utilized in MEC are carbon cloth, carbon fiber, carbon felt, carbon mesh, carbon paper, and granular carbon (Logan 2009b).

Increasing the surface area enhances the performance of the reactor by increasing the volume of the biofilm and hence the ARB reactive sites. For example, Yasri and Nakhla (2017) found that filling the anode chamber with granular activated carbon increases the efficiency and the corresponding H_2 conversion rate. However, this improvement is still limited considering the faster H_2 production rate achieved in some biological system, i.e., dark fermentation (Lee et al. 2010). Thus, effort was made to favor adhesion of microorganisms to positively charged anode by treating anode surface with ammonia at a high temperature (700 °C, 5% ammonia gas for 1 h), which results in faster startup of H_2 production (Cheng and Logan 2007b). Several similar methodologies such as surface pretreatment of carbon cloth anode (or carbon mesh as a cheaper alternative) with aqueous ammonia, phosphate buffer, metal doping (Yasri & Nakhla 2017), or nitric acid have been investigated (Zhang et al. 2014b). Moderate to slight increase in anode performance was attributed to the enhancement of electron transfer and better MCI on the anode surface (Zhang et al. 2014b). Factors affecting the MCI conditions at the anode, such as applied voltage, electrolyte conductivity, electrode arrangement, pH, substrate types, and electrode porosity, have been extensively studied (Wang et al. 2010b).

The effect of applied voltage on the MEC system performance was inconclusive. Commault et al. (2013) noted an influence of different anode potentials on the type of *Geobacter* strains grown in MECs (Commault et al. 2013), i.e., different strains will grow from mixed culture inoculum at different potentials. However, Logan et al. (Zhu et al. 2014) suggested that the same exoelectrogenic communities self-regulate their exocellular electron transfer pathways to adapt to different anode potentials. To understand the effect of potential, the voltammograms obtained from grown biofilm have to be analyzed to answer the question, how different sets of potentials affect the performance of the bioelectrochemical system?

The porosity of the anode surface represents also an impotent factor to improve the mass and charge transport limitations of the electrolyte, which highly influence the performance of bioelectrochemical systems (Dhand et al. 2014; Sleutels et al. 2009, 2011). Increasing the porosity will increase the surface area of the biofilm on the interface and hence increase the active reaction sites (Dhand et al. 2014). Reports indicate that increasing porosity as well as conductivity of the electrode can be achieved by modifying the anode surface with various nanoparticles such as Fe (Xu et al. 2012) or conductive polymer such as poly (3,4-ethylenedioxythiophene) (PEDOT) (Liu et al. 2015). The role of varying the porosity or conductivity of anodes using Fe nanoparticles or sulfur-containing chemical (such as PEDOT) is not clearly understood. For example, it has been reported that the conductivity of the electrolyte in the anolyte chamber has a significant effect on the performance of ARB (Lacroix et al. 2014; Rousseau et al. 2013) and that the H_2 increased from 0.13 to 0.82 m³ H_2 /m³ per day when the electrolyte conductivity increased from 7.5 to 15 mS/cm (Verea et al. 2014). This phenomenon was related to an increase in electron-shuttling effect between the biofilm and the electrode surface, which reduces the inner resistance

