

The Role of Electrochemistry and Electrochemical Technology in Environmental Protection, a review.

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Abstract

Electrochemical technology has a very broad range of environmental protection applications and generally aims to improve the environment in a number of ways. Environmental electrochemistry is a novel field of study that has appeared recently. Environmental electrochemistry is the use of electrochemical methods to remove poisons from industrial wastewater before it is discharged into the environment. The main goal of this article is to provide a full review of the choices of electrochemistry and electrochemical technology to clean the environment. We cover industrial applications for the electrochemical removal of heavy metals from diluted solutions. A careful survey of the various electrode types and cell designs like rotating cylinder electrode cells, Swiss-roll cells, fixed packed bed cells, fluidized bed cells, and spiral wounded steel electrodes is presented. All of these cells are used to extract toxic heavy metals from industrial solutions and waste liquids. These cells' activity is governed by a number of operating factors. These operational parameters that control reactor performance and efficiency are reviewed. We cover the advantages and disadvantages of various techniques for electrochemical recovering metals and cleaning up pollution is reviewed. The use of bench-scale cells from Central Metallurgical R & D Institute (CMRDI) researchers in this research proves the following: Copper refiners' solutions were reduced using packed column electrode cells, and Swiss-roll cells. Toxic chromium was electrochemically removed from electroplating and tanning solutions using rotating cylinder electrode cells. In a three-dimensional cell, the electro-removal of cadmium employing a spiral-wound steel electrode from the solution was evaluated.

Keywords: CMRDI, Environmental Protection, Electrowinning, current efficiency, reactor design.

1. Introduction

Environmental pollution and protection applications for electrochemical technology are highly diverse, and the technology's overall goal is to enhance the environment in several ways. Recent years have seen the emergence of the novel field of study known as environmental electrochemistry. Using electrochemical techniques to eliminate contaminants from industrial effluent before it is discharged into the environment is known as environmental electrochemistry.

Individual metals and metal complexes, also known as "heavy metals," are toxic to humans when inhaled as small particles or consumed through food and

The drink can have negative health effects. "Major pollutants" refers to 126 contaminants, including heavy metals and certain organic chemicals.

The primary goal of this article is to provide a thorough overview of the potential applications of electrochemistry and electrochemical technology in environmental cleaning. We outline practical uses for electrochemical cells that remove heavy metals from diluted liquids.

1.1. Toxicity of Dumped Metals on Human Health

The effluents and electroplating wastes have had strong harmful effects on the organisms. Heart problems include allergy illnesses of the respiratory system, dermatomes, and eye infections will develop from a high amount of exposure to it in people (mostly Chromium, Cadmium, Lead, Copper, Platinum, Palladium, Mercury, Arsenic and Zinc). Cadmium is an extremely harmful carcinogenic with obvious dangers associated with its use. Abnormal skin absorption of heavy metal substances decreases blood hemoglobin levels and liver functions. Heavy metals are used in many different industrial applications. The effects of heavy metals on people are important. Aphthous ulcers, eczema, and severe allergic reactions are all caused on by long-term exposure to heavy metals (Silver, Chromium, lead, and Copper). Due to the gastrointestinal/coetaneous absorption of Ag brought on by its contact with sweat, saliva, or skin, allergic reactions might be brought on. The most serious side effects of long-term Ag exposure include chronic abnormal skin and eyes. Also, breathing in large amounts of soluble metal ions components might cause significant respiratory tract irritation in the upper (nose and neck) and lower (chest) respiratory systems.

1.2. Environmental Effects of Industrial Pollutants & Environmental Regulation

Solid or liquid trash dumped on the ground or in unsuitable landfills is susceptible to weathering and leaching by rain. Some of the harmful substances in these wastes make their way into adjacent surface waters, aquifers, or ground waters, contaminating the water as well as the aquatic biota by infecting their tissues and posing health risks to the local population. Marine life is negatively impacted by marine pollution caused by releasing hazardous compounds from industrial waste products. Through the food chain, these chemicals that bio-accumulate in the fatty tissues of marine species are passed on to humans. The enrichment of these contaminants causes a high level of heavy metal contamination in many soils, lakes, and rivers. Industries need new technologies and solutions that improve treatment efficiency and are protective of the environment and public health as industrial discharge increases and regulations governing such discharge tighten. Toxic heavy metals can be extracted from some industrial effluents using electrolysis. Environmental deterioration brought on by industrialization is significant.

Table 1. shows the wide range of pollutants associated with some selected industries [1]. Heavy metals are

present in many effluents of metal electrorefining, electroplating, and metal finishing plants as well as in mining and metallurgical industries.

Table1. Effects on the Environment of Several Industries

Private Sector	Air	Water	Soil/Land
substances, both organic and inorganic, except petroleum products.	SO ₂ , NOX, CO, CFCs, VOCs, and other organic chemical emissions, as well as odors	Using cooling water, water PCBs, organic matter, heavy metals	disposal issues with chemical process wastes mud caused by water pollution
Nonferrous metals	SO ₂ , NOX, CO, and hydrogen sulphide emissions, HCl, HF, Al,, Cr, Cd, Cu, zinc, Hg, Ni, Pb, Mg, F, silica, Mn, hydrocarbons	Scrub metal-of-water effluents of gas-scrubbers, fluorinated, and hydrocarbon-rich	Sludge from effluent treatment, electrolysis cell coatings, and refinery cells
refinery byproducts, petroleum	SO ₂ , NOX, hydrogen sulphide, HCs, benzene, CO, and organic compounds	cold water HCs, oil, Cr.	Toxic trash, effluents sludge's, discarded
tanning and leather	emissions that include Cr compounds, CO ₂ , hydrogen sulphide, and leather dust	wastewater from many harmful solutions Cr	Sludges of Cr

The environment and general public health are significantly impacted by these effluents. For treating these diluted metal-containing fluids, electrolytic metal recovery has achieved particular industrial recognition.

The main potential sources for dilute metal waste solutions originate from metal plating, metal electrorefining and electrowinning industries. Aircraft, printed circuit board manufactures, metal finishing, mining/metallurgy and other chemical industries produce different kinds and concentrations of cation waste solutions.

Most of these industries discharge what is commonly referred to as "spent chemicals" into the sanitary systems or directly into the running water canals. Each of these spent chemicals has its own characteristics, nomenclature and harmful limits to the environment.

Individual metals and metal complexes, also known as "heavy metals," that are toxic to humans when inhaled as small particles or consumed through food and drink can have negative health effects. A list of 126 distinct pollutants, called major pollutants, contains heavy metals and certain organic compounds. A subset of "toxic pollutants," as that term is used in the Clean Water Act, are the priority pollutants [2]. Due to their frequent occurrence in wastewater, these 126 contaminants were given a high priority for inclusion in the establishment of water quality standards and effluent restriction guidelines. Numerous heavy metals are listed as environmental contaminants. Below is a list of some important metals to watch out for and their main sources:

- Antimony: - Foil, batteries, ceramics, safety matches, and textiles are made with antimony. Deaths are not frequent. Stibine is released when antimony-containing metals are treated with acid. The tissues and mucous membranes are irritated by antimony. Hemolysis, or the breakdown of red blood cells, and central nervous system irritation are both brought on by stibine.

Arsenic: from fossil fuel combustion and industrial discharges. In Asia, South and North America, and Europe, arsenic in drinkable water has led to serious health issues.

Cadmium: Alloys, plated surfaces, electroplating waste, and industrial discharges all corrode to produce cadmium. Chromium: hexavalent chromium Cr^{6+} ions are toxic and carcinogenic. Chromium is used in the production of steel, electroplating, leather tanning, and as an anti-rust inhibitor for radiators. damages and disturbs cells. Chromium effluents contain some metallic impurities such as Nickel, iron, Zinc, Copper, and trivalent chromium ions tanning baths contain mainly Cr^{3+} .

Mercury: from natural erosion and industrial discharges; the manufacturing of thermometers, felt, paints, explosives, lamps, electrical equipment, and

batteries use mercury. When treating seeds, diethyl and dimethyl mercury compounds are applied.

Copper: copper ions, as a pollutant, do not accumulate in the human body, but with massive doses, can cause death. As example, the copper limit concentrations are, nearly, the same as that of the cyanide ions.

Lead: Pb was released through batteries, leaded gasoline, paints, and storage batteries.

Zinc: from tires, galvanized metal and exterior paints and stains.

Manganese: -is employed in the production of dry cell batteries and steel.

It has been established that high concentrations of mercury, copper, and cadmium pose major risks to both human health and the environment. Environmental laws in place in the last years are now phasing out some of the sources mentioned above, lead in gasoline and heavy metals in some paints [2]. All plants must comply with the following limit values before the discharge of industrial wastewater into the sewer system [3]. Table 2. shows the maximum tolerable concentration for humans and the environment. In many industrial waste streams, approximately 60% of the metal dumped and its value are not recovered. Metals are difficult to recover from products or specific waste streams when utilized in tiny quantities for specialized uses that don't require bulk [4].

Table 2. Wastewater Effluent Limit Values before Discharge [3].

Parameter	Maximum value/ ppm
Arsenic	0.1
Cadmium	0.1
Chromium hexavalent	0.1
Chromium total	0.5
Copper	0.2
Cyanide free	0.2
Mercury	0.01
Nickel	0.5
Lead	0.2
Zinc	2

1.3. Heavy Metal Industrial Effluents and Wastewater Treatment Methods

According to environmental protection laws, metal-contaminated waste solutions must be treated to extract or decrease their metal contents to the permissible limits [5-6]. Industrial wastewater generally contains contaminants like heavy metals at levels considered hazardous to the environment and could pose a risk to public health.

These contaminated waste solutions have a big impact on the environment. They have to be treated to minimize their toxicity and to recover, if possible, some of these valuable metals, for their own values and to control environmental pollution

The metal removal processes include the following traditional treatment techniques: such as precipitation, adsorption and biosorption, evaporation, reverse osmosis, ion exchange, cementation, membrane separations, solvent extraction, electrodialysis and electrocoagulation. The different physical and chemical methods applied for the treatment of metal-containing waste effluents are summarized and compared in the following Table 3. Physical and chemical methods of treating metal-containing waste solutions, generally require various processing steps. In addition, these treatments, generally, achieve low reaction efficiencies, non-saleable products, and also contributes to environmental problems.

Table 3. Treatment of Effluents Containing Dissolved Metals.

Treatment	PRODUCT
Precipitation of metal salts	Sludge
Ion exchange	Concentrated solutions
Solvent extraction	Concentrated solutions
Evaporation	Concentrated solutions
Electrodialysis, Membrane processes e.g. RO	Concentrated solutions
Cementation	Mixed metal solid
Electrorecovery and Electrodeposition (ED)	Metal, and oxides

The main potential sources for dilute metal waste solutions originate from metal plating, metal electrorefining, and electrowinning industries. Printed circuit board manufactures, metal finishing,

mining/metallurgy and other chemical industries produce different kinds and concentrations of cation waste solutions, Fig. 1. Most of these industries discharge what is commonly referred to as “spent chemicals” into the sanitary systems or directly to the running water canals.

