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ELECTROCHEMISTRY AND RADIOACTIVE WASTES: A SCIENTIFIC OVERVIEW

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Abstract: Radioactive wastes are arising from nuclear applications such as nuclear medicine and nuclear power plants. Radioactive wastes should be managed in a safe manner to protect human beings and the environment now and in the future. The management strategy depends on collection, segregation, treatment, immobilization, and disposal. The treatment process is a very important step in which the hazardous materials were converted to a more concentrated, less volume and less movable materials. Electrochemistry is the branch of chemistry in which the passage of electric current was producing a chemical change. Electrochemical treatment of radioactive wastes is widely used all over the world. It has a number of advantages and hence benefits. Electrochemistry can lead to remote, automatic control and increasing safety. The present work is focusing on the role of electrochemistry in the treatment of radioactive wastes worldwide. It contains the fundamentals of electrochemistry, the brief story of radioactive wastes, and the modern trends in the electrochemical treatment of radioactive wastes. An overview of electrochemical decomposition of organic wastes, electrochemical reduction of nitrates, electro- precipitation, electro- ion exchange, and electrochemical remediation of soil are outlined. The main operating factors, the mechanism of decontamination, energy consumption and examples of field trials are considered.

Keywords: Radioactive wastes, electrochemistry, organic wastes, nitrate, sludge, energy consumption, electro-ion exchange, contaminated soil, electro-flocculation.

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List of abbreviations		List of notations	
LLW	Low Level Waste	E	Energy consumption (kWh/m^3)
MLW	Medium Level Waste	C	Concentration (mol/m^3)
HLW	High Level Waste	F	Faraday constant (Coulomb/mol)≈ 96500
ELW	Exempted Level Waste	I	Applied electric current (A, mA)
VSLW	Very Short Lived Waste	E_{cell}	Applied cell voltage (V)
VLLW	Very Low Level Waste	t	Time (s, h)
EKR	Electro-Kinetic Remediation	i	Current density (A/m^2)
PWR	Pressurized Water Reactor	Q	Electric charge (Coulomb)
EIX	Electrochemical Ion Exchange	$E°$	Standard electrode reduction potential (mV)
DF	Decontamination Factor	m	Mass (g, kg)
VRF	Volume Reduction Factor	m_{eq}	Equivalent mass (g, kg)
DC	Direct Current	φ	Current efficiency
EF	Electro Floatation/Flocculation	z	Valence of the counter ion
TBP	Tri Butyl Phosphate	*MBq*	Mega Becquerel
ZrP	Zirconium Phosphate	*mCi*	Milli- Curie
SS	Stainless Steel	*M*	Molar concentration

Introduction

In recent years a lot of works have been carried out for handling, treatment and management of different types of radioactive waste in a safe manner [1]. Treatment of radioactive wastes can be classified into two main categories: Traditional and non-traditional treatment techniques. Evaporation, chemical precipitation, and ion exchange techniques were considered as traditional treatment methods while electrochemical treatment was considered as a non-conventional one. Electrochemical treatment of radioactive wastes is well known worldwide with different waste streams [2-4] such as:

1) Aqueous wastes *e.g.* LLW/MLW containing ^{137}Cs, ^{60}Co.

2) Organic wastes *e.g.* TBP, extraction solvents, oils, and scintillation cocktails which are used most commonly for measuring ^{3}H and ^{14}C, and less widely for ^{125}I, ^{32}P and ^{35}S.

3) Hazardous sludge produced after chemical or electrochemical precipitation *e.g.* sludge thickening and removal of suspended solids by electro-flocculation.

4) Nitrate wastes resulting from nuclear fuel fabrication plants and hot cells.
5) Radioactive and heavy metal contaminated soils.

In such treatment methods, radioactivity or hazardous materials were removed by different electrochemical processes such as wet oxidative degradation, reduction, cathodic deposition, and anodic dissolution. The most contaminant transportation mechanisms are listed below [5, 6]:

1) Electro-migration.
2) Electro-precipitation.
3) Electro-dialysis.
4) Electro-coagulation.
5) Electro-flocculation.
6) Electro-flotation.
7) Electro-osmosis.
8) Electro-chemical ion exchange (EIX).

The electrochemical treatment options for a specific type of wastes, experimental setup, safety requirements, decontamination efficiency and the final products of the process were depends mainly on the major operating conditions which can be categorized into the following:

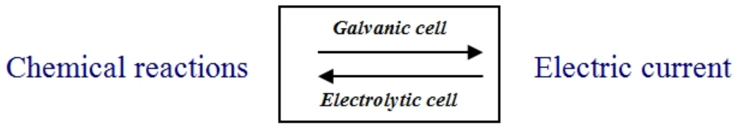
1) Radiological factors, including: level of radioactivity, type and half-life of the isotope.
2) Physico-chemical factors, including: the physical state of wastes (solid, aqueous or organic), treatment time, pressure, temperature, chemical composition, chemical concentration, and pH of waste solution.
3) Electrical factors, including: applied voltage, current density, cell constant, types and dimensions of operating electrodes.
4) Economic factors, including: energy consumption and availability of chemicals, instruments, etc.

Each electrochemical treatment process has its own advantages and disadvantages. In general, electrochemical methods show several advantages and hence benefits. The external process control of applied potential can modify to remote, automatic control system that increase safety and prevent direct exposure to radioactive wastes. Minimization of secondary waste can be achieved by being able to conduct reactions without the need of chemical additions. Mild operating conditions, enhancement of process effectiveness through electrical form and smaller plants with minimum energy consumption in turn saving in both capital and running costs now and in the future [6]. Although both electrochemical methods and radioactive wastes are well known separately, the combination between them is less known. The objective of the present work is to highlight the role of electrochemistry techniques in the treatment of different types of radioactive wastes, show the feasibility of combining between them and finally to investigate the effect of operational variables on practical performance, so the present paper is a scientific review for the following:

1) Fundamentals of electrochemistry and the chemical changes occurs during hydrolysis.
2) A brief story of radioactive wastes (sources, classifications & management strategies).
3) Application of electrochemistry concepts in the treatment of radioactive liquid wastes.