(Lacroix et al. 2014; Rousseau et al. 2013; Verea et al. 2014). However, the conductive material may be a natural favorite to attract bacteria, and the enhancement of ARB performance may be not due to their conductive properties. For example, metal sulfides, especially those containing Fe, Ca, K, or Mg, play a major role in microbial growth under anoxic and oxic conditions and are found at the active centers of a wide variety of redox and catalytic species (Bertini et al. 1994; Lapinsonnière et al. 2012; Picot et al. 2011). These species include simple soluble electron transfer mediators (e.g., Fe(II)/Fe(III), sulfate/sulfide redox couple (Schroder 2007), Ca^{2+} ions (Fitzgerald et al. 2013), membrane-bound components of electron transfer chains, and some complex metalloenzymes (Amend et al. 2004; Bertini et al. 1994; Ghasemi et al. 2013; Lapinsonnière et al. 2012; Lovley and Phillips 1986; Schippers 2004; Weber et al. 2006). Despite the neutral attraction of ARB to these materials, research emphasizes the importance of increasing conductivity of anode surface modification with suitable conductive chemicals to induce cultivation of ARB, stimulate catabolism, conduct electrons, and consequently improve current density (Baudler et al. 2015; Gnana Kumar et al. 2014; Kang et al. 2015; Kato et al. 2012; Li et al. 2011; Luckarift et al. 2012; Tang et al. 2015; Zhao et al. 2010). For example, Kang et al. (2015) observed superior biocatalytic enhancement when PEDOT was coated on carbon felt anode and inoculated in an effluent originating from palm oil mill waste to catalyze acetate oxidation. Although PEDOT, which was used for anode modification, contain element sulfur that may stimulate bacterial growth, the enhancement was attributed to the better conductivity of the modifying material. The unanswered question is whether the improvement in the performance of MEC system is due to surface conductivity or due to the attraction of bacteria to attach to trace element present in the electrode.

On the other hand, the anode arrangement can be considered as an effective parameter to reduce the inner resistance (Li et al. 2014). For example, Liang et al. (2011) separately placed two anodes, either on one side or both sides of cathode in parallel within a membraneless MEC. They found that the MEC with anodes on both sides of cathode improved current and H_2 production rate by 72% and 118%, reaching $621.3 \pm 20.6 \text{ A/m}^2$ and $5.56 \text{ m}^3 \text{ H}_2/\text{m}^2 \text{ per day}$, respectively.

The limitation of pH inside the anolyte compartment is an important factor affecting current, bacterial growth, and electron transfer which is also tied to proton transfer within the biofilm (Babauta et al. 2012b). Babauta et al. (2012b) confirmed this effect and concluded that (a) pH can vary within the biofilm at different growth phases, (b) pH is not always a limiting factor in a biofilm, and (c) biofilms respire in a unique internal environment that variation of pH and redox potential are associated only with the biofilm.

Substrates are considered as the feed sources for ARB, existing in the effluent, and are converted or oxidized within the MEC system. Kadier et al. (2014) have reviewed the substrates used in MECs (ranging from simple to complex effluent resulted from real wastewater, fermentable and non-fermentable organic materials), their performance, and future potential usage for sustainable system. The substrates discussed include from complex to simple sources such as molasses industrial (methanol rich), food processing, winery, potato processing, dairy manure, refinery,

swine, and domestic wastewater. Of these, the complex substrates help in establishing a diverse and electrochemically active microbial community, while simple substrates degrade easily and improve H_2 production rate.

Thus, although the microbe/electrode interactions stem from the abilities of bacteria to extracellular electron transfer to solid metals as terminal electron acceptors, electron transfer to electrodes does not necessarily share identical cellular components (Babauta et al. 2012a). Thus microbe/electrode interactions remain enigmatic with both ecological and evolutionary origins. Further research is needed to shed more light on these bioelectrochemical processes.

Cathode System

Hydrogen production in MEC occurs at the cathode surface, located in the catholyte chamber and operated in air-saturated electrolyte. The hydrogen evolution reaction (HER) on plain carbon electrodes is very slow and requires a high overvoltage (-0.42 V) to drive H_2 production (Logan et al. 2008). To reduce the overvoltage barrier, Pt is usually used as a catalyst. Pt-catalyzed electrodes are commercially available and also are easily prepared by mixing commercially available Pt/carbon powder with a chemical binder (Cheng et al. 2006). This forms a paste in which the Pt loading can be varied by changing the mass of Pt in the paste.

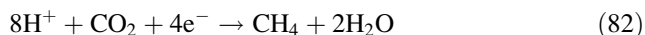
Major disadvantages of using Pt are high cost and the possibility of being poisoned by chemicals such as sulfide, which is a common constituent of wastewater. Various other metals, alloys, modified electrode surfaces, or reducing biofilms are used as alternative for Pt as cathode (Rozendal et al. 2008). Kundu et al. (2013) reviewed the type of cathode material, catalysts, and modifications that are suitable for H generation in microbial electrolysis cell. Among the materials used, stainless steel, Ni alloys, Pd nanoparticles, and decorated cathode are very good for H_2 evolution. Nevertheless, cost-effective catalysts are the key to successful industrial application of MEC.