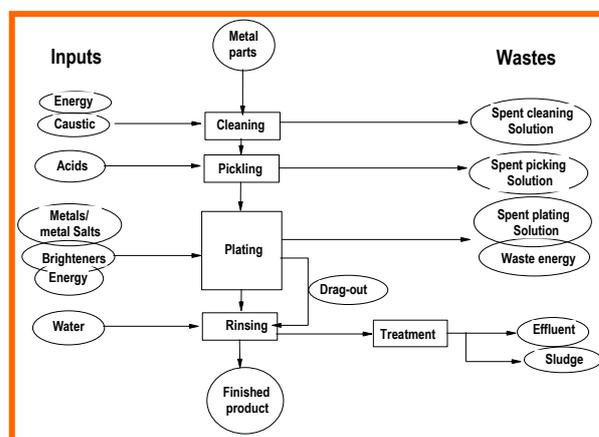


Fig. 1 Inputs and Wastes of the Electroplating Process

The kind and volume of the waste stream, as well as disposal regulations, will determine the equipment type and treatment chemicals that are chosen. The entire cost of treatment includes operational costs such as power, labour, treatment chemicals, sludge disposal, and maintenance. If the extraction and recovery of metals from waste solutions is feasible and economical, this will encourage the industry to treat their waste solutions.

According to environmental protection laws, metal-contaminated waste solutions have to be treated to extract or decrease their metal contents to permissible limits. The conventional techniques for the treatment of metal-contaminated waste solutions can be classified under three main roots, the physical, the chemical, and the electrolytic process. The metal removal and recovery processes include the following techniques: like drag out, precipitation, adsorption and biosorption, evaporation, reverse osmosis (RO), ion exchange, cementation, membrane separations, solvent extraction, cementation, electrodialysis and electrocoagulation (EC). physical and chemical methods of treating waste solutions require various processing steps. These treatments of heavy metal ions achieve low reaction efficiencies, non-saleable products, and contribute to environmental problems.

The different physical and chemical methods applied for the treatment of metal-containing waste effluents are summarized and compared in the following Table 3. On the other hand, the electrochemical methods consist of only one, or limited steps with the direct recovery of saleable metals without adding additional chemicals.

These processes had the ability to remove metal selectively from a mixture. Also, metals may be recovered in their most valuable metallic form. Electrodeposition is a promising process for recovering heavy metals without damaging the environment (environmentally friendly technique). Electrolysis refers to the chemical changes occurring at the expense of an applied electrical current in an electrical cell. Recovery of valuable and toxic metal ions (including Silver, Gold, Cadmium, Cobalt, Chromium, copper, nickel, lead, Zinc, and platinum) via electrowinning (EW) is in principle a simple process that is based upon the reduction of the toxic metal ions at the cathode and gas evolution at the anode. The electrowinning cell consists of an anode, a cathode, an electrolyte and a power supply. The metalbearing waste solutions serve as an electrolyte in the electrochemical cell. Applying a voltage across a pair of electrodes confined in the solutions can be used to generate a cathodic reduction reaction. The concentration of toxic metal ions (copper (II), hexavalent chromium), in industrial dilute solutions, are not suitable for traditional (conventional) two-dimensional electrolysis cells. New generation of three-dimensional (3-D) bed electrodes and extended (2-D) two-dimensional electrode cells with a larger specific surface area than the conventional planar electrode cells are essential for such electrochemical recovery and electroextraction treatments. The high cathodic surface area of these cells enables them to act, in spite of the low current density, at a total high current for the new generation electrochemical cells.

2. Applications of Electrochemical Technology in Environmental Remediation

Numerous research projects have recently focused on using electrochemical technology for environmental cleanup [7-13]. Toxic metals utilized in the extensively used electrodeposition (ED), electrowinning (EW), and electrorecovery (ER) processes are cathodically deposited during electrolytic procedures [14-30]. Also, hazardous organic molecules are electro-oxidized and degraded either directly on the anode surface or through oxidants produced on the anode or the cathode surface. Due to the effective production of hydrogen peroxide from the reduction of oxygen using electrochemical electrodes, the electro-oxidation, and degradation of dangerous organic materials are of major importance [8] or more recently using cross-flow electrodes even with the application of high pressures leading to more efficient processes. Electrocoagulation (EC) is an alternative to conventional coagulation, in which the coagulant is provided by the dissolution of sacrificial electrodes [31-

32]. Electrocoagulation technologies can be used to break up emulsions in industrial wastes, remove colloid contaminants from those wastes, and cleanse surface water. They are also begun by the electrolytic discharge of coagulants from a sacrificial anode [9]. In addition to electro dialysis [11] and capacitive deionization [13], which allow for the concentration of ions in liquids, electrochemically aided separation techniques also allow for the transport of species in solid-liquid combinations like soil or sludge. The unit of electro dialysis containing many anion and cation exchanger membrane pairs is common and the concentration of supporting electrolyte must be low [33-34]. Electrodeposition (ED), electrocoagulation (EC), and electroflotation (EF) are electrochemical processes that are frequently employed to remove hazardous metals. Particularly for diluted solutions, electrochemical treatment is favored.

2.1. Environmental Electrochemistry and Electrochemical Techniques

Environmental electrochemistry uses electrochemical techniques to remove pollutants from industrial effluent before it is released into the environment. Electrolytic recovery is used in the wastes from plating and metal finishing. Also, used in the electronics and printed circuit board for the removal and/or recovery of metals in solution [30, 35-37]. By utilizing insoluble anodes during electrowinning, various metals that are found in industrial wastewaters can be electro recovered [38 -49]. The feeding electrochemical cell and electrolyte are the metal-containing waste solutions [14-30]. Metals recovered through electrolysis are equally pure (virgin) plating materials.

2.2. Metal Removal and Recovery via Electrochemistry (EW)

Electrodeposition (ED), electrocoagulation (EC), and electroflotation (EF) are electrochemical processes that are frequently employed to remove hazardous metals. Particularly for diluted solutions, electrochemical treatment is favored. Electrodeposition (ED) is a safe and reliable technique typically used to recover metals from wastewater. To maximize the ED of metals from low-concentration solutions, a condition for electrowinning (EW) that is required is currently lower than the limiting current. Diluted metal solutions, especially those containing heavy metals and precious metals, are treated using electrowinning.

For the appropriate reaction to occur the applied voltage must be higher than the potential of the reversible

electrode Erev. The desired reaction also needs a voltage greater than the reversible electrode potential. It must take into consideration additional cell voltage drop caused by the solution's resistance, which depends on the conductivity of the solution. The difference between the applied voltage and the potential of the reversible electrode is known as the voltage over potential.

In an electrochemical cell, the amount of charge passed, q , in a time interval, t , is given by

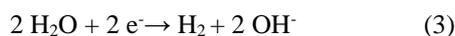
$$q = \int Idt \quad (1)$$

The amount of metal deposited (in mols) is calculated from Faraday's law of electrolysis as [50]:

$$m = q / nF \quad (2)$$

Where F is the Faraday constant and is equal to 96485 C/mol.

The main reaction is the metal electrodeposition at the cathode where metal is eliminated. Another side reaction cathode is the hydrogen gas evolution, which signifies a reduction in Faradic, or current efficiency, CE.



The current efficiency (reactor key parameter) is the yield of a process based on the charge passed and can be defined as:

$$CE = \frac{\text{charge consumed in forming product}}{\text{total charge consumed}} \quad (4)$$

Experimentally the current efficiency (CE) is obtained from the measure of the amount of product formed, reactant consumed, m_{act} , and the theoretical amount, m , i.e.,

$$CE = m_{act} / m \quad (5)$$

From Faraday's Law this is:

$$CE = m_{act} nF / q \quad (6)$$

The total current at an electrode is the sum of the currents (reactor cell parameter), I_j , of the individual reactions, and the CE at any instant can thus be expressed in terms of current as:

$$I = \sum I_j \quad (7)$$

$$CE = I_j / I \quad (8)$$

The cell design affects energy consumption values. The energy consumption, EC (reactor key parameter), is calculated from the following expression:

$$EC = nF E_{cell} / 3600 M (CE) kWh/kg \quad (9)$$

Where E_{cell} is the cell voltage and M is the relative molar mass.

The energy consumption (EC) can be minimized by making the cell voltage as low as possible. The current efficiency (CE) is efficient at moderate metal ion concentrations but not very satisfactory at low concentrations due to mass transfer limitation and the competing hydrogen evolution reactions.

Increase the surface area of the cathode as much as possible to avoid the mass transfer limitation with diluted liquids. Moreover, It is necessary to vibrate the electrodes or circulate electrolytes to decrease the thickness of the cathodic boundary layer in order to eliminate the mass transfer limitation with diluted solutions [51]. As known from Fick's law [50], representing the relation between the flux (rate of diffusion of a species to a unit area of the electrode surface) and the bulk concentration of the ions in solution, the flux is proportional to the concentration gradient.

$$\text{Flux} = -D \left(\frac{dc}{dx} \right)_{x=0} = -D \frac{C_b - C_e}{\delta_N} \quad (10)$$

Where D = Diffusion coefficient of the species, δ = Thickness of the hypothetical diffusion layer, C_b =Bulk concentration, C_e =Concentration at the electrode-electrolyte interface. The steady-state concentration is given by

$$i = -nFD \frac{C_b - C_e}{\delta} \quad (11)$$

Ion concentrations drop with time during electrolysis. As the C_e depletes, C_e becomes zero and the limiting current density (i_L) reaches its maximum, resulting in poor quality and a side reaction that includes hydrogen evolution [52-53].

$$i_L = -nFD \frac{C_b}{\delta} \quad (12)$$

With diluted solutions, metal ion depletion occurs quickly and limiting currents quickly reach the area where hydrogen evolved, poor deposits occur, and energy consumption increases [51]. If the potential of mixed metal ions (Cu^{2+}) is sufficiently negative, a second reaction (Hydrogen gas evolution) could start and occur simultaneously. The reaction that needs the least positive potential occurs at the anode if the same principle is employed at the anodic side, unless the potential of the anode is sufficiently positive to permit for a second reaction (evolution of oxygen gas). Various metal ions will be present in the treatment of aqueous electrolyte in

low quantities [54-55]. By carefully controlling the electrode voltage and solution media, it's also possible to perform electrochemical separation of mixed metals.