Electrochemistry

Electrochemistry is the branch of chemistry which studies the chemical changes due to passing the electric current and vice versa. A galvanic cell is the cell in which the electrical potential was produced from a chemical reaction while electrolytic cell is the cell in which a chemical reaction takes place due to the passage of electric current [7].



Simple dry cell, lead cell and fuel cell are examples of the galvanic cell while a water hydrolysis cell is an electrolytic cell. Any electrolytic cell consists mainly of a direct current source (DC-Power supply), anode compartment, cathode compartment, porous barrier (semi-permeable membrane, porous glass or semi-permeable ceramics, pottery material) and an electrolyte solution (contains mobile ions). Electrodes may be chemically active (involved in the chemical reactions) electrode such as metal electrodes e.g. Ag, Pb, Cu, Fe, Zn and Al electrodes or chemically inactive (inert, does not involve in the chemical reactions) electrode such as graphite, Pt and Au electrodes [8].

Anodic Processes

Oxidation of the metal to metal ions occurs when chemically active metal was used as the anode and the oxygen gas will produce if the inert anode was used according to the following equations [6, 9]:

$$\text{At active anode: } M \dashrightarrow M^{z+} + ze^- \quad (1)$$

$$\text{At inert anode: } 2H_2O \dashrightarrow O_{2(g)} + 4H^+ + 4e^- \quad (2)$$

$$4OH \dashrightarrow 2H_2O + O_2 + 4e^- \quad (3)$$

$$\text{In the presence of } X^-\text{: } 2X^- \dashrightarrow X_2 + 2e^- \quad (4)$$

From the above reactions, we can notice the following:

1) The oxidation process produces electrons which are responsible for the passage of electric current in the electrolyte and then the cell as shown in equations (1) to (4).
2) Metal corrosion, weight loss of anode and increase of metal ion concentration in the solution is accompanied by the conversion of $M \dashrightarrow M^{z+}$.
3) Appearing of H+ ion in equation (2) and consumption of the OH^- ion in equation (3) decreases the pH value at the anode compartment.
4) The rate of metal corrosion and the rate of O_2 gas production depends on the external applied potential between electrodes.

5) Both metal anode dissolution (main cell reaction) and production of oxygen gas (side reaction) at anode compartment can take place simultaneously if over-voltage is applied to the cell.
6) Halogen gases X_2 may be liberated at the anode if the electrolyte solution contains halogen anion X^- as shown in equation (4).

Cathodic Processes

On the other side of the electrolytic cell, reduction of metal ions (M^{z+}) to metal atoms or production of hydrogen gas will occur at the cathode according to the following equations [6, 9]:

$$\text{At active cathode: } M^{z+} + ze^- \dashrightarrow M \quad (5)$$

$$\text{At inactive cathode: } 2H^+ + 2e^- \dashrightarrow H_{2(g)} \quad (6)$$

$$2H_2O + 2e^- \dashrightarrow 2OH^- + H_{2(g)} \quad (7)$$

From the above reactions, we can notice the following [10]:
1) Overweighing of the cathode and decrease of metal ion concentration can take place due to deposition of metal on the surface of the cathode as shown in equation (5).
2) In order for the metal deposition to take place, the metal ion M^{z+} must be found in the electrolytic solution.
3) Hydrogen gas is evolved only if the electrolytic solution does not contain any metal ions of positive electrode reduction potential (Ag^+, Cu^+, Cu^{2+}, Bi^{3+}).
4) Hydrogen gas is also evolved if the solution contains only metal ions of negative electrode reduction potential (less than the electrode potential of hydrogen = zero) e.g. ions of group I (Li^+, Na^+, K^+, Cs^+, Rb^+) and group II (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}).
5) For electrolytes which contain more than one metal ion (mixed ions), the metal of the highest standard electrode reduction potential (E°) was deposited first e.g. the electrolyte contains Ag^+, Cu^{2+} and Fe^{2+} mixed together, silver will be deposited first on the cathode then copper and finally iron, because $E°_{Ag} = +0.8$ V > $E°_{Cu} = +0.52$ V > $E°_{Fe} = -0.44$ V.
6) Consumption of H^+ in equation (6) and production of OH^- in equation (7) at the cathode raise the pH value (lower the acidity and increasing the alkalinity).

All cathodic and anodic chemical and physical changes occur in any electrolytic cell can be summarized in Table 1 [11], from which it was noticed that what happens at the anode is the opposite with that occurs at the cathode completely and vice versa [12].

Table 1. Chemical and physical changes in any electrolytic cell.

At anode (+ve pole)	At cathode (- ve pole)
Oxidation of active metal anode or oxidation of water at inert anode	Reduction of metal ions or reduction of water
Production of electrons	Consumption of electrons
Metal anode corrosion	Metal cathode deposition
Weight loss of metallic anode	Overweighing of cathode
Production of O_2 or X_2	Production of H_2
OH^- consumed	H^+ consumed
H^+ produced	OH^- produced
pH decreases (becomes acidic)	pH increases (becomes basic)
M^{z+} produced	M^{z+} consumed
M^{z+} and H^+ migrate to cathode	OH^- migrates to anode

Deposition versus Precipitation

From radioactive waste point of view, metal ion (M^{z+}) deposition on the cathode surface corresponds to the removal of metal ion from solutions or decontamination of radioactive liquid waste. The process is not easy and depends on the chemical nature and the standard electrode reduction potential (E°) of the counter ion. According to the electrochemical series, metals can be classified into four main categories towards cathodic deposition [10, 13, 14]:

(1) Easily deposited metals which have a positive value of (E°) higher than the electrode reduction potential of hydrogen = zero. This group includes: Au^+, Au^{3+}, Pt^{2+}, Hg^{2+}, Ag^+, Hg^+, Cu^+, Cu^{2+} and Bi^{3+}, respectively.

(2) Possible deposited metals which have a negative value of (E°) closer than the electrode reduction potential of hydrogen = zero. This group includes: Fe^{3+}, Pb^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+}, respectively. External overpotential and withdrawal of generating OH^- from the cathode compartment facilitate deposition of these groups of metals.