Unlike plain carbon materials, carbonaceous cathode doped with nanoparticles containing, e.g., MoS_2 , has been reported effective and even competes with Pt cathode (Hou et al. 2014; Tenca et al. 2013). Nevertheless, due to the toxicity of most metal ions and for the purpose of keeping the MECs as environmentally friendly technology, replacement with nonmetallic composition becomes advantageous. Many successful applications have been reported using nanocomposites of carbonaceous materials doped with nitrogen (Zhang et al. 2014a), phosphate (Munoz et al. 2010), sulfur, or their mixtures (Ghasemi et al. 2013, Zheng et al. 2014).

Membrane

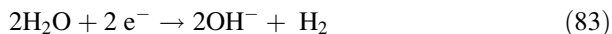
The use of membrane in MEC system is to separate anaerobic microbial condition at the anode from aerobic condition at the cathode, to minimize H_2 losses, and to

prevent mixing with CO_2 in the anode chamber. However, the presence of membrane disadvantages the system by increasing potential losses and reducing energy recovery associated with the resistance accompanied by its existence (Logan et al. 2008). Although membraneless system can be employed, research shows the production of methane in combination with H_2 due to the growth of cathodic reducing bacteria (methanogenic bacteria) that reduce of CO_2 according to Eq. 82 (Bajracharya et al. 2015).



Membranes used in MEC can be either CEMs or AEMs (Logan 2008). The use of CEMs allows transportation of H^+ and other cations present in solution, such as Na^+ , K^+ , NH_4^+ , Ca^{2+} , and Mg^{2+} , toward the catholyte chamber. However, typical pH of wastewater and the inoculating medium of MECs is about neutral (pH ~ 7.0), and the proton concentration is about 10^{-4} mM (Rozendal et al. 2007), which is far less than the concentration of cation species other than protons in wastewater (typically 4–5 orders of magnitude higher). As a result, electrodialysis of cation mainly occurs in the MECs provided with CEM by the transport of cation species other than protons through the membrane. The cation transportation to catholyte chamber other than protons will therefore alter the anolyte medium surrounding the bacteria, as well as create a pH difference (gradient) between the catholyte and the anolyte chambers which will negatively affect the MEC performance by creating an extra potential loss and competing reactions other than hydrogen evolution at the cathode surface (Rozendal et al. 2007).

The utilization of AEM instead of CEM is useful in a sense that electrodialysis of anion toward the anode from the cathode rather than the transport of cations from the anode to the cathode will prevent the transportation of the other cation to the catholyte chamber (Rozendal et al. 2007). The transport of hydroxide (OH^-) anion toward the anolyte chamber will leave behind hydronium (H_3O^+) ions that react at the cathode surface to evolve hydrogen. The electrolysis of water (Eq. 83) at the cathode will provide, in this case, the extra hydroxide ions that diffuse through membrane via the effective ion transportation mechanism toward the anode that equilibrates the exchange of charges and electrons in the system.



Concept of MEC System

Understanding the principles and behavior of electrochemical interface reactions between biotic entities in biofilm, substrate utilization, and abiotic surface phase of electrode is important to continue advancements in MEC systems. Electrochemical studies for MECs include voltammogram analysis of the interface reactions, performance of the biofilm in both cathode and anode (Yoho et al. 2015), and determination of the kinetic parameters of biofilm growth on electrodes.