The success of selective electroextraction is ensured by the difference in standard electrode potential for electrical scraps and printed circuit boards containing copper constituents [30, 37, 56-61]. A selective electroextraction process of mixed metals can be performed by stabilizing the cathode potential at the metal potential (referred to standard reference electrode) [33, 62]. The transport of ions in dilute solutions (1g/l) is controlled by mass transfer. When it is electrolyzed, the concentration of ions will transfer from the electrolyte's bulk to the electrode's surface, where it will be zero (metal ions will deposit in metallic structures) at the limiting current density, forming a diffusion layer (or boundary layer) with a thickness of less than 0.5 mm (in unstirred solution). Fig. 2 depicts the boundary layer that occurred between the electrode surface and the bulk of the electrolyte. Depletion of ions starts in the diffusion layer. The metal ions are forced to flow by convection and migration mass transfer in addition to the concentration gradient. Diffusion is the most successful way to move dilute ions up through the boundary layer. The diffusion layer (EDL) thickness (δ) must be suitable for dilute metal ions to flow through it to enable metal ions to be removed and deposited on the electrode. If the thickness is expanded and the current density is raised above the point in which the ion concentration at the electrode surface is zero, the current efficiency of the metal deposition process will decrease because of the evolution of hydrogen (the consequence of side reaction). [39-40, 42-43, 46, 49, 52-53]. The diffusion rate is inversely proportional to the ion concentration and the rate of concentration drops. The (δ) value rapidly increases as the ionic concentration drops. After that, there is a gradual decrease in the forces moving the ions toward the electrode. With a faster rate of deposition, the maximum current density (Limiting current density) quickly lowered and achieved [63]. To maximize the ED of metals from low-concentration solutions, a condition for electrowinning that is required is a current that is lower than the limiting current

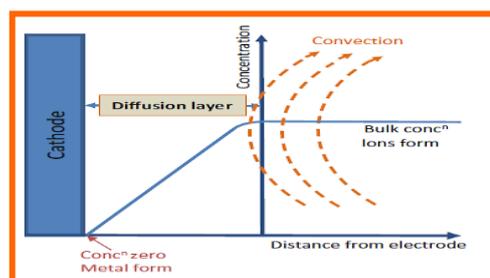


Fig. 2 A layer of Diffusion is produced between the Solution and the Cathode Surface

2.3. Classification of Electrochemical Reactors

Conventional two-dimensional electrowinning techniques are efficient at moderate cation concentrations. Low-concentration (dilute) solutions require special treatment, such as cell design, electrode type, and information relevant to the process' activity, characteristics, and status. Numerous classifications have been suggested to classify the wide range of identified cell designs [52]. Probably the most useful of these is based upon the electrode geometry and electrode motion, Fig. 3.

A given reactor will have a certain electrode area per unit, and contained electrolyte volume (active specific area), and thus the production capacity can be expressed on a volumetric basis. This in fact is the space time yield (STY) in units of mol m⁻³ s⁻¹. Space-time yield is defined as volumetric quantity of the metal produced per unit time per unit volume of the process reactor. it is an important key parameter. The design optimization of an electrolyzer aims for maximum productivity with minimum power consumption use at the lowest cost. The space-time yield, therefore, depends on the current density and the specific cathode area. In general, the roll structure of such a simple suitable design produces higher space-time yield, simple construction, large active electrode area, close inter-electrode distance, low power consumption, low heat evaluation, large mass transfer rates, cheap pumping, and uniform current density distribution [51]. The current density, current efficiency, space-time yield, current potential distribution, and cell voltage are the key parameters for reactor performance in the electroremoval of harmful species.

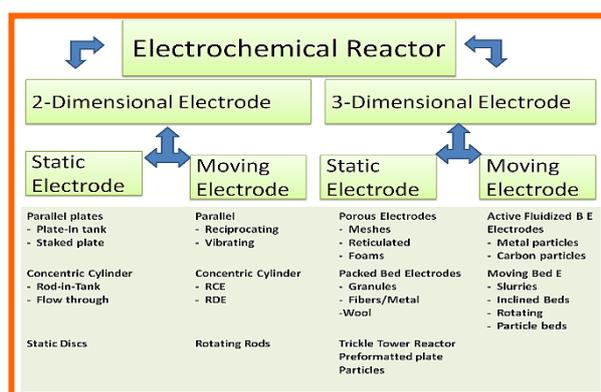


Fig. 3. Classification of Electrochemical Reactors according to the Motion and Geometry of the electrodes

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. These designs include: fluidized beds, circulating or moving beds, slurries, rotating and tumbling beds, vibrated beds and pulsed beds. Beside these bed electrodes, inclined fluidized bed electrode cells, vortex bed cell and spouted bed cell electrodes were described [51]. According to the size of the particles used the rate of electrolyte flow used, from down to upward, the cell can be ascribed as fixed or fluidized cell. Depending on the electrode material, some reactors were classified as extended two- or three-dimensional geometries.

In conventional cells, new expanded two-dimensional electrodes or particle beds are used instead of the conventional planer plate cathodes. Comparatively, these designs have a greater surface area per unit volume than the (conventional) traditional two-dimensional cells. In order to increase mass transport within the cell, a number of electrolytic cell designs have been proposed forth [64]. In these cells, agitation is coupled with an electrode surface area that is considerably higher per unit electrode volume [65-68]. Rotating electrodes, mechanical solution stirring, air agitation, turbulence promoters, slurry, or fluidized bed agitation are all used for agitation techniques [68-75].

2.3.1. Extended Two-Dimensional Electrodes: Swiss-Roll cells (SR)

The Swiss-roll cell (SR) was suggested and designed by Robertson. Robertson designed the "Swiss roll" cell, an extended surface electrolysis cell with a helix sandwich electrode structure [40, 46, 76-77]. A flexible

sandwich of electrodes and separators is rolled around a central axis to make the Swiss roll cells, which are then housed in a container. The components of the sandwich may be selected from the wide range of materials available today. These include electrode sheets, expanded metal, or nets that can be stashed together, see Fig. 4 a, b.

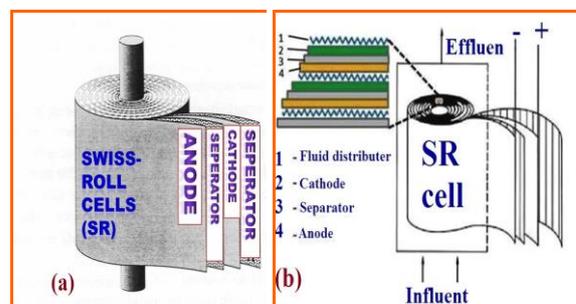


Fig.4 The 'Swiss roll' (SR) Reactor (a) Configurations cell and (b) system, respectively

Elsayed et al. [40] and Elsayed [46] reported that copper could be removed to 0.1 ppm with current efficiency of 78 % using Swiss roll cell.

2.3.2. Three-Dimensional Electrode Cells

The term three-dimensional electrode is used to describe electrodes in which the electroactivity is distributed in three dimensions by using suitable porous structures. Three-dimensional electrodes are employed in cell geometries where a HSA per unit volume is essential. This cell design gives acceptable space time yields at low ion concentrations and at low current densities. These electrodes were available as fixed bed, porous bed, fluidized bed, slurry and circulating beds, see Fig. 5.a,b. Three-dimensional electrode cells have been investigated [51, 65, 69, 78]. Depending on whether they are static beds or moving beds, they can be divided into two general categories [76, 79]. The electrode material in fixed (static) beds can be either porous, where it has the shape of a matrix material, or fixed packed column electrode (PCE), where it is made from loosely contacting materials. The name "moving beds" refers to a number of designs in which the particulate electrode is moved mechanically or hydraulically as a result of electrolyte flow [51]. The cell can be classified as a fixed static or fluidized bed electrode cell (FBE) depending on the size of the particles employed and the rate of electrolyte flow used, from downward to upward.

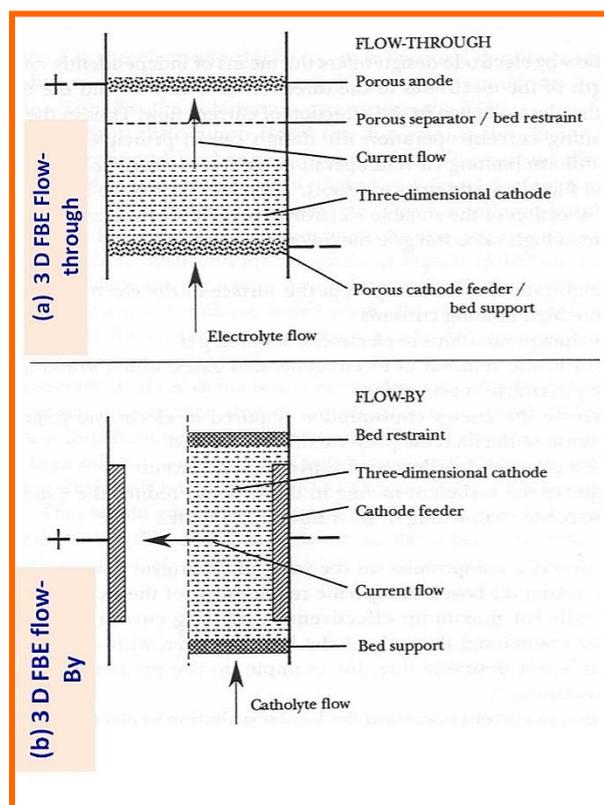


Fig.5 Three-Dimensional Electrode Configurations involv: (a) Flow-through Cell and (b) Flow-by Cell.

2.3.2.1. Fixed Bed Electrode cell (packed column electrode cell (PCE))

As shown in Fig. 5 a, b, fixed bed electrode cells are also known as packed column electrode cell (PCE) [41, 46] are composed of a bed of conducting particles held up by sinter. The current is introduced to the bed by a conducting wire, plate or mesh, named the current feeder, that is housed into the particles of the bed. The anode is usually a plate, a grid, or cylindrical gauze electrode located just above the cathode bed or inserted into it in the presence of a separator. By selecting particles of a suitable size electrode surface area is greatly increased over that of conventional plate electrode for the same cell geometry. The extremely high specific surface area of these cells make suitable for using in numerous electrochemical processes which can only be successful at low current densities [41, 46]. Elsayed [46] reported that copper could be removed to 0.1 ppm with a current efficiency of 87.2% using a packed column electrode cell (PCE).

2.3.2.2. Fluidized Bed Electrode cell (FBE)

In order to produce a fluidized bed electrode (FBE), the electrolyte must travel through an unrestricted particle bed in which the particles will move around, contact, and usually move [65-67, 69-72, 81], see Fig. 5 a, b.

A fluidized electrode phase has the following potential benefits:

- 1) The electrode's dispersion structure gives it a high surface area value (HSA).
- 2) The interaction between the particles causes the formation of HSA.
- 3) Mass transport is greater than for electrodes on a fixed bed.
- 4) May provide a uniform potential and current distribution at specific conditions.
- 5) The removed metal may be regularly recovered from the reactor.
- 6) The circulation rate should be increased with the use of more coarse and high specific densities particles [82-83].

Three-dimensional electrodes face more distribution problems than two-dimensional electrode cells. FBE disadvantages lead to the use of the so-called spouted bed electrode and AKZO FBE cells [53, 84-86]. The separators may be chosen to increase turbulence as is the case with cotton cloths, or even to decrease the mass transfer rates, in which case porous materials are housed and cover the electrodes as in Fig. 6 (AKZO Fluidized cathode cell [53]). Akzo Zout Chemie developed one of the industrial designs for fluidized-bed electrodes [53].

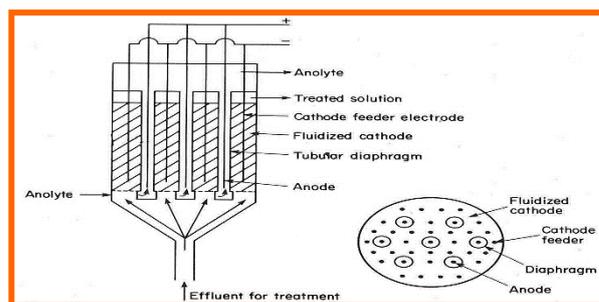


Fig. 6 The AKZO Fluidized Cathode Cell for Effluent Metal Recovery [53]

2.3.3. Chemelec Cell

Using a fluidized bed cell called a Chemelec cell, which uses inert beads as the fluidizing medium, different kinds of metal recovery were performed.