(3) Difficultly deposited metals which have a negative value of (E°) lower than the electrode reduction potential of hydrogen = zero. This group includes: Fe^{2+}, Cr^{3+}, Zn^{2+} and Al^{3+}, respectively.

(4) Very difficult or non-deposited metals which have a higher negative value of (E°). These groups include: Mg^{2+}, Ca^{2+}, Ba^{2+}, Na^{+}, K^{+}, Cs^{+} and Li^{+} respectively.

In general, metals of group (I) directly form soluble metal hydroxides *e.g.* NaOH which remains as soluble ions in the solution forever. For metals of group (II), there is a competition between deposition and precipitation as metal hydroxides $M(OH)_2$, the preferred routes depend on applied potential, pH value around the cathode and the presence of solid impurities. Metals of group (III) prefer precipitation and the freshly generated hydroxide precipitate appears as a white gelatinous cloud around the cathode in case of Al^{3+}. Metals of group (IV) such as Pb^{2+} usually form stable hydroxide precipitates while metals of group (V) such as Bi^{3+} undergo both precipitation and deposition. Inner transition elements, especially the ions of gold, silver, platinum, mercury and copper mostly deposited as pure metals on the cathode surface. These transition metal ions do not undergo precipitation at all because their hydroxides are not stable compounds and do not exist.

Radioactive wastes

There are many uses of radioactive materials which improve or facilitate human activities and quality of life. These uses are given in different fields of technology, ranging from power generation to medical and industrial uses. All these applications generate radioactive wastes that may represent risks to the environment and to the human being, so it is necessary to have special attention to the management of radioactive wastes [15].

Sources

In general, there are two main sources of radioactive wastes [16]:

1) Nuclear fuel cycle sources: These include mining and milling of natural uranium and fissionable materials, nuclear fuel fabrication, the use of fabricated fuel rods in nuclear power plants, and reprocessing of spent nuclear fuel. Radioactive wastes arising from isotope production facilities, radioactive laboratories and hot cells are related to nuclear fuel cycle sources. All steps of nuclear fuel cycle produce different types and different levels of waste stream such as:

(1) Contaminated solvent extracts with α and γ activity due to the presence of U^{234}, U^{235}, U^{238}, Pu^{234} and Th^{234}.
(2) Solid and aqueous waste contaminated with fission products, e.g. Cs^{137} and H^{3}.

II) Non-Nuclear fuel cycle sources: These include industrial and medical applications of radioactive isotopes in diagnoses and treatment e.g. I^{125}, I^{131}, Tc^{99m} and Ir^{192} sealed sources.

Classifications

Radioactive wastes can be classified into six categories [17-19]:

1) Exempted Level Wastes (ELW): Wastes that meet the criteria for clearance, exemption or exclusion from regulatory control for radiation protection purposes [20].

2) Very Short Lived Wastes (VSLW): Wastes that can be stored for decay over a limited period of up to a few years and subsequently cleared from regulatory control, according to arrangements approved by the regulatory body, for uncontrolled disposal, use or discharge; this class includes wastes containing primary radionuclides with very short half-lives often used for research and medical purposes. Decay storage for the common short lived radioisotopes is normally routinely applied to segregated low level waste from radionuclide users in hospitals, universities, and research laboratories. Radioactivity concentrations of 3.7 to 37 MBq/m^3 (0.1 to 1 mCi/m^3), decay storage of ten half-lives (giving a 36 reduction of greater than 1000) potentially reduces the residual radioactivity content to below the limits for unconditional release/disposal [21].

3) Very Low Level Wastes (VLLW): Wastes that do not necessarily meet the criteria of the ELW, but that do not need a high level of containment and isolation and, therefore, are suitable for disposal in near surface landfill type facilities with limited regulatory control. Such landfill-type facilities may also contain other hazardous wastes. Typical wastes in this class include contaminated soil with low levels of activity concentration.

4) Low Level Wastes (LLW): Wastes that are above clearance levels, but with limited amounts of long lived radionuclides. Such wastes require isolation of containment for periods of up to a few hundred years and are suitable for disposal in engineered near surface repository site. This class covers a very broad range of wastes. LLW may include short-lived isotopes at higher levels of activity concentration, and also long lived radionuclides, but only at a relatively low level of activity concentration.

5) Medium Level Wastes (MLW): Wastes that are, because of their contents, particularly of long lived radionuclides; they require a greater degree of containment and isolation that are provided by near surface disposal. However, MLW needs no provision, or only limited provision, for heat dissipation during its storage and disposal. MLW may contain long-lived radionuclides, in particular, alpha emitting radionuclides that will not decay to a level of activity concentration acceptable for near surface disposal during the time for which institutional controls can be relied upon. Therefore, waste in this class requires disposal at greater depths, of the order of tens of meters to a few hundred meters.

6) High Level Wastes (HLW): Wastes with levels of activity concentration high enough to generate significant quantities of heat by the radioactive decay process or waste with large amounts of long lived radionuclides that need to be considered in the design of a disposal facility for such wastes. Disposal in deep, stable geological formations usually several hundred meters or more below the surface are generally recognized option for disposal of HLW.

Management Strategy

A responsible management strategy of radioactive wastes requires the implementation of measures aimed to protect human health and the environment. The basic steps of management strategy are part of a global system, ranging from waste generation to final disposal are: waste minimization, pretreatment, characterization, treatment, conditioning, transportation, storage, and final disposal [19]. A management system should be applied in all steps in order to ensure that activities, facilities, equipment, and waste product in meeting the overall safety, health, environment, security, quality, and economic requirements, with safety and environmental protection being of primary importance [22, 23].

Traditional treatment of aqueous wastes

Options and selection of treatment process for radioactive aqueous wastes depend upon its radiological and physicochemical characterization and quantity of the wastes [21, 24]. The processes available for treating aqueous radioactive wastes are listed as follows:

*Chemical precipitation (coagulation, flocculation).
*Ion exchange & sorption (cation and anion exchange).
*Evaporation.