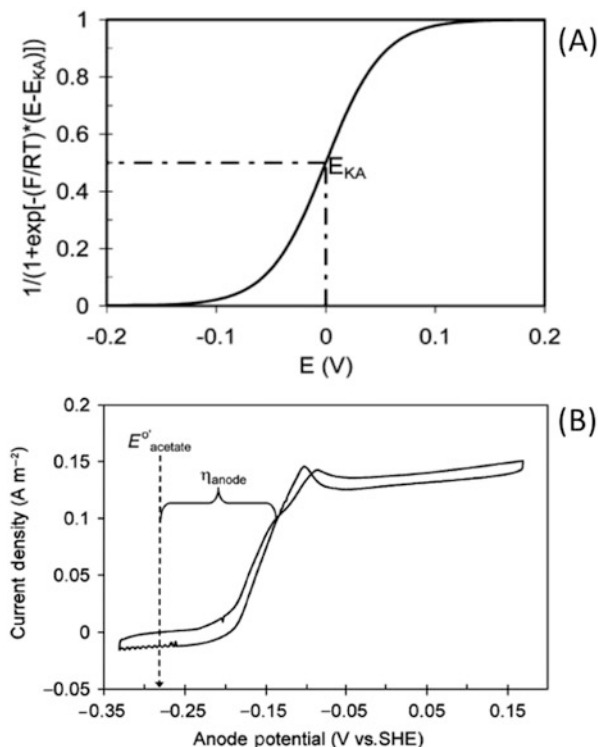
The correlation between current generation, ARB, and the electrode has been well established, indicating that the electron generation is a consequence of biocatalytic substrate utilization to transfer via various extracellular electron transfer (EET) to the final electrode port (Lovley 2008; Reguera et al. 2005; Richter et al. 2009). However, information about the interfacial anodic voltammogram at the electrode-biofilm is limited. Generally, the kinetic response of electron shuttles at the electrode interface (i.e., current density-voltage, J-V response) is defined by mass-transport processes according to Butler-Volmer equation (Torres et al. 2008). However, in the case of biofilm interface, the production of conductive matrices (wiring within the biofilm), which is directly attached to the anode, will be considered as an extension of the anode material, and thus the biofilm containing a solid conductive matrix can be called a “biofilm anode” (Torres et al. 2008). The bacterial kinetics and the J-V response model in this case will differ from Butler-Volmer equation and that variance directly affected by the bacteria should be considered.

Electrochemists commonly use Nernst model to describe redox potential as a function of electron concentration at the electrode interface. Biologists, on the other hand, use Monod kinetics to describe the dependence of biological growth on the concentration of electron donor and acceptor (substrate) (Wang et al. 2010d). Marcus et al. (Kato Marcus et al. 2007) combined the above two models and proposed the Nernst-Monod model (Eq. 84) to describe the bacterial kinetics under the influence of the anode potential E (V), where the reduction potential of interface electron controls the bacterial donation activity, i.e., current exchange at the interface.

The ideal electrode J-V representation for ARB influences electron shuttling through self-produced mediators and is a sigmoidal-shape voltammogram presented in Fig. 10a (Kato Marcus et al. 2007; Torres et al. 2008). An experimental current response of the biofilm anode to potential at slow scan rate (1.0 mV s^{-1}) is presented in Fig. 10b. Usually when applying a slow scan rate, the voltammogram shows an ideal “steady state”; that is, the catalytic current does not depend on the scan direction (Marsili et al. 2008) to allow ARB to reach a steady metabolic condition at all potentials, i.e., reach a steady state. In bioelectrochemistry, the low-scan cyclic voltammetry (LSCV) is a powerful technique, as it measures the steady-state response of ARB as a function of the anode potential (Torres et al. 2010).

The main assumption for the use of the Nernst-Monod model is that microbial kinetics controls the rate of current generation. This is usually performed by evaluating the anode potential losses APL (η_{anode}) in an ARB biofilm anode. The APL (η_{anode}) is defined as an electrocatalytic potential of active site as close as possible to the redox potential of the substrate being oxidized. Characterizing these potential losses is an important factor in the development of MFCs and MECs. The main postulation of this hypothesis is that, lower APL will translate to a higher catalytic current, higher energy output, and hence higher efficiency of the process. Thus, the twofold task in optimizing MEC system is to produce a high current density using minimum anode materials at a low anode potential (being as close as

Fig. 10 Ideal plot of the Nernst-Monod model for $E_{KA} = 0$ V and $T = 30$ °C (Torres et al. 2008) (a) and low-scan cycle voltammetry of ARB biofilm for acetate as substrate (b) (Adapted from Torres et al. 2010)



possible to the redox potential of the substrate being oxidized). Thus, the practical goal in MECs is to find an ARB community (or system) that can achieve both aims by producing a high current density at a low anode potential (Torres et al. 2010).

$$J = J_{\max} \left(\frac{1}{1 + \exp - \frac{F}{RT}(E - E_{KA})} \right) \quad (84)$$

where J = current density (A m^{-2}); $J_{\max}$ = maximum current density (A m^{-2}); R = ideal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$); F = Faraday constant ($96,485 \text{ coulomb per mol}^{-1} \text{ e}^{-1}$); T = temperature (303.15 K); and E_{KA} = potential at which $J = \frac{1}{2} J_{\max}$.