The mobility of the fluidized beads in the Chemelec cell (Fig.7) enables the concentration of metal ions to rise closer to the high surface area (HSA) electrode,

increasing the recovery rate. The performance of some of these cells is limited at the low end and does not reach the discharge limit, which is usually less than 5.0 ppm and often below 1.0 ppm, while some of these cells can be effective in solutions with metal ion concentrations of 50-150 mg/l [87-88].

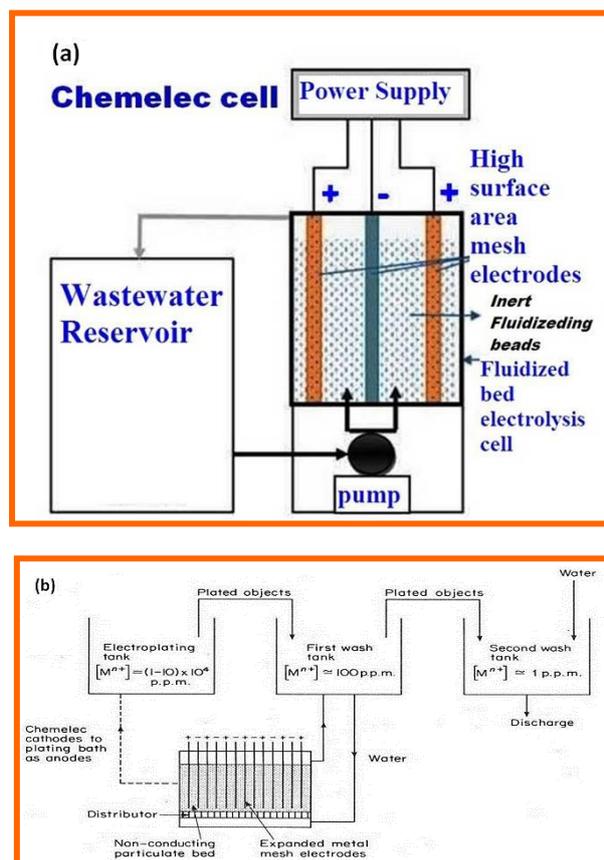


Fig. 7 The Chemelec Cell of the Three-Dimensional Electrode Reactor with Inert Beads that have been "Fluidized" in a small cell system and industrial layout, respectively [53, 76, 87-88].

2.3.4. Rotating Cylinder Electrode Cells (RCE)

By rotating an electrode, mass transport can be enhanced without significantly affecting the residence time of electrolyte in the cell [51]. The rotating cylinder cell RCE is used for the recovery of metals from effluents in which it operates in a continuous mode with axial flow of electrolyte in an annular channel formed between the inner, rotating electrode and the surrounding membrane. The use of a rotating cathode cell greatly improves the efficiency of metal recovery from relatively dilute solutions. The main reasons for this are: 1. The rotation of the cathode gives rise to turbulent flow

conditions in the electrolyte, thereby enhancing the mass transfer of ions in solution to the cathode surface, 2. The mass transfer rate is further enhanced by the deposition of a rough metal deposit, which acts to promote turbulence at the cathode surface boundary layer. Electrochemical methods for the treatment of chromium waste solutions, originating from electroplating industries using RC cathodes were applied at the chemical and electro-processing department at (CMRDI) [44] as shown in Fig. 8.

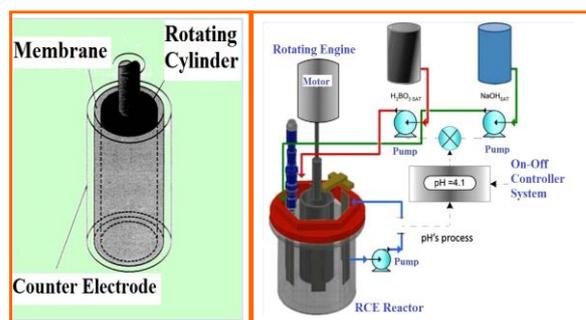


Fig.8 Diagram of the Rotating Cylinder Electrode Reactor (RCE) cell and reactor system, respectively.

Our studies verified that Cr^{6+} can be removed and reduced from industrial effluent to a zero level using a rotating cylinder electrode cell (RCE) [39, 44]. The hexavalent chromium concentration was reduced from 5 g/l to 1.5 g/l Cr^{6+} using a solution of chromic acid that is 10 to 1 H_2SO_4 and applying a current density of 100 mA/cm². 36% current efficiency was obtained. The electrorecovery of silver from rinse water (1.3 g/l) from cyanide media was evaluated using laboratory scale RCE. Using two rotating cylinder electrode reactors: bench scale and pilot plant, the electrorecovery of Ni from synthetic and real electroplating rinse effluents (1.2 g/l) Ni^{2+} was investigated [89]. Because of uniform flow produced at low rotation speed, the controlled mass transport rate, and the uniform current distribution, the RCE is appealing for turbulent studies of metal recovery and electrolytic investigations [90].

2.3.5. Spiral Wound Steel Cell (SWS cell)

High surface area cathode (HSA) creates Spiral Wounded Steel Cells' (SWS cells') cathode. This spiral wounded steel and HSA cathode are housed inside a small, efficient Pyrex glass cell column. A flow-by cell with a spiral wound steel high-surface-area (HSA) cathode (Spiral Wound Steel Cell) has effectively been used to remove cadmium from diluted acidic solution [43], Fig. 9 a, b. The flow rate of 20 ml min⁻¹, along with

a current density of 400 A/cm², at the SWS flow-by cell cathode, proved to be the most effective experimental setups for removing cadmium. The maximum and quickest recovery of about 95% of the cadmium present in the solution is achieved in 45 minutes at 400 A/cm². Under this regime, cadmium was electrolyzed with a current efficiency of 35% and a 4.8 kWh/kg cadmium energy consumption. Cadmium levels have decreased from 500 to less than 5 ppm, almost entirely [43].

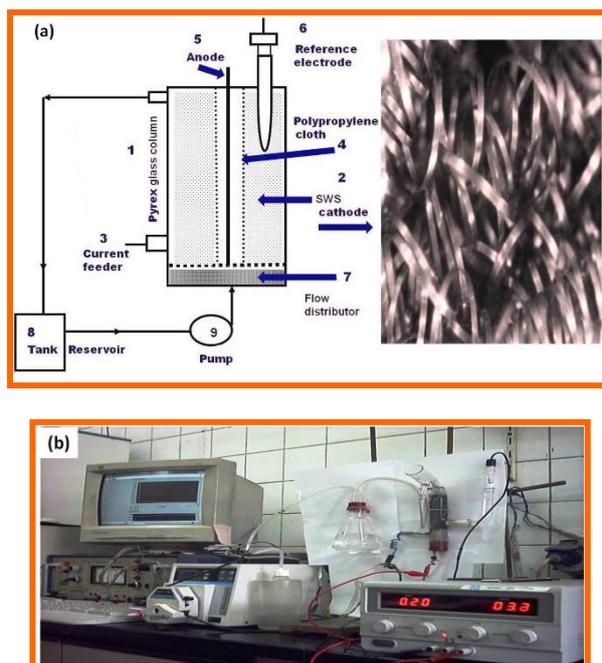


Fig. 9 Photomicrograph of the SWS flowing-by Cell Cathode and a schematic representation of the Reactor System, respectively.

2.4. Guidelines of Electrochemical Reactor Design

The current density, efficiency, space-time yield, current potential distribution, and cell voltage are the key parameters for reactor performance in the electroremoval of harmful species. The following principles of the cell construction are controlled by key factors. These are some fundamental principles of cell design, such as the ones listed below:

- The cell design should be as simple as in order to meet the electrowinning conditions
- Simplicity: operational simplicity and stability
- Mixture and ability to adapt:
- The size and space needed for the reactor's interior.
- Engineering reaction factors
- Uniformity of the potential and current distribution.
- A uniformly high mass transfer over the electrode.

- Achieve a high space-time yield (STY) electro-active area per unit reactor volume.
 - Cheap operating and cell component costs is needed.
 - The existence or absence of separators and their material,
 - The arrangement of electrodes,
 - The distance between the anode and cathode,
 - The cell construction materials
- These elements are vital and essential to reactor effectiveness [52-53].

2.4.1. Potential and Current Density Distribution

Potential and current distribution are the most important key parameters in the electroremoval of harmful species. A uniform potential distribution and a uniform current distribution are important goals of cell design. The following variables affect the distribution of current between electrodes, which itself is strongly related to the distribution of potential, see Fig. 10.

- 1) The electrodes' and reactor's geometry
- 2) Conductivity of the electrolyte
- 3) Conductivity of the electrodes
- 4) Overpotentials produced by charge transfer (electrode material) or mass transport forces at each electrode (hydrodynamics)
- 5) The current distribution is affected by the potential distribution and the local concentration of metal cations
- 6) Distribution of current is influenced by the type of over-potential.
- 7) Potential distribution is affected by the anode and cathode's surface profiles.

The disadvantages of a non-uniform current distribution include:

- 1) Lower space-time yield (STY),
- 2) Irregular electrode degradation
- 3) Increased cell voltage with large overpotentials
- 4) Reduced current efficiency and increased energy consumption (key parameter).

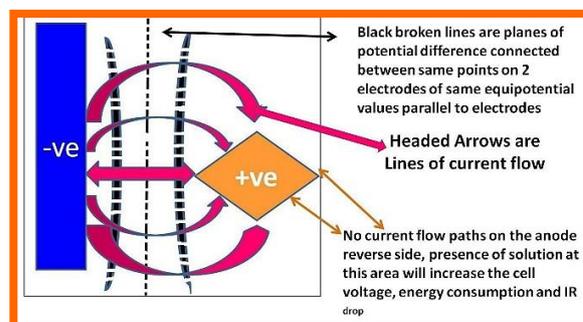


Fig. 10 Electrode Geometry affects Current Distribution and Polarization values.

2.4.2. Mass Transport Regimes (Modes of Operation)

Batch processes are usually used for processes and small-scale operations. In a semi-batch mode of operation, one or more reagents are continuously injected while another exists in a batch. Continuous stirred tank or plug flow reactors and non-ideal flow patterns and circulation mode. Electrochemical reactors can be operated periodically for the distribution of product species in batches or continuously as flow cells with or without a high degree of mixing. The scale of the process will often govern the modes of operation (batch, semi-batch and plug flow process). The amount of metal electrodeposited per square meter of cathode determines the cell's design capacity. The size and design of the system are affected by the volume and concentration of species [53]. Some decisions made during the designing of cells are shown in Table 4.

Table 4. Some decisions in the process of Cell Design.