Aqueous wastes containing suspended matter must be treated to remove particulates before and after the main treatment process. Physical or mechanical processes such as sedimentation, decantation, filtration, or centrifugation are used commonly to clarify the effluent wastes [21, 25].

Chemical precipitation

Chemical precipitation processes are regularly used for removing radioactivity from LLW and MLW at fuel reprocessing facilities, research laboratories, and the power station. Precipitation process is greatly versatile, low-cost process and may be used to treat large volumes of effluents containing relatively low concentrations of radionuclides. In some cases, a pretreatment stage, such as oxidation of organics, pH adjustment, and change of the valence state should be applied prior to the formation of the precipitate in order to improve the process. Radionuclides can be removed by precipitation, co-precipitation with a carrier or sorption onto particulates present in the waste solution [21].

Ion Exchange

Ion exchange methods have extensive applications that remove soluble radionuclides from liquid wastes produced in nuclear fuel cycle operations, radioisotope production plants, and research laboratories. It is very effective at transferring the radioactive content of a large volume of liquid into a small volume of solids. Ion exchange processes involves the replacement of cations or anions between an insoluble solid matrix containing ionizable polar group and a liquid solution.

When the ionic groups are negatively charged, the exchange will involve cations and when they are positively charged they involve anions, the process is selective, stoichiometric, and, as a rule, reversible; therefore, ion exchangers can be regenerated and radioactive liquid wastes recovered with high activity content or if the exchangers becomes exhausted they are removed and treated as radioactive solid wastes. A wide range of materials is available for the ion exchange treatment of radioactive aqueous wastes: (a) natural ion exchangers (clays, zeolites, cellulose, charcoals, collagen) and (b) synthetic materials such as zeolites, hydrous oxide gels of metals or organic resins formed by highly polymerized cross-linked hydrocarbons containing ionic groups (sulfonic acid, carboxylic acid, amino group, *etc.*). Ion exchange processes can be operated in batch or continuous modes and if the wastes contain high concentrations of salts, suspended solids, organic contaminants or the radionuclides ionic form not suitable, the liquid wastes will have to be pre-treated before exchange process [21, 26].

Evaporation

The evaporation process is effective in concentrating or removing salts, heavy metals and a variety of hazardous materials from waste effluent, reducing large volumes of liquid wastes with high decontamination factor and volume reduction factor. The process is commonly used for the treatment of HLW, MLW, and LLW effluents and may be carried out through the use of commercially available evaporator. However, evaporation has some important limitations: Unsuitable for waste effluents containing a large concentration of inactive salts, expensive because its large energy requirement and the presence of some organic compounds can produce explosions during evaporation [21].

Treatment of radioactive organic wastes

Liquid scintillation, extraction solvents, *e.g.* tributyl phosphate (TBP), oils and diverse biological fluids, generated in nuclear research centers, medical and industrial establishments are considered as radioactive organic liquid wastes. These wastes may present radioactive, chemical and biological hazards requiring treatments to remove or destroy radio-chemically or biochemically hazardous components. The objective is to eliminate the organic components to enhance compatibility of the treated waste with secondary conditioning process with cement.

Incineration, wet oxidation, acid digestion, and distillation can be applied for treating radioactive organic liquids [21, 27].

Treatment of radioactive solid wastes

Solid wastes are produced by all applications and used of radioactive materials, in normal operations and maintenance activities.

Solid, low and intermediate level wastes are generally segregated into combustible, compactible, and non-compactible forms. Treatment of solid wastes is used to reduce the waste volume and/or convert waste into a form suitable for handling, storage, transportation and disposal [21, 24, 26]. Instruments and solid equipment were decontaminated chemically, mechanically or electrochemically. Compaction, cutting, crushing, shredding and incineration are suitable treatment processes for almost solid wastes.

Electro-chemical trends on the treatment of radioactive wastes

Electrochemical treatment of nitrate/nitrite wastes

It is reported earlier that [28, 29] nitrate (NO_3^-) and nitrite (NO_2^-) are two of the major hazardous species present in HLW and mixed wastes. After removal of the bulk radioactivity, the decontaminated salt solution will be disposed in a cement waste form referred to as saltstone or borosilicate glass waste form. Reductive destruction of the nitrate and nitrite prior to disposal of the decontaminated salt solution in saltstone eliminates the possible groundwater contamination from the leaching of nitrate and nitrite from the waste form. Destruction of nitrate and nitrite prior to vitrification would significantly reduce the size of the off-gas system by eliminating the formation of NO_x gases. In the electrochemical destruction of sodium nitrate and nitrite, sodium hydroxide is the major liquid phase product of the process.

If the sodium hydroxide could be recovered and recycled, significant reduction in the quantity of waste requiring disposal would be realized. On-site use of the recovered sodium hydroxide would include neutralization of fresh waste and as a corrosion inhibitor in the waste storage and evaporation facilities. Thus, the quantity of sodium hydroxide available for recovery and recycle would increase by converting the sodium nitrate and nitrite into sodium hydroxide. Modern electrochemical reactor designs make it relatively simple to scale the treatment facility to the size of the waste stream by the addition of modular reactor units. Aqueous electrochemical processes operate at moderate temperature ($\leq$ 90 °C) and near the atmospheric pressure. The electrochemical reactions can be shut down instantaneously by shutting off the power to the electrochemical reactor. No additional chemicals are added in the process, and therefore there is minimal or no secondary wastes generated by the process. The obtained results for a bench scale electrochemical reactor show that the concentration of NO_3^-/ NO_2^- was reduced from 5 moles to 1 mole with charge $\approx 2.75\times10^6$ coulombs using 316 SS cathode and Ni anode [30].

Electrode materials, cell design, and other experimental parameters are the main operational variables affecting on the NO_3^-/ NO_2^- reduction using electrochemical flow cell. Lead (Pb) was found to be the best cathode material in terms of current efficiency, which improved in divided cells due to the elimination of anodic oxidation of nitrite. Operation of the divided cells at high current densities (i = 300–600 mA/cm^2) and moderate temperatures (80°C) provides more efficient reduction process. Greater than 99% of the NO_3^-/ NO_2^- were removed from the synthetic waste mixture batch in the 1000 h tests at an overall destruction efficiency of 55%. N_2, N_2O, and NH_3 were the only products formed and identified as shown in the equations (8) to (11) [28, 31].