Figure 10b depicts an example LSCV curve produced with freshly formed ARB biofilm producing maximum current density of about 0.15 A.m^{-2} (Torres et al. 2008). The voltage is scanned back and forth between -0.33 and $+0.15 \text{ V}$ vs. the standard hydrogen electrode (SHE) at 1 mVs^{-1} . The forward and backward curves are similar to each other, indicating steady-state conditions that are not affected by the scanning direction. η_{anode} can be measured from this curve by calculating E_{donor} (for acetate as electron donor in this case, $E_{\text{acetate}}^{\circ} = -0.285 \text{ vs. SHE}$). At $E_{\text{anode}} = E_{\text{donor}}$, ARB cannot gain any energy-transferring electrons to the anode;

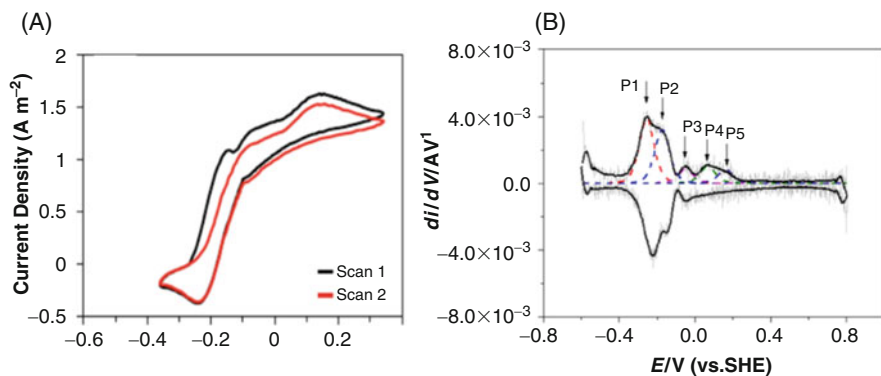


Fig. 11 Two consecutive cyclic voltammograms of *Geoalkalibacter subterraneus* inoculated in Fe(III)-containing cultures, recorded at 1 mV s^{-1} after day 7 of biofilm growth (a) (Adapted from Badalamenti et al. 2013). Derivative CVs suggest multiple electron transport pathways pointed out by arrows, and dashed lines represent Nernst-Monod fit (b) (Adapted from Yasri and Nakhla 2016)

therefore, $J = 0$. As E_{anode} becomes more positive, the ARB metabolic rate increases (indicated by the increase in J) until saturation.

The Nernst-Monod equation is proved to be a good model to describe the kinetics of bioelectric current that generates from pure bacterium culture and electron-shuttling pathways. However, in the real experimental situation when mixed culture is inoculated (instead of pure culture) and when the pristine material of electrode is made of mixed composition (not pure material), the J-V voltammogram may show in some cases sigmoidal shape, but the interpretation of kinetic data becomes complicated. In these cases, the CV curves will not fit the Nernst-Monod model, even with the selection of an appropriate J_{max} and E_{KA} . This is largely due to the occurrence of several EET pathways. For example, results from Badalamenti et al. (2013) show sigmoidal-shape CVs with various convex shapes indicating multiple EET pathways (Fig. 11a). The CV curve will emphasize significant deviations from Nernst-Monod model (Yasri and Nakhla 2016; Yoho et al. 2015, 2014).