Factor	choice A more simple in design	choice B (complex) Expensive
Mode of operation, mass transfer regime	Batch recirculation	Continuous stirred tank reactor CSTR
Number of cathodes or anodes	single	multiple
Electrode movement	Static	Moving
Electrode geometry	2-Dimensional	2-Dimensional
Electrode connections	Mono polar	Bipolar
Inter-electrode gap	moderate	capillary
Electrolyte manifolding (types)	External	Internal
Division of cell	Undivided	Divided
Sealing of cell	Open cell	Closed cell

2.4.3. Operating Variables that Affect Reactor Key Parameters.

Applications of electrochemical reactors in pollution remediation contain the electroreduction,

electrorecovery, degradation of organic and electrooxidation of toxic metals. The reactor has to be optimized to fulfill the requirements of the treated dilute solution. It may involve cathodic reduction reaction (e.g. heavy metal ions deposition, nitrates reduction), or anodic reaction (e.g. anodic decomposition of organic pollutants, production of highly oxidative species). In the case of cathodic reduction the main intention is to overcome problems related to the low concentration of treated species [74]. Operating variables have had an effect on reactor design and decision (Physical and chemical parameters) [13, 64, 91-93].

Electrolysis variables optimization is needed to achieve the best possible (key parameters) performance, productivity, effectiveness, and efficiency from the electrochemical reactor. The reactor key parameters are affected by these important electrolysis variables. Physical and chemical variables are included in Tables 5 and 6.

Table 5. Operating Factors in Electrochemical Reactors (Physical Factors) [64, 91].

Physical factors	Factor description
Types of electrolytes	The choice of the electrolyte is determined by requirements for reactant solubility and low electrical resistivity. Aqueous solution, organic solvent, inorganic liquid [94-95].
Types of electrodes	Anodes: consumable, insoluble, solid polymer type; Cathodes: rigid metal, insoluble, porous, conducting polymers [69, 96-100].
Separators	Microporous plastic, ceramic, ion exchange, liquid membranes, polypropylene [13, 65, 91, 101].
Cell construction	Undivided, divided cells, mono- or bi-polar electrodes, tank cell
Modes of operation	Batch or semi-batch mode:- Mass transport regime [13, 75, 93].
Electrode configuration	Two- or Three-Dimensional, dynamic or static, at the separator (zero gap) and away from the separator [13, 66].
Reactor products	Soluble, insoluble liquid, Powder, thin film, metallic deposit
Reaction species	Dispersions, inorganic and organic, solid metals, and redox species
Cell arrangement and electrode movement	Energy consumption decreases when there is a good cell arrangement and solution mass transfer [13, 53].

Table 6. Operating Factors in Electrochemical Reactors

Electrochemical Factor	Factor description
Current density and cell voltage effects (key parameters)	At higher voltages/ cell densities there is evidence of higher removal efficiencies. Energy consumption increases with increasing cell voltage or current density [94].
Inter-electrode distance effect and Anode to cathode space.	For metal electro winning, the ideal electrode distance is necessary. Mass transfer is enhanced and surface diffusion is reduced by the short distance between 2 electrodes [13, 92, 94].
Particle electrode dosage effect high active surface area (HSA).	Three-Dimensional cells had a (HSA) than 2D cells. The 3D bed reactor uses more energy and costs more money [93, 95].
Electrolyte-Impurities percentage-foreign ions	Energy consumption increases and current efficiency of metal removal decreases with increasing impurities (foreign cations) in the EW solutions [94-95].
Electrolyte conductivity	Energy consumption decreases with increasing conductive cations and anions in the EW electrolyte [13, 53].
Electrolyte PH effects	Highly acidic pH conditions enable higher removal efficiency

2.5. Electrodialysis

Electrodialysis is used for a range of processes, such as the desalination of seawater and metal removal from industrial effluent before its disposal. An alternate arrangement of anion exchange membranes (AEM) and cation exchange membranes (CEM) is placed in a cell (Stack), and a potential field is applied between two electrodes placed at either end of the stack to force current through the stack (cell). To allow electricity to pass between the electrodes, ions must be transported between each of the membranes. The membranes are thin plastic sheets that can either be CEM or AEM in nature. Alternating sheet of AEM and CEM is placed between two electrodes. It is possible to force ionic salts to pass from the dilute stream to the concentrated stream by placing the feed to the numerous intermembrane compartments. Metal ion separation can be performed by increasing the electrodialysis membrane technology. Ions must be transported across each membrane in it. Metal ions are driven across an ion-selective membrane by electromotive forces (in reverse osmosis (RO), pressure is the driving force; in ion exchange, the driving force is chemical attraction. The electrolyte circulates past the system's electrodes. Oxygen and hydrogen are evolved. Ions move from the positive terminal to the negative

terminal and vice versa. Metal separation can be achieved by introducing substances that preferentially complicate (face) one group of elements and prevent transit across the CEM, while allowing flow of other hydrated cations (Mask or EDTA) [33-34].

Fig. 11 illustrates the fundamental idea of the separation procedure employing electrodialysis with improved CEM and AEM [34]. Briefly, the separation in a three-compartment electrodialysis cell (Fig. 11b) is accomplished by taking advantage of the increased stability of the complexing agent, such as EDTA, with one of the metal combinations (Nickel (II), Cobalt (II),..). In a three-compartment electrodialysis cell, for instance, the Ni-(EDTA)₂ complex and hydrated Co²⁺ ions are separated by electro-transferring from the feed solution to the electrodialysis anolyte and catholyte chambers, respectively [33], (see Fig. 11a,b). Separation process will be affected by several parameters (e.g., pH, cathode material, type of hydrated metal ions, and concentration). Abdel-Ghafar et al [11] conducted seawater desalination with high salt content of NaCl (42 g/l) utilizing Ion Tech electrodialysis unit at CMRDI workers. they evaluated the partial desalination process in two different tests, batch and continuous operation. It was established that the theoretical and experimental limited current densities were 1.49 A/m² and 1.15 A/m², respectively. Additionally, the precise energy consumption (7.15 kWh/m³) was computed [11].

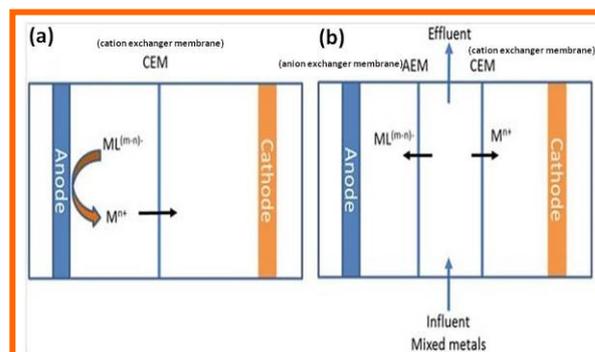


Fig. 11 Electrodialysis Cell with (a) Two Compartments and (b) Three Compartments.

In contrast, it has limited efficiency in desalinating saltwater and high operational costs. Its ability to desalinate saltwater is limited by the high operating costs and its limitations for highly high saline water. Low flow rates are recorded. Adsorbents need regeneration since they regenerate slowly.

2.6. Electrochemical Technology Applications for Organic Pollution Treatment

Numerous electrochemical engineering applications for the removal of environment pollutants have appeared in recent years [13]. Applications of electrochemical reactors in pollution cleaning involve anodic oxidation reactions, anodic decomposition of organic pollutants, production of highly oxidative species and the electrolysis of industrial waste to remove highly dangerous or refractory environmental pollutants.

Electrocoagulation (EC), electro-oxidation (EO), Fenton's electroadsorption, and electrobiological oxidation are examples of electrochemical processes that are useful for organic remediation [69-71,79,102-107].

2.6.1. Electrocoagulation (EC)

The process by which particles aggregate and separate from a colloidal suspension is known as flocculation or coagulation [108]. The wastewater treatment technique called as electrocoagulation (EC) includes both coagulation and electrochemistry principles. It has been suggested to use electrocoagulation to remove certain contaminants from waste, such as metallic ions, dyes [108], industrial effluents which contain both organic pollutants and heavy metals. These electrocoagulation (EC) method can be used as an alternative to chemical precipitation processes to remove dissolved and suspended organics from solutions. Basically, EC includes the electrochemical dissolution of iron Fe or aluminum Al anodes into an electrolyte solution to coagulate with contaminants under the given circumstances. The electrostatic repulsion forces between the colloidal particles in the solution are reduced during coagulation. Moreover, a number of the toxic heavy elements (copper (II), hexavalent chromium ions) which are electro-reduced and removed at the cathode from effluents by use of this technique. Also, it is a low-cost technique that helps decrease the organic content of wastewater [108]. In opposition, it is limited and restricted method. Electrocoagulation produces large particle sludge and has poor efficiency in removing ions and metals from wastewater.

2.6.2. Electroflotation (EF)

Electroflotation (EF) are used to clean up effluents which include heavy metals and organics. Pollutants are transferred to the surface by the solid/liquid separation process known as electroflotation (EF), which uses bubbles of oxygen and hydrogen gas produced during water electrolysis. A number of the toxic heavy elements (copper (II), hexavalent chromium ions Cr^{6+}) are electro-reduced and removed at the cathode from effluents by use of this technique [108].

2.6.3. Electro-Fenton's Oxidation

According to the Fenton's process, hydroxyl radicals are produced when ferrous (II) ions and hydrogen peroxide (H_2O_2) combine. Since this discovery, substances that contain both H_2O_2 and Fe^{2+} are referred to be Fenton's reagents. H_2O_2 is dissociated and consumed throughout the process, while ferrous ions promote the oxidation of organic-enriched electrons [109]. The CMRDI workers compared the photo-fenton oxidation method and the fenton process as advanced treatment techniques for treating tannery effluent [110-111]. The photo-Fenton process is a good technology for decomposing organic pollutants from tannery wastewater because of the cheap cost iron sulphate and high chemical oxygen demand (COD) reduction [110].

2.6.4. ElectroOxidation (EO)

Electrochemical oxidation, also referred to as "anodic oxidation," has been used to treat wastewater from industries related to the textile industry and dyes. In an electrolyte that allows the transfer of ions between two electrodes, electrochemical oxidation occurs. For anodic oxidation, an electrochemical cell has a two-electrode setup with a cathode and anode (mesh or plate). The oxidation mechanism, the products, and the efficiency of the oxidation process are all affected by the types of anode material and electrolyte.

High oxygen evolution, stable, non-sacrificial anodes are necessary for electrolysis. Often, graphite, titanium, or mild steel cathodes are used on the cathodic side of the cell [104, 106, 112-113]. Dye molecule degradation can result in unwanted degradation products for the environment like aromatic amines and chloro organic chemicals. When the effluent's conductivity is low, NaCl electrolyte should be added to a bath during the electrochemical oxidation (EO) of organic waste to increase the conductivity and help in the oxidation process. There are two main mechanisms in electrochemical oxidation (EO) for cleanup organic pollutants [114]:

- 1) The direct anodic oxidation at the electrode-solution interface and
- 2) Indirect anodic oxidation is done by surface-active species generated.