Cathodic reactions (Reduction):

$$NO_3^- + H_2O + 2e^- \dashrightarrow NO_2^- + 2OH^- \quad (8)$$

$$NO_2^- + 2\ H_2O + 3e^- \dashrightarrow 1/2\ N_2 + 4\ OH^- \quad (9)$$

$$2\ NO_2^- + 3\ H_2O + 4e^- \dashrightarrow N_2O + 6\ OH^- \quad (10)$$

$$NO_2^- + 5\ H_2O + 6e^- \dashrightarrow NH_3 + 7\ OH^- \quad (11)$$

Electrochemical remediation of contaminated soils

Electrochemical treatment of contaminated soils with organic or inorganic pollutants is known as electro-remediation or electro-kinetic remediation (EKR). It is easy to operate and involves the installation of electrodes into the soil and the application of a low voltage gradient or direct current (DC) [32]. EKR is capable of mineralized organics into CO_2 without emission of any toxic materials like dioxins. Metal oxidizing systems like Ag/Ag^+, Ce^{4+}/Ce^{2+}, Co^{3+}/Co^{2+}, Fe^{3+}/Fe^{2+}, *etc.*, have been examined for EKR in pilot and commercial scale [33-35]. Due to the passage of electric current, some transportation such as ion migration (electro-migration), electro-osmosis (movement of water), and electrophoresis (movement of charged bulk molecules or solids) occurred in the liquid phase of soil [36, 37]. The nature of transportation depends on the chemistry of pollutant [38-40]. Inorganic pollutants such as salts of heavy metals can be removed by electro-migration because soluble salts dissociate into movable ions while organic compounds can be removed by electro-osmosis. Migration of cations towards the cathode and anion towards anode are electro-mechanical process [41-44].

EKR has the capability to remove heavy metals (Pb, Hg, Cd, Ni, Cu, Zn, Cr); hazardous anions (NO_3^-, SO_4^{2-}, CN^-); mixture of organic and ionic pollutants; hydrocarbons; oils; polychlorinated biphenyls and radioactive species (^{137}Cs, ^{90}Sr, ^{60}Co, ^{238}U) from saturated and unsaturated soils [41, 45, 46]. Efforts have been made to improve the EKR and to reduce the removal time. For example, modification of pH and the current density, introducing chemical compounds on electrolyte chambers [47, 48], and the addition of chelating agents to desorb the pollutant from soil particulates [49, 50].

Ti, Pt, Au, Ag and stainless steel electrodes were used in EKR. Chemically active electrodes, e.g. Ag, Zn and Al suffer a kind of corrosion, generating an oxide film on their surfaces, which cover the active sites and raise the electrical resistance of the cell. For that reason, it is necessary to pre-treat or pre-active the electrode surface before using to increase roughness or surface active sites. Also, carbon electrodes have been used in EKR because it is inert, low-cost and high availability [51-53]. In order to increase the active sites, eliminate passivation phenomenon, increase electrode life and improve the oxidant activity, it is necessary to modify electrode surfaces to obtain high over-potentials. Consequently, some electrode materials have been modified with metallic oxides forming a thin layer on a base metal (usually titanium), *i.e.* Ti | SnO_2/Sb_2O_3, Ti | IrO_2/Ta_2O_3, Ti | IrO_2, Ti | RuO_2 and C | TiO_2 [43, 53].

There are some aspects of EKR that require attention before the technology can be successfully implemented in the field, such as soil characterization, type and concentration of pollutant, electrode materials as well as electrode array configuration and spacing.

Electrochemical treatment of radioactive organic wastes

The use of polyvalent metal ions for removal of organic pollutants from effluent streams is well known. In these techniques, a coagulant is added as an external source of the polyvalent metal ion [54]. The examples are alum and ferric chloride with Al(III) and Fe(III) being the corresponding metal ions, respectively. In electrocoagulation, the desired metal ions are generated in situ by using a sacrificial anode (Fe or Al) dipped in the effluent and applying a DC electrical current. The effluent is creating a flock of metal hydroxides by electro-dissolution of sacrificial anode [55].

The Al(III) ions and the hydroxyl ions generated at anode combine to produce several monomeric and polymeric hydroxylated species which finally precipitate as $Al(OH)_3$ [56-58]. These freshly formed $Al(OH)_3$ aggregates, owing to their large specific surface area, allow rapid adsorption of organic pollutants onto them. Colloidal impurities are also trapped inside. The flocks so formed either settle to the bottom or float with the generated hydrogen bubbles [59]. In some cases, they can also form complexes with organics. In a variation of the process called the "peroxy electrocoagulation process", the added hydrogen peroxide in excess generates Fenton reactive system and synergistically works with electrocoagulation [60, 61].

Beside the adsorption of organic molecules on the surface of freshly prepared flocks, organics can be incinerated or destructed into gases (CO and CO_2) electrochemically according to the following equations:

$$\text{Acidic pH; at Anode: } H_2O \dashrightarrow OH^{\bullet} + e^{-} + H^{+} \tag{12}$$

$$\text{Alkaline pH; at Anode: } OH^{-} \dashrightarrow OH^{\bullet} + e^{-} \tag{13}$$

Equations (12) and (13) show that the hydroxyl radicals just generated, react with the organic pollutants due to their very high oxidizing power, ultimately leading to mineralization of organic pollutant with the production of CO_2, H_2O and other inorganic ions [54].

Electrochemical ion exchange (EIX)

The concept of electrochemically controlled ion-exchange was first developed in the USA [62] during a program to investigate methods of desalinating brackish water (1953-1970-US). This effect was based on local pH changes induced at an electrode surface by the passage of small electrolytic currents. When the electrode contained weakly acidic cation exchange groups, these become activated to cation absorption at cathodic potentials. Conversely, at anodic potentials these cations were eluted by a reversal of this process. Most of the US work was devoted to the use of carbon electrodes chemically modified with carboxyl (-COOH) groups by surface oxidation, although towards the end of the program, weak cation ion-exchange resins physically bonded to the carbon felt were introduced.