In these cases, however, derivative cycle voltammetry (DCV) can be used to distinguish multiple EET pathways (red curve in Fig. 11b), which are reflected by the multiple convexes appearing on the DCV (Yoho et al. 2015). The results from Yasri and Nakhla (2016) indicate possible fitting of the forward DCV scan portions using multiple derivatives of Nernst-Monod equations (Fig. 11b). The derivative of the Nernst-Monod equation is best described by convex shape of dI/dV (mA V^{-1}) versus anode potential (V) (Yasri and Nakhla 2016; Yoho et al. 2015). Fitting first derivative of Nernst-Monod equation to the DCVs can provide an important tool to differentiate EET pathways under multiple EET conditions (Yasri and Nakhla 2016; Yoho et al. 2014, 2015). The forward and the backward DCV scans reveal that there are multiple visible convex and concave shapes, respectively, that may be associated with different electron transport pathways (Yasri and Nakhla 2016).

The use of the derivative of the forward CV scan for fitting with multi-Nernst-Monod equations is to provide the overall response of the oxidation part of the scan (Yasri and Nakhla 2016). These forward curves can be fit using various derivatives of Nernst-Monod equation ($n = 1$) at the midpoint potential of each convex shape by adjusting the current values. Each Nernst-Monod fit represents one electron transfer pathway. Thus, from the DCV shapes and from the multi-Nernst-Monod fits, we could presume the existence of multiple EET pathways associated with various potentials using different types of electrode. The variations in the potential of EET pathways for different electrodes can be an indication of the various types of ARB growing on the electrode (Yasri and Nakhla 2016; Yoho et al. 2015).

It is interesting at this point to discuss the driving force for the interface reactions. For example, the DCV in Fig. 11b shows four main pathways corresponding to four values of E_{KA} in Nernst-Monod model. The lower E_{KA} value (pathway 1) corresponds to lower bioelectrocatalytic potential. Comparing the overall bioelectrocatalytic potential (E_{KA}) of different biological communities on different electrodes will provide idea about the corresponding potentials of pathways and hence the anode potential losses (APL, η_{anode}). Thus, the lower APL (lower E_{KA}) will translate to a higher current density and hence higher energy output and efficiency (Torres et al. 2010). In a similar approach, Zhu et al. (2014) studied the effect of different anode potentials on the CVs of non-turnover (starving biofilm conditions) to assess microbial community variations. They similarly observed that the faster electrocatalytic processes were accompanied by a shift of the anodic peaks toward the negative direction (Zhu et al. 2014). Further research is needed to optimize electrode materials or growth of biofilms to reduce energy required to catalyze the substrates being oxidized.

Conclusions and Perspectives

Interfacial electron transfer between electrodes and aqueous phases containing pollutants can be successfully exploited in electrochemical systems for remediation of environmental pollutants. Proper design of reactors, careful choice of materials, and systematic control of parameters can lead to effective pollutant remediation, material recovery, and even energy generation from waste streams. The concentrator technique can be used to recover valuable heavy metals from dilute waste streams and return the metals back to the industrial cycle. In case of waste streams containing multiple metallic constituents, each can be simultaneously recovered and separated by selective electrochemical deposition or in electrodialysis system. Exploiting the stability of metal complexes with suitable masking ligands readily performs these.

Electrochemical remediation of organic constituents can be achieved by implementing various electrochemical designs and principles. Among these, the techniques for remediating waste and simultaneously generating energy are the most promising. The utilization of the basic chemical principles of coagulation,

flotation, Fenton oxidation, chemical oxidation, and adsorption in electrochemical cell provides enhancement in the performance of different electrochemical techniques such as electrocoagulation, electroflotation, electro-Fenton oxidation, electro-oxidation, and electroadsorption. Each process exhibits certain technical advantages and disadvantages. The cost of electrochemical remediation is generally lower than their chemical remediation counterparts. However, future developments in electrochemical remediation technologies should be dictated not only by the cost but also by the need to meet the public expectations and the regulatory guidelines. An advantageous direction for new research is to explore the use of organic wastes as resources for cost-effective energy generation. In this regard microbial electrochemical techniques show promise. However, there are challenges to overcome such as the low current density, slow rate of remediation, limited scale-up, poor portability, etc. Generally, the investment in electrochemical remediation processes would be more promising if research focuses on integrating the electrochemical technique to assist other remediation process as sources of electron donor and acceptor at the electrode interface.