2.6.5. Electroadsorption (EA)

To eliminate dilute hazardous substances from effluents, adsorption is often used. This is performed in an electroadsorption (EA) cell using activated carbon adsorbent particles and an applied electric field. This

technique increases the adsorption property of the adsorbent and helps in increasing oxidation by producing a bipolar force on the adsorbent particles. The adsorbent particles placed in the electric field produce micro-anodes and micro-cathodes at their two terminals. This generates a large number of micro electrolytic cells to form. The effective number of cells formed improves the adsorption characteristics while destroying impurities [101, 115]. The EA technique was effective at removing organic pollutants like dyes [33]. The possible uses of graphite materials, particularly granule activated carbon and graphite particles, as electrode oxidizers and adsorbents in so-called three-dimensional electrode systems [76]. In a three-dimensional electrode system (3D), the electrochemical system is filled with graphite and carbon particles as a packed bed (see Fig. 12) or a fluidized bed to function as an electroadsorption (EA) cell [69]. The design of three-dimensional (3D) electrolysis allowed the classic two-dimensional (2D) electrolysis problems, such as mass transfer and low current restrictions, to be solved. [65]. In the 3D electrochemical system, these particles (bed electrodes) were kept between the two electrodes, the anode and the cathode [116-118]. The system is subjected to an electrical voltage, which forces the particles to become polarized. The polarized particles behave like microelectrodes, with one surface acting as an anode and another surface nearby acting as a cathode. In opposed to 2D electrochemical systems, which theoretically produce intermediates that form insoluble pollutants, 3D electrochemical systems allow for the complete electrowinning of heavy metal as-deposited metal or the degrading of pollutants [119]. On the other hand, due to the poor carbon adsorption capacity, the treatment of effluents with an EA unit alone is not effective in treatment [76]. Electroadsorption units are not suitable for efficient remediation due to their insufficient ability to adhere to carbon and graphite particles (3D bed).

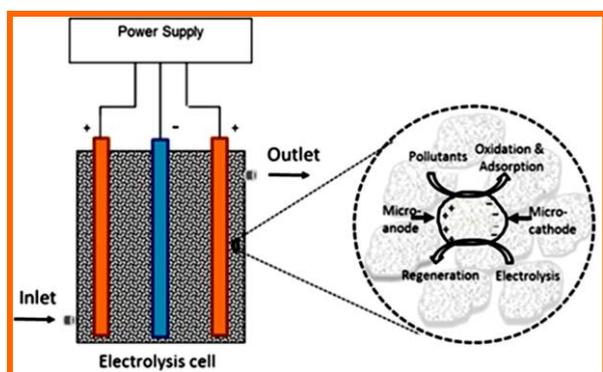


Fig. 12 Electroadsorption cell for Electroadsorption.

3. Roles of the Author and the CMRDI Department in Environmental Protection

The CMRDI department researchers conducted a significant amount of studies using both chemical and electrochemical technologies in the fields of environmental protection and the treatment of toxic metals. Abdel-Aal and his CMRDI coworker [110] developed procedures for material removal via oxidation to purify industrial wastewater. In order to remove organic pollutants from wastewater, Abdel-Aal et al. have investigated advanced oxidation processes (AOPs) based on the generation of highly reactive species, particularly hydroxyl radicals. Fenton and photo-oxidation Fenton's processes were two of them. The photo-fenton process is a good technology for degrading organic pollutants from tannery wastewater due to the cheap cost iron sulphate and high chemical oxygen demand (COD) elimination. Abdel-Aal and his CMRDI colleges [111] use two different methods (Co-precipitation) routes involving NaOH and MgO to remove Chromium leather tannery effluent. The optimum pH range for precipitating chromium either with MgO or NaOH produced total chromium removal rates of 99.1 and 99.7%. Compared to the NaOH method, the MgO route had little sludge and a shorter settling time (3 hours).

Abdel-Ghafar and his CMRDI coworker [11] used an Ion Tech electro dialysis device to successfully treat the seawater and achieve seawater desalination with a high NaCl (42 g/l) salt content. They produced electrochemical treatment for wastewater and environmental protection. Under a batch mode procedure, operation factors including voltage applied, and desalination time were investigated. The limiting current density was 1.15 A/m², and the specific energy usage was 7.15 kWh/m³.

3.1. Author's role in using Electrochemical Technology in Industrial Wastewater Treatment.

The author contributes to the use of electrochemical technology for the protection of the environment and the cleanup of industrial wastewater. At CMRDI, a variety of important facilities are ready for use in working on each of the electrochemical environmental investigations.

3.1.1. Facilities of Chemical and Electrochemical Processing Department (CMRDI)

Department Facilities: The Chemical and Electrochemical Processing Department (CMRDI)

includes a number of significant facilities that are ideal for conducting studies on the electrochemical removal of hazardous metals from the environment. For example, the computerized Volta Lab 21 Potentiostat / Galvanostat model (PGP 201, France) instrument in our department is supported by electrochemical software. Also, rotating disc electrode set up (RDE) with a high-speeds rotator (EG&G Instruments, INC. model 616, USA), a digital Multimeter (Keithly Model 617 programmable electrometer, U.S.A), constant D. C. Power Supply, Variable Resistance, the Battery Tester, a Vacuum Oven, an X-ray diffractometer, a SEM, a TEM, a Surface Area Analyzer, Anticorrosion Circulating Pumps (Model MasterFlex, USA), Water Flow Pumps (March, UK), Spectrophotometer (Perkin Elmer Lambda 1100), FTIR analyzer, an EDX analyzer, and elemental analysis by ICP and XRF. It has a Flame Photometer to detect alkali cations in water. It has a number of tools that are perfect for doing research on pollution protection, like electrochemical and electro dialysis units that can gather plating chemicals from recovery units in a novel way. Moreover, it has equipment like a Fluidized Bed Adsorption Unit for studying the adsorption of heavy metals utilizing various adsorbent materials.

The author's work at the CMRDI was concentrated on electrochemical studies for the treatment of industrial wastewater using (EW) techniques, toxic metals removal from leather effluents, hexavalent chromium removal from plating wastewater, Pb effluents, Cu pickling /rinse water, Cu refiners, and Zinc liquors [39, 40-41, 44, 46, 49, 120].

Elsayed and his CMRDI coworker at the chemical and electro processing department [39-49] performed electrochemical studies on the electrowinning (EW) and removal of harmful metals from IWW, electroextraction, from leather processing, toxic Cr^{6+} from electroplating wastewater, zinc liquors, and copper refiners for the treatment of industrial wastewater.

The author's work in electrochemical environmental protection techniques and his work to treat industrial wastewater using various electrochemical cells (non-traditional).

3.1.2. Electroremoval of Copper from Cu Plant Effluents using PCE and SR Cell

As copper is one of the important waste and pollutant metals, it was essential to examine some of the factors and electrolytic cells which can lead to efficient and economical electrolytic process solutions.

The author with cooperation of his coworkers [40-41, 46, 49] recovered toxic Cu from industrial dilute wastewater

using different non-traditional electrochemical cells. For this, two different advanced cathodes were tested: a high surface area (HSA) Swiss roll cathode (SR) [40] and a Packed Column Electrode Cell (PCE) [41] as mentioned and shown prior at Fig. 4 a and Fig. 5 a.

Our studies have shown that this electrochemical method are capable of reducing the copper metal to levels less than 1 ppm using a Packed column electrode cell and Swiss-roll cell.

The Packed Column Electrode cell (PCE) was made up of a Pyrex glass tube with a diameter of 50 mm as shown in of Fig. 5.a. Where the Cu particle bed was housed, its lower portion was filled with a bed of glass wool and fixed with mesh Polyvinyl chloride PVC. Copper particles in the form of small Cu wire 5 mm length and 0.5 mm diameter (amounting to 1000 cm^2 total bed surface area) served as the bed cathode. The cathode current feeder was made of copper wire. The anode was made of lead-4% antimony alloy rod covered by a plastic PVC diaphragm.

The Swiss-Roll (SR) Electrode Cell was constructed from copper cathode of area 20 cm^2 and 4% lead-antimony anode sheets. Both electrodes are sandwiched with polypropylene cloth and housed in a glass tube container. All were rolled up and placed within the cell container, which is depicted in Fig. 4a, b, inside a pyrex tube. The polypropylene membrane with its configuration prevent any potential contact between the deposited copper and short-circuiting. Experiments were carried out with solutions containing 5g/l copper concentration, in a batch recalculating mode using both PCE and SR cell.

The Packed Column Electrode Cell (PCE) was also constructed from copper particles cathode of area 300 cm^2 and 4% lead-antimony anode sheet. Both electrodes are housed in a Pyrex glass column. With the progress of electrowinning process, the concentration of the copper cations deplete with time. This decrease in concentration brings up lowering of the maximum density of the current. An experiment was carried out depending, mainly, on the cathodic potential measurements. The limiting diffusion current density was determined from the polarization curve under galvanostatic conditions. The potential-time dependence curve is plotted in Fig.13 a, b. The electrolysis was continued until a sharp rise in the cathodic polarization occurred Fig.13 b. All deposition currents were chosen to be 0.8 of the limiting diffusion current, before the process became diffusion controlled [40-41, 46]. According to the resulted parameters a stepwise decreasing current mode was performed and consists of five regime steps, (Table 7 and Table 8). The input current was galvanostatically

decreased with time, keeping its value close to 0.8 of the limited diffusing current, of the new concentration achieved by the continuous depletion of copper during electrolysis Fig.13 a, b. The optimum deposition time and currents registered in Table 7 were adopted using Packed Column Electrode Cell. The deposition run was performed in a five stepwise decreasing current regime, namely, 2 mA/cm² for 87 min, 1 mA/cm² for 64 min, 0.66 mA/cm² for 32 min, 0.26 mA/cm² for 64 min, and finally at 0.20 mA/cm² for 128 minutes. Measuring the cathodic potential using preplanned program monitored the reaction. After the electrolysis run, copper concentration was determined at each step. After performing out five step-wise decreasing current regimes, the overall final current efficiency was 87%, and the Cu²⁺ concentration was reduced to 0.005 g/l.

Table 7. Optimum Conditions for Copper Electrowinning from Solutions that acidified by 100 g/l H₂SO₄ Using Packed Column Electrode Cell (PCE).

Cu, initial g/l	5	2	0.94	0.6	0.3
Cu, Final g/l	2	0.94	0.6	0.3	0.005
Current, mA	600	300	200	80	60
Time of deposition, min	87	64	32	64	128
Current density, mA/ cm ²	2	1	0.66	0.26	0.2
Cell voltage, V	1.91	1.89	1.83	1.82	1.81
Current efficiency, %	87	84	81	80	62.7
Total electricity consumed, C	3134	1152	389	307	460
Energy Consumption, kw.h/kg	1.898	1.898	1.902	1.919	2.4

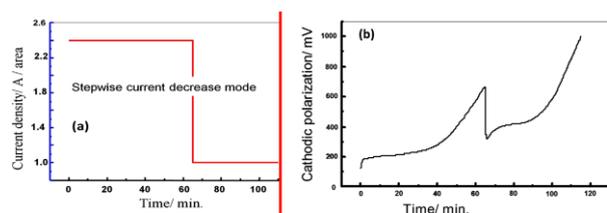


Fig. 13 The Stepwise Regime of Cu Electrorecovery using a PCE and SR Cell, (a) stepwise decreasing current with time, (b) stepwise decreasing electrode polarization with time.

Using a Swiss-Roll Cell (SR) in batch recalculating mode and solutions with a concentration of 5 g/l Cu²⁺, experiments were carried out based on cathodic potential measurements. The results obtained were found to agree closely with those based on the preplanned stepwise decreasing current modes. The containing 100 g/l of H₂SO₄ and 5 g/l of copper was continuously introduced into a Swiss-roll cell (SR) at a flow rate of 3.75 l/h.