In the US work terminated in 1970, when it was realized that other techniques were proving more cost-effective for the desalination of brackish water streams, which were relatively high in dissolved the ionic material and had a very low operating cost target for the production of potable water. No other work was reported on this technique between 1970 and the commencement of the Harwell's work in 1981 on its potential application in the treatment of radioactive wastes. The early part of the Harwell program experimentally evaluated both modified carbons and ion-exchange electrodes, finding the latter to be superior in having higher capacities, better life under extended cycling conditions and the potential of cation selectivity. Further developments included the introduction of a restrained electrode structure between a platinized titanium mesh current feeder and counter electrodes. This provided an effective, reliable and robust system which has formed the foundation of subsequent developments. The sandwich structure of the used electrochemical cell comprised a pair of outer counter electrodes in contact with the EIX membrane of powdered ion-exchanger bonded together with an elastomeric binder onto an internal current feeder [63]. This not only gave mechanical rigidity and support to the exchange medium, but also improved performance at low cation concentrations and reduced electrical power requirements, due to the minimization of the inter-electrode gap. As a result, cells were demonstrated that could remove Cs with high decontamination factors (DF≈ 2000) up to a higher exchange loading (≈75%) using the EIX unit in an analogous way to a normal ion-exchange column, in which the feed stream introduced at the bottom was progressively decontaminated as it passed up the cell.

Subsequent quantitative elution into the water could be accomplished by polarity reversal to give concentrated products (>0.25M), compatible with vitrification. Complete absorption/elution cycles, which required only 0.25% of the energy needed for the equivalent concentration by evaporation, were repeated over 2000 times during 2 years of continuous use, with no signs of visual deterioration or loss of EIX performance. Once the stability of EIX modules had been demonstrated, their specificity for particular cation removal could be sensibly measured. As expected, conventional, organic resins did not display any significant selectivity between Group IA cations, in agreement with their performance under conventional ion-exchange conditions. Towards the end of the period of 1983-1985, inorganic absorbers were noted for their selective absorption properties under normal chemical driving forces were screened for their ability to behave as electrochemical exchanges. These materials which classed as strong acid exchanges [e.g. MnO_2, Sb_2O_5, $Ti(HPO_4)_2$] did not respond electrochemically to Cs absorption in solutions of pH 4-11. Zirconium phosphate $Zr(HPO_4)_2$ (ZrP) was found to behave in a way very similar to the weak cation resin exchanges [64].

A research program in 1985/86 [65] concentrated mainly on the development of ZrP to maximize the selectivity of ^{137}Cs removal from a sodium-bearing waste. In preliminary trials, multiple absorption and elution between two ZrP electrodes by polarity reversal gave an enhancement of Cs removal over Na by a factor of 17. As radioactive Cs was being concentrated in the EIX electrode during the treatment of the waste stream, and eluted only periodically to give a small volume of waste for subsequent immobilization, the electrodes had to be resistant to radiolytic degradation. Trials in an external gamma field demonstrated that no deterioration in EIX behavior was observed up to at least a dose of 10 MGy. Also, the field of work was broadened from the consideration of fission product containing wastes to include those containing plutonium. Preliminary studies comprised the adsorption of Pu(IV) from nitric acid solutions (1-5 M) onto Pt, Ti, stainless steel and graphite electrodes as a function of Pu concentration (0.001-1 g/L) and potential. The most significant effect was observed under these conditions when ion-exchange might be expected at electrolytically formed surface oxide films. The virtually complete desorption could be affected by changing the applied potential. EIX has been firmly established as an effective process for the treatment of a wide range of liquid radioactive wastes, including LLW of PWR and primary coolant drain wastes, fuel storage pond water, research center waste (LLW and MLW) and fuel fabrication wastes [25, 26].

A low-cost current feeder electrode has also been developed, with a projected lifetime of > 6 years. While cation EIX can be used for the treatment of low-salt content streams combined with anion EIX to control the pH can extend its range of application to > 30 meq/L.

At the same time, it is also able to remove activity complexes in an anionic form. EIX technique has also demonstrated its ability to remove radionuclides with insoluble hydroxides (e.g. Co, U and Pu) from both high and low salt content streams. EIX has been successfully scaled-up from the bench-top scale of 0.16 L/h to 1 m^3/h -firstly by increasing the electrode size by a factor of 11, and then by operating five units in parallel. An improvement in performance of by a factor 3 was observed over a simple increase in the area, due to the minimization of edge effects in the larger units. Despite the hand-made nature of the electrodes, their performance was within 3%. This has demonstrated the practicality of the multi-modular approach to scale-up. In a comparison with flocculation, ion exchange and evaporation, EIX was able to give equal, if not better DF performance (10-1000) with a system simply controlled through an automatic power supply. However, the most significant advantage of EIX is its compactness -with plant sizes of <1/10 of its competitors. This has important cost implications in minimizing the size and hence the cost of the controlled area.

EIX has a significantly lower energy requirement than evaporation, thus minimizing running costs, and is able to achieve volume reduction factors comparable to those expected from flocculation (>1000). The key variables of EIX operation are the choice of absorber, current density, flow rate and pH. In order to systematize the information obtained from flow cell experiments, a cell parameter (CP) has been derived and calculated, so that cells of different sizes can be compared and estimates of future cell performance predicted. Four variables combine to give the CP: Cell current (A), cell efficiency (E), flow rate (F), and feed concentration (N).

At CP = 1, the cell is working at 100% efficiency. The higher the CP is, therefore, the poorer its performance and the larger electrode area are required to treat the waste. Typical results indicate that a CP of 2.5 is required for 99% cation removal, i.e. an overall electrical efficiency of 40% [63].

Electro- flotation / precipitation / flocculation

The electro - flocculation principle has been known since the beginning of the 20th century. Oil/organic polluted water is a problem in many different industries. Demands from the authorities and general public for a cleaner environment will increase, and the authorities might reduce the legal effluent concentrations to 20 mg/L of organic substances. When the effluent is characterized as hazardous waste, it is illegal to drain it into the sewers. It might only consist of 0.6% oil, while the rest is pure water. These huge volumes of low- concentration oily waste are expensive to treat. If the oil could be separated from the water, it would be much less costly to treat the oily waste, because of the low volume. The oily sludge can probably be incinerated, and the water reused in the industrial process with a reduction in the cost.