List of Notations/Abbreviations and Symbols

Notations/abbreviations

3-D: three dimensional	EEC: electrochemical energy consumption
ACE: average current efficiency	EET: extracellular electron transfer
AEM: anion exchange membrane	EF: electrochemical flotation
APL: anode potential losses (η_{anode})	EFO: electro-Fenton oxidation
ARB: anodic respiring bacteria	EO: electro-oxidation
ATP: adenosine triphosphate	HPR: hydrogen production rate ($\text{m}^3 \text{H}_2/\text{m}^3/\text{d}$)
BDD: boron-doped diamond	HRT: hydraulic retention time
CAO: catalytic advance oxidation	ICE: instantaneous current efficiency
CE: coulombic efficiency	LSCV: low-scan cyclic voltammetry
CEM: cation exchange membrane	M/MO: metal/metal oxide
CET: concentrator electrochemical technique	MCI: microbial cell immobilization
CM: concentrator material	MEC: microbial electrolysis cell
COD: chemical oxygen demand	MFC: microbial fuel cell
CV: cycle voltammetry	MNP: metal nanoparticles
DC: direct current	MO: metal oxide
DCV: derivative cycle voltammetry	PEDOT: poly(3,4-ethylenedioxythiophene)
DMRB: dissimilatory Fe-reducing bacteria	POPs: persistent organic pollutants
DO: dissolved oxygen	RH: organic molecules (pollutants)
DSA: dimensionally stable anodes	SCE: saturated calomel electrode
EA: electroadsorption	SCOD: soluble chemical oxygen demand
EC: electrochemical coagulation or electrocoagulation	SHE: saturated hydrogen electrode
ED: electrodeposition	TCOD: total chemical oxygen demand
EDTA: ethylenediaminetetraacetic acid	TOC: total organic carbon
	UV: ultraviolet

Symbols

η_{act} : activation overvoltage η_H : hydrogen overvoltage η_r : resistance overvoltage R_{H_2} : overall H_2 recovery (%) W_{H_2} : energy content of the hydrogen (J) Y_{H_2} : hydrogen yield n_{CE} : H_2 production from current (mol) n_{th} : theoretical maximal production of H_2 (mol) ΔH : enthalpy (kJ/mol) ΔG : nucleation energy (J) A : atomic weight of metal (g) C : concentration D : diffusion coefficient d : thickness of the diffusion layer E : voltage (volt) E_{KA} : potential when $J = \frac{1}{2} J_{max}$ E_{PS} : the applied voltage (Volt) e_0 : elementary charge of the electron F : Faraday constant (96,485 coulomb per $\text{mol}^{-1} \text{e}^{-1}$) I_{90} : current (A) for 90% of the charge accumulation I_{appl} : applied current (Amp) I_{ef} : effective current (Amp) J : current density (Amp m^{-2}) J_{max} : maximum current density (A m^{-2}) K_{abs} : the kinetic rate constant of reaction	N^* : number of atoms per nucleus growth n : ion valence, η : overvoltage N : transport number η_c : concentration overvoltage η_E : energy recovery based on external electric energy input η_{E+S} : energy recovery based on external electric energy input and substrate input n_{H_2} : number of moles of the hydrogen (mol) η_S : energy recovery based on substrate input n_S : number of moles of the substrate utilized (mol) p : pressure (atm) Q : electric charge (coulomb) R : ideal gas constant) r_{cat} : cathodic hydrogen recovery (%) R_{ex} : ohmic external resistance (ohm) t : duration time (s) T : temperature (303.15 K) V_S : solution volume (L) W_{in} : energy input to the system (J) W_R : energy loss on the external resistor (J) W_S : energy added by substrate (J) z : metal valence α : percentage removal or efficiency (%) $\phi(N)$: variation in surface tension
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Volume 2: Non-Biological Approaches

Anjum, N.; Gill, S.S.; Tuteja, N. (Eds.)

2017, XIII, 374 p. 65 illus., 50 illus. in color., Hardcover

ISBN: 978-3-319-55422-8