The optimum times and current densities deduced from Table 8 were adopted. A deposition run was performed, applying the deduced program. This program consists of five stepwise decreasing currents, namely, 1.36 mA/cm² for 128 min, 1 mA/cm² for 128 min, 0.66 mA/cm² for 64 min, 0.26 mA/cm² for 64 min and 0.13 mA/cm² for 128 min. The current is reduced to the next stage after the first step of the electrolysis process is complete, and so on. The potential-time dependence data and the operating parameters are given in Table 8. Final concentration achieved was 0.005g/l copper, and the total current efficiency was about 70%. The concentration of copper was reduced to 0.005 g/l after performing the five step-wise decreasing current regime.

Table 8. Optimum Conditions for Copper Electrowinning from Solutions that acidified by 100 g/l H₂SO₄ Using Swiss-Roll Electrode Cell (SR).

Cu, initial g/l	5	2.5	1	0.5	0.215
CU, Final g/l	2.5	1	0.5	0.215	0.005
Current, mA	408	300	207	80	39
Time of deposition, min	128	128	64	64	128
Current density, mA/cm ²	1.36	1	0.66	0.26	0.13
Cell voltage, V	1.58	1.7	1.98	1.735	1.72
Current efficiency, %	70	65.36	61.9	84.5	60.6
Total electricity consumed, C	3133	2304	768	307	199
Energy Consumption, kW.h/kg	1.9	2.19	2.69	1.92	2.46

The same methodology is used to examine both the Swiss-roll cell (SR) and the (PCE). For the treatment of wastewater, the PCE cell is superior to the SR cell. Also, these CMRDI Pyrex reactor designs include: PCEs,

moving or circulating beds, slurries, rotational and tumbled beds, vibrated beds and pulsed beds.

3.1.3. Hexavalent Chromium Recovery from Industrial Electroplating Effluent using rotating cylinder electrode cell RCE Cell

Chromium salt is highly toxic, particularly in its hexavalent form [108, 110-111]. Elsayed and his colleagues at CMRDI investigated and evaluated the removal of hexavalent chromium using a rotating cylinder electrode cell RCE [39, 44, 120]. Hexavalent chromium can be removed and reduced from industrial effluent to a zero level, according to investigations by Elsayed et al. The results reveal that Cr^{6+} was reduced from 5 g/l to 1.5 g/l using a chromic acid solution with an H_2SO_4 concentration of 10 to 1 and a current density of 100 mA/cm². In fact, the current efficiency was 29.25%. We studied the relationship between cathodic current density, foreign cation presence, free acid ratios, and cathode rate of rotation with respect to cathodic current efficiency [39, 44, 120], (Fig. 14). The RCE Cell used in chemical and electro processing department consisted of a double-wall glass vessel with a holed Perspex lid that included holes for mounting the electrodes. The cathode was a rotating brass cylinder with area 40 cm² that was placed in the middle of the cell. The anode had been a lead cylinder with a uniform distribution at the containers wall surrounding the cathode. The lead anode area was 120 cm² (see Fig. 8). The RC Cathode was moved by a motor with variable speed. Experimental results of Fig. 14 showed that the CE increased with the increase of the Cr concentration in solutions. The CE of solutions containing 5 g/l Cr^{6+} increases as the current density, reaching a maximum deposition rate of 29.25% at 100 A/m², and solutions containing 2.17 g/l Cr^{6+} also show an increase in current efficiency with rising current density, reaching a maximum deposition rate of 27.51% at 100 A/m². Good metallic deposits of chromium were obtained from all solutions.

3.1.4. Chromium Electroreduction from Leather Fabrication Wastewaters using RCE Cell

Elsayed and his colleagues at CMRDI [39, 44, 120] have been electro reduced toxic hexavalent chromium Cr^{6+} ions to Cr^{3+} using bench scale (RCE) cell model. The working cylinder electrode was a rotating lead electrode of area 40 cm², (brass coated by lead/Cr), which placed at a distance 0.5 cm from the counter electrode. Graphite rods of 5 cm² area 120 cm² were used as the counter electrode. In order to investigate Cr^{6+}

reduction, we performed a set of LSV in an acidic solution containing 1.5 g/l of Cr^{6+} and 27.5 g/l of H_2SO_4 acid (Cr^{6+} to H_2SO_4 molar ratio: 1: 10). Fig. 15 shows two regions where the LSV curves were displayed. The first region was defined as the reduction of Cr^{6+} to Cr^{3+} . The second area was formed due to the evolution of hydrogen gas, which decreases the reduction current efficiency. Also, as RCE rotation increases, the reduction LSV current density increases too.

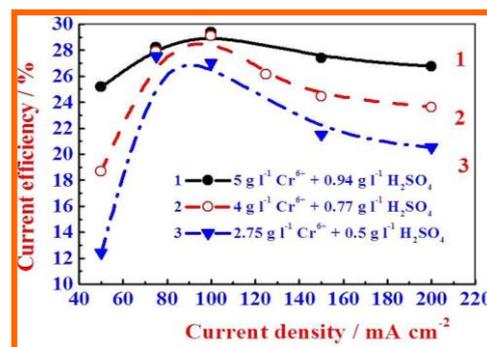


Fig. 14. Influence of Current Density on the Current Efficiencies for Removing Chromium from 5, 4 and 2.75 g/l of Cr^{6+} with (10:1) H_2SO_4 using RCE Cell.

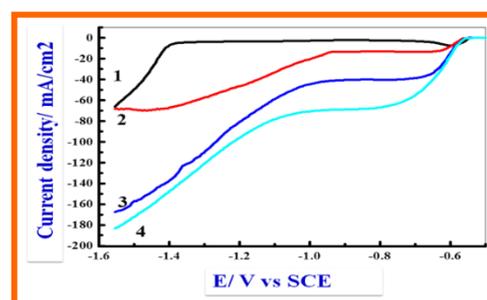


Fig.15 Lead RCE at varied Cathode Speeds (1) 0.0, (2) 150, (3) 600, (4) 2000 rpm at 1.5 g/l Cr^{6+} + 27.5 g/l H_2SO_4 .

The optimal operating parameters for Cr^{6+} reduction are 115 min, 225 mA/cm², and 1.5 g/l of concentration. Ideal current efficiency was 15%. Chromium was decreased from 1.5 g/l to less than 1 ppm. The Cr^{3+} is precipitated into chromium hydroxide.

The current efficiency of Cr^{6+} reduction is strongly correlated with the Cr^{6+} and sulfuric content, Fig. 16. Also, Fig. 17 depicts that, when cathode rotation speeds rose up to 600 rpm, current efficiency of reduction reaction was increased while energy consumption decreased. Fig. 18 demonstrated that the existence of sulfuric acid in the bath promotes the current efficiency of Cr reduction. Then, successful production of Cr^{3+} from acidic tannery and industrial wastewater that contains 1.5 g/l Cr^{6+} . Also, 20% current efficiency is also

achieved after 80 min at a current density of 225 mA/cm² (Cr⁶⁺ to H₂SO₄ molar ratio 1: 60).

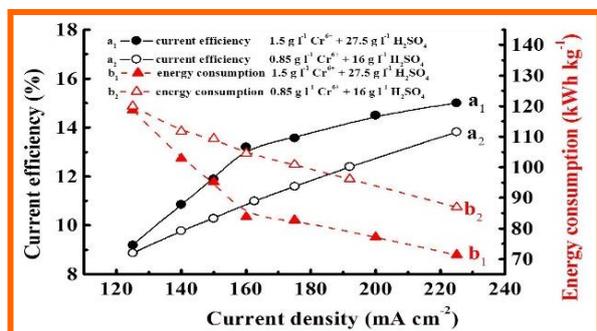


Fig. 16 Influence of Current Density upon Current Efficiencies and Consumption of Energy for electroreduction of Cr⁶⁺ from (a) 1.5 g/l Cr⁶⁺ + 27.5 g/l H₂SO₄, (b) 0.85 g/l Cr⁶⁺ + 16 g/l H₂SO₄ with 600 revolution/minutes.

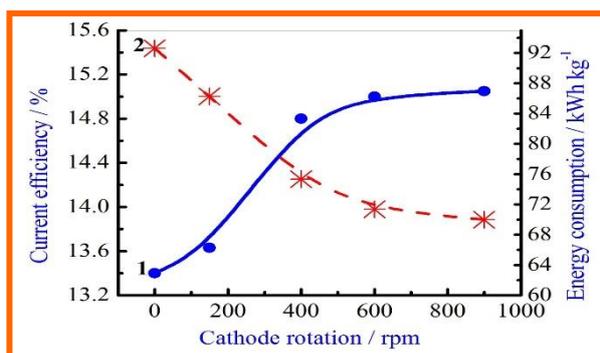


Fig. 17 Effect of cathode Rotation on Current Efficiency and Energy Consumption during Cr⁶⁺ reduction from 1.5 g/l Cr⁶⁺ + 27.5 g/l H₂SO₄ and at 225 mA/cm² RCE cell.

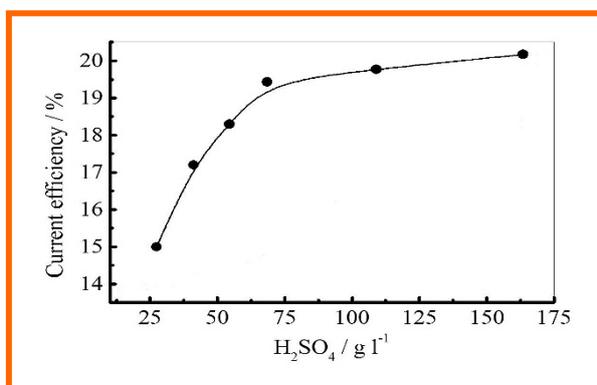


Fig. 18. The change in Current efficiency of Cr⁶⁺ reduction with H₂SO₄ at 225 mA/cm² using RCE cell. bath concentration was 1.5 g/l Cr⁶⁺ solution.

3.1.5. Electrochemical Elimination of Cadmium from Effluents using Spiral Wound Steel (SWS) Electrode.

Our activity at the CMRDI focused on using advanced and nontraditional flow-by cells to help remove cadmium from wastewater before to discharge [43]. We used a spiral wound steel electrode (SWS) to eliminate cadmium from industrial effluent. Using a flow-by cell with a spiral wound steel high-surface-area (HSA) cathode, as depicted in Fig. 9 a, b. The flow rate of 20 ml/ min, a current density of 400 uA/cm², and the SWS flow-by cell cathode were found to be the most effective experimental setups for removing cadmium.

At 400 uA/cm², the rate of cadmium deposition is accelerated. In 45 min at 400 uA/cm², the highest and fastest recovery of about 95% of the cadmium contained in the solution is obtained. Under this regime, cadmium was electrolyzed with a current efficiency of 35% and a 4.8 kWh/kg cadmium energy consumption.

Fig. 19 illustrates the influence of current density on the rate of cadmium removal. Also, the cyclic voltammogram of cadmium on the surface of the (SWS) cathode is shown in Fig. 20. Furthermore, Fig. 21 shows how cadmium ion decreased under these circumstances from 500 to less than 5 ppm in under 90 min. Applying a SWS cathode for electrolysis, safe waste is generated, energy consumption is decreased, and safe effluent is created.