The electro-flocculation unit is capable of separating many kinds of organic substances and heavy metals in addition to the oil. The degree of separation is in most cases above 99%, and the power consumption is about 1 kWh/m^3 of wastewater [66]. Current units can treat about 1m^3/h of wastewater in a continuous process. The best results are when the wastewater contains 5000 ppm organic substances or less [66].

Electrolytic processes to separate oil in wastewater were described in the patent literature as early as 1903. The process was used to treat condensed water from steam engines, before it entered the steam boiler as feed water. The unit used iron sheets as the anode material; the iron was oxidized during the process, and had to be replaced after a while. The electrolysis cell operated with a potential of 150 V and with a fairly high current [67]. This process was further developed by Weintraub, Gealer, Golovoy and Dziecіuch into a continuous process to clean oily wastewater from metal-cutting, forming, rolling and finishing operations. An electrolytic cell which can treat 3.8 L/min of wastewater was designed and patented in 1980. The wastewater which was fed into the unit contained from 300 to 7000 mg oil/liter of water. The processed water contained less than 50 mg/L for 90% of the time, and less than 26 mg/L for 83% of the time. The unit can be improved to reach an effluent oil concentration of 10 mg/L. The power consumption was calculated to be 1.6 kWh/m3 [67]. One of the first experiments with electroflotation was in 1911, treating domestic sewage in the United States. This method has not become generally used because the electrodes tended to scum after a while and, because of this, the efficiency decreased with time [68]. In 1946, Rivkin *et al.* [69] obtained a patent for a method for electroflotation of ore. They designed several laboratory-scale electroflotation cells, which gave an improved flotation rate compared to other flotation techniques. Kaliniichuk *et al.* have described an electroflocculation unit which can be used to separate an oil/water emulsion. They achieved a degree of separation of more than 99% with a power consumption of 0.48 kWh/m^3 of water, but they used a residence time of 10-20 min. [70].

Electro-flotation

In flotation processes, air or gas is bubbled through a liquid containing particles which float or emulsify in the water. The process consists of four basic steps: (1) gas bubble generation, (2) contact between gas bubble and oil drop, (3) gas bubble adsorption on the surface of the particle, and (4) rising of the gas bubbles and oil drops to the surface [71]. At the surface a layer of foam will be created [66]. This foam consists of gas bubbles and the floated particles, and can be removed by skimming. The rate of flotation depends on the following: the surface tension; the gas bubble diameter; the size of the particles; the water residence time in the electrolytic cell and the flotation tank; the particle and gas bubble zeta potentials; and the temperature; pH and particle size distribution.

There are many different flotation methods. The conventional process is to use a compressor to blow air through nozzles in the bottom of the flotation tank. The problem is the distribution of the air bubbles, and to make bubbles small enough. Small gas bubbles are more efficient than larger gas bubbles, since they have a larger surface area per unit volume of gas. Smaller gas bubbles also have the advantage that they have lower buoyancy, and so will have a longer residence time in the electrolyte. This increases the possibility for collisions between bubbles and oil particles. Another method is dissolved-air flotation, which gives a better bubble distribution in the water. The disadvantages are that it is not a continuous process, and it is difficult to control the bubble flux. During the process, air is injected into the water under pressure; when the pressure is released, the water is supersaturated with air, which is released as air bubbles [72]. This is the same process that happens when a bottle of carbonated water or beer is opened. A method which follows the same principle, but which uses a very low pressure, is vacuum flotation. The water is saturated with air at atmospheric pressure, and when vacuum is applied, air bubbles will be released. This process has the same advantages and disadvantages as dissolved-air flotation.

Electroflotation is a continuous method. The bubbles are generated by electrolysis of water; the water flows between two electrodes, and is reduced to hydrogen at the cathode and oxidized to oxygen at the anode. One advantage is that the gas bubbles generated are essentially at the same, very small, size. However, the power consumption can be high if the process is not well designed and optimized. Another advantage is that it is easy to adjust the gas bubble flux, by varying the current across the electrodes. The distribution of the gas bubbles is also good, because the bubbles are produced over the whole area of the electrode.

Electro-precipitation

Electro-precipitation is a flocculation process where the flocculating agent is the metal ions which are precipitated from the anode. The metal ions will settle in the electrolyte, but on the way down, they collide with particles in the electrolyte, and adsorb onto the surface of these particles. The best anode material is Fe or Al, because they give trivalent ions; most other cheap and easy accessible metals give bivalent ions. Trivalent ions have a higher ability to absorb onto particles in the water than bivalent ions, because they have a higher charge density. The mechanism which breaks down emulsions is not fully understood. Weintraub et al [67] suggested that the breakdown of emulsions is brought with the assistance of hydroxyl radicals, which are generated during ferrous-ion oxidation as shown in the equations from (14) to (17).

$$Fe^{2+} + O_2 + H^+ = Fe^{3+} + HO_2 \quad (14)$$
$$Fe^{2+} + HO_2 + H^+ = Fe^{3+} + H_2O_2 \quad (15)$$
$$Fe^{2+} + H_2O_2 = Fe^{3+} + HO + OH^- \quad (16)$$
$$Fe^{2+} + HO = Fe^{3+} + OH^- \quad (17)$$

The ferrous ion/hydrogen peroxide solution taking part in reactions (16) is recognized as Fenton's reagent, and is a powerful oxidizing system. The emulsion is destabilized by both oxidative destruction of the chemical emulsifier and by neutralization of the emulsion/droplet charge [67]. No mechanism has been suggested with aluminum as the anode. Aluminum ions are very unstable, and it is suggested that aluminum ions react with hydroxyl ions and make a network as soon as they are released from the anode. The network of aluminum hydroxide will adsorb onto colloidal particles. The process depends on pH and temperature to create the correct crystals. At 25°C the pH in the water must be between 4 and 10, while, at 100°C between 3 and 7, in order to create large crystals. Outside these pH ranges, the aluminum ions will react to make less complex compounds with hydrogen and oxygen [73].

Electro-flocculation

Electro-flocculation is a combination between electroflotation and electroprecipitation. Electroflocculation unit consists of an electrolytic cell with an aluminum anode and a stainless-steel cathode. The anode must be more easily oxidizable than the cathode to give the correct effect. Balmer and Foulds [74] tried many different electrode materials, such as iron, steel, copper, brass, zinc, alloys of aluminum, bronze and phosphor bronze. All of these materials produced enough flocks, and gave a high degree of separation. They concluded that the cheapest and most easily accessible electrode materials should be used. An electrolytic cell can be designed in many different ways. A famous electroflocculation cell which has been designed and patented by Jan Sundell is called the 'Purifier'. The distance between the electrodes is 3 mm; this distance is an important design variable when it comes to optimizing the operating costs of the unit. The operating costs are dependent on the power consumption, which can be expressed as:

$$P = U \times I = R \times I^2 = U^2 / R$$

To reduce the power consumption without changing the current and the degree of separation, one can reduce the resistance in the electrolyte. Reducing the distance between the electrodes or increasing the conductivity of the electrolyte will reduce the power consumption without changing the degree of separation, because the current is not changed. In some types of wastewater the conductivity is too low, and it is necessary to add some salts to increase the number of dissolved ions in the electrolyte. The simplest method is to add table salt, NaCl, but it has also been reported that 0.01 N $CaCl_2$ has been used to increase the conductivity of the electrolyte [67]. When the current in the electrolytic cell is increased, the gas bubble flux increases; this increases the separation effect.

However, when the concentration of gas bubbles is increased, the possibility that two gas bubbles collide also increases. This reduces the separation effect since larger gas bubbles are less effective than smaller gas bubbles, because they have a smaller surface area/volume ratio. In addition, gas bubbles have a lower conductivity than the electrolyte; this increases the power consumption. When the gas bubble concentration increases, the result is that the degree of separation increases as the current increases up to a certain level.

Concentration of the gas bubbles gives a large contribution to the electrolyte resistance, and eventually too many of the gas bubbles will coalesce. The degree of separation will then slowly decrease as the current across the electrodes increases [75]. The electroflocculation cell reactions can be written as follows:

$$\text{At cathode: } 2\ H_2O + 2\ e^- = H_2 + 2\ OH^-,\ E° = -\ 0.83\ V \tag{18}$$

$$\text{At anode: } 2\ H_2O = O_2 + 4\ H^+ + 4\ e^-,\ E° = +\ 0.40\ V \tag{19}$$

$$\text{At anode: } Al = Al^{3+} + 3\ e^-,\ E° = -1.66\ V \tag{20}$$

$$\text{Total cell reaction: } 2\ Al + 6\ H_2O = 2\ Al^{3+} + 6\ OH^- + 3\ H_2,\ E° = +0.83\ V \tag{21}$$

From Equations (18) and (19), hydrogen gas will evolve on the cathode, and oxygen gas will evolve on the anode; oxygen gas will only evolve at high current densities. It is an advantage that hydroxyl ions are developed at the cathode, because they maintain the pH in the electrolyte. The effective aluminum ion flocks were produced as in the Equations (20) and (21). To create the correct aluminum complexes, the pH must be close to 7. There are many mechanisms which are at work in the electrolytic cell. These include an electrophoresis mechanism, which makes the negatively charged oil particles attracted to the anode. This results in a faster flocculation than would be the case with conventional flocculation or flotation methods [74].

Conclusion

Electrochemistry and radioactive wastes are strongly related to each other, especially in recent researches. Several electrochemical processes can be applied to treat radioactive and hazardous wastes such as: organic wastes, aqueous wastes and contaminated soil in turns to human being and environment.

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Türkçe öz ve anahtar kelimeler

ELEKTROKİMYA VE RADYOAKTİF ATIKLAR: BİLİMSEL BİR BAKIŞ

Öz: Radyoaktif atıklar nükleer tıp ve nükleer güç santrallerinde olduğu gfibi nükleer uygulamalardan sonra ortaya çıkmaktadır. Radyoaktif atıklar şimdi ve gelecekte insanları ve çevreyi korumak için güvenli bir şekilde yönetilmelidir. Yönetim stratejisi toplama, ayırma, muamele etme, tutuklama ve atma işlemlerine dayanmaktadır. Muamele etme süreci, zararlı maddelerin daha derişik, daha az hacim kaplayan ve daha az hareketli bir hale dönüştürüldüğü çok önemli bir adımdır. Elektrokimya, elektrik akımının kimyasal değişim meydana getirdiği bir kimya dalıdır. Radyoaktif atıkların elektrokimyasal olarak muamele edilmesi dünyanın her yerinde geniş ölçüde kullanım alanı bulmaktadır. Bu yöntemin çok sayıda avantajı ve getirdiği faydalar bulunmaktadır. Elektrokimya uzaktan ve otomatik kontrol sağlayabildiği gibi güvenliiği de artırmaktadır. Bu çalışma dünya çapında radyoaktif atıkların muamele edilmesinde elektrokimyanın rolüne odaklanacaktır. Çalışma elektrokimyanın esaslarına, radyoaktif atıkların kısa bir hikâyesine ve radyoaktif atıkların muamele edilmesinde modern elektrokimyasal yöntemlere değinecektir. Organik atıkların elektrokimyasal ayrışması, nitratların elektrokimyasal olarak indirgenmesi, elektro-çöktürme işlemleri, elektro-iyon değişimi işlemleri ve toprağın elektrokimyasal olarak canlandırılması işlemlerine göz atılacaktır. Temel işlem faktörleri, temizleme mekanizmaları, enerji tüketimi açıklanacak ve alandan örnekler verilecektir.

Anahtar kelimeler: Radyoaktif atıklar, elektrokimya, organik atıklar, nitrat, sulu atık, enerji tüketimi, elektro-iyon değişimi, kirli toprak, elektro-topaklanma.