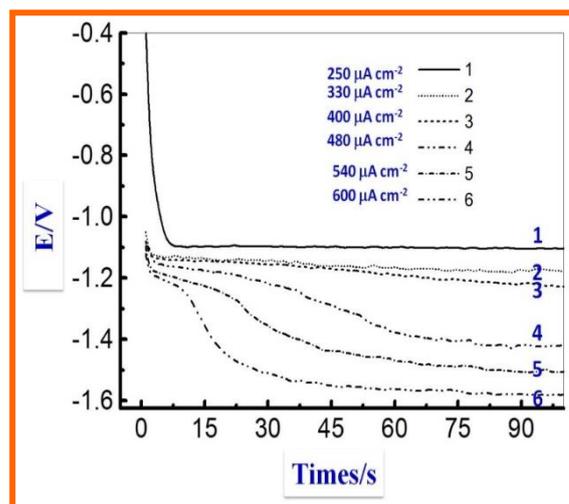


Fig. 19 E-t Curves of a SWS Cathode Flow-by Cell with 0.5 g/l Cd in a 0.5 M Na₂SO₄ solution.

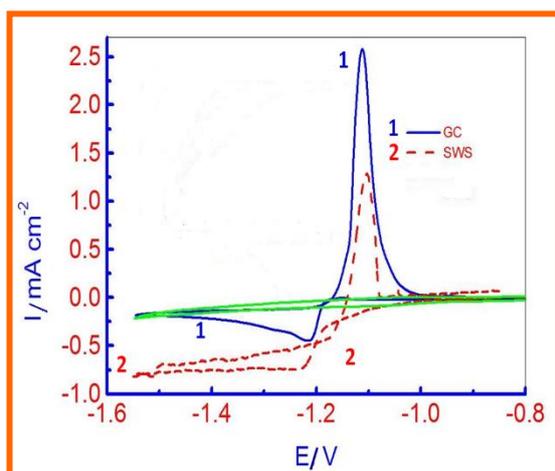


Fig.20 Cyclic voltammograms of: 1) Glassy Carbon Electrode (GC) and 2) SWS electrode in solution of 0.5 g/l Cd + 0.5 M Na₂SO₄.

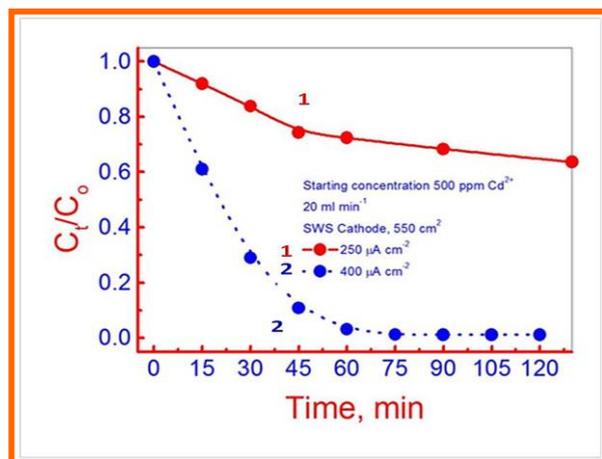


Fig. 21 Concentration-Time Curves for 0.5 g/l Cd in a SWS Cathode Flow-by Cell in a 0.5 M Na₂SO₄ solution at: (1) 250 μA/cm², (2) 400 μA/cm².

4. Future Approaches and Recommendations

There were a lot of Challenges (bottleneck) enabling environmental applications of electrochemical technology [7]. Treatment of industrial wastes, effluent control, energy-related problems, and the creation of novel electrode materials for treatment were all challenges to be solved. Biological treatment is cheap but unsuccessful and limited. The three electrochemical treatment methods were electro dialysis, electrocoagulation, and electrodeposition. The electrodeposition method has a number of advantages, like excellent control, small chemical requirement, nontoxicity, and low sludge output. It involves the removal and deposition of cations at the cathode. It is strongly influenced by the mass

transfer of the species to be recovered, the cathode surface area, and hydrogen gas evolution.

In environmental electrochemistry, the main electrolysis key parameters are the current density, current efficiency, space-time yield and energy consumption, which is usually controlled by cell voltage and electrode over potential. It's critical to search for techniques that can produce active sites and innovative cell geometries. The design optimization of an electrolytic cell aims at a high productivity.

We should create and develop new cell designs in the future. to develop product, material removal electrochemical cells (environment cleaning). We recommend the following suggestions as a way of resolving these challenges and achieving these goals while keeping the following important factors in mind:

- 1) The cell must offer excellent fluid flow per pass (offer excellent removal /pass).
- 2) High key factors, such as high current-potential distribution, high space-time yield, and high efficiency at low concentrations, should be fulfilled by the cell.
- 3) The cell must distribute current and voltage in an uniform way across the whole electrode surface area.
- 4) The EDL in the cell is to have a steady, uniform concentration distribution.
- 5) The cell's size, interior, electrode shape, and geometry should be simple.
- 6) The cell must have uniform electrode arrangement inside it.
- 7) At very diluted solutions, the cell must satisfy a high limiting current density.
- 8) The cell allows for the small inter-electrode distance between the electrodes.
- 9) The cell should be built and run with low-cost pumps, pyrex body (Teflon alternatives) and cheap material.
- 10) The cell should increase the mass transfer systems and flux gaps between the electrode bed molecules. The cell should increase the flow and mass transfer systems between the particles of the bed. The following suggestion methods allow us to achieve this goal.
 - i. mass transportation made possible by high flow rates and turbulence promoters (stirring).
 - ii. improve mass transfer (MT) by injecting air or sparging (distributing) air..
 - iii. Agitate the cell body by Hydraulic agitation (Move the cell body).
 - iv. rotate electrode in a vortex, a spouted, a pulsed, or a tumbling motion.
 - v. The fluidized bed of cathode (FBE) is limited and restricted. It has a lot of disadvantages, like irregular bed conductivity, irregular flow of solution, and irregular

potential distribution between bed particle. Metals aggregate and deposited near to separator/feeder.

Moreover, we have to prepare novel innovative modified electrode of ideal properties. It should meet (fulfill) the needs and requirements listed below:-

- a) It should be stable chemically, must be cheap, simple, and environmentally safe
- b) It needs to have an active electrode with low cell voltage value.
- c) High current efficiency must be provided.
- d) meet low power consumption standards,
- e) It must be reliable, hugely efficient, and able to prevent quick H₂ evolution.
- f) offer the highest active specific surface area (mesh expanded, net shape), as in Table 9.

Table 9 Summary of Some Novel Innovative Modified Electrode Materials

Cathodes in Electro removal process of electrode materials	Anode materials
<u>Using porous 3D electrodes includes:</u> Carbon Felt electrodes- Microporous Felt/ Cloth	Pt, PT/Ti, PT-Ir
Reticulated Vitreous Carbon RVC bed	Graphite C forms
Reticulated Foam metal as (Cu, Cu, Ni, SS)	Pb in acid-sulfate media
Conductive fibers- Spiral SWS. Stacked beds	PbO ₂ on Ti, Nb, C.
Complex Porous Electrodes (narrow porosity)	Ni in Alkaline media
Porous Mesh Coated/Cu,	
Net coated/C Mesh expands- Staked meshes-	Mixed Ru-Ti oxide on Ti for Cl ₂
Metal based Mesh	
3-Dimensional packed beds, FBE of glass bed coated by Cu, steel, SS, Conducting ceramics coated/Cu,	Conducting Ceramics e.g. Ti ₄ O ₇
Cheap Scraps of Cu, Al, SS,	
<u>3 D Printed Flow electrode (Printed Cells)</u>	IrO ₂ on Ti for O ₂
Catalyst Ni on SS scaffold, Pt/C catalyst on SS . Coated by Electrodeposition, Spray coatings, Drop casting. Prepared by computer numerical control (CNC) manufacturing methods.	

g) can provide uniform surface area to distribute current and potential uniformly. The space-time yield values are controlled by this.

h) These electrode materials should produce the highest reactor capacity.

i) These ideal electrodes should prevent the high pressure drop and plug with a solid product (feeder/membrane).

j) Over potential of ideal electrode should be as low as possible.

Our solution is to use as an answer to these difficulties.

Use inert anode materials such as lead-4% antimony alloy, PbO₂, C, Graphite and Pb which have high oxygen over potential.

Our suggestion is using cheap of pump of (PTFE)Teflon alternative valves (Artelon is cheaper than Teflon valves).

Our idea is to use cheap reactor body (Perspex or acrylic) to overcome this problem. preparing novel modified cell geometry as follow (Some decision and suggestions of

Modified electrode Geometries and design

- I. Rotating Cylinder Hall Cell (RCH Cell)
- II. Recessed Rotating Cylinder Electrode (rRDE)
- III. Reticulated Vitreous Carbon Rotating Cylinder Electrode (RVCRC E)
- IV. Rotating Ring Disc E (RRDE)
- V. Double Rotating Cylinder Electrode (DRCE)
- VI. Rotating Wire Electrode (RWE)
- VII. Double Rotating Conc Electrode (R RCE)
- VIII. Rotating Hemisphere Electrode (RHs E)
- IX. Microline Rotating Cylinder Electrode (Micro-LERCE).
- X. Bi-metalic R C E (BRCE)

5. Conclusions

Environmental electrochemistry uses electrochemical techniques to remove pollutants from industrial effluent before it is released into the environment. Electrodeposition is a promising method for recovering heavy metals without damaging the environment. This article's main goal is to provide a thorough overview of electrochemistry's potential applications while also highlighting how advanced reactors in the field are used in the surface finishing, mining, tanning, and electroplating industries as well as environmental remediation, which includes removing heavy metals from waste liquids. First, it is mentioned how various industrial waste sources harm and damage the environment. After that, the techniques and procedures for conventional waste water treatment are listed.

Furthermore, the subject of electrochemical technology's applications in environmental remediation is covered. The direct electrolysis is thoroughly discussed

together with the necessary processing parameters, specifically electrowinning from sources of dilute industrial effluents. The advantages and disadvantages of chemical and physical treatment methods are mentioned. Also, a summary of the various electrochemical cell and reactor types used in environmental cleanup is given, such as: extended two- and three-dimensional electrodes, such as FBE, AKAZO SR, Chemelec, RCE, and SWS cells. The advantages and disadvantages of some electrochemical cells are reviewed. The current density, current efficiency, space-time yield, current potential distribution, and cell voltage are the key parameters for reactor performance in the electro-removal of harmful species.

Key parameters influencing reactor performance include reactor effectiveness, productivity, and removal rate. There are several important variables that affect the decision-making process in process of the design of the reactor. These important electrolysis variables have an effect on the reactor key parameters (performance parameters). These important physical and chemical factors are discussed and addressed briefly. The roll of Chemical and Electrochemical Processing Department (Central Metallurgical Research and Development Institute) in environmental protection using electrochemical PBEC, SR, SWS, and RCE cells was mentioned and reviewed. The author also discusses his hopes and ideas for overcoming challenges in environmental electrochemical technology applications by using (toxic metal removal) modified cell geometries like RCH, rRDE, RRDE, DRCE, and BRCE, as well as innovative electrode materials like in table 9.

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