From the Editor's Desk

Electrochemistry–for Green and Clean Environment

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Energy has become an index of the economic growth of a country. The role of energy in contributing towards human welfare has increased in stature, along with industrialization and over population. At present 88% of the world energy demand is met by fossil fuels. In order to meet the vast energy requirement in different sectors man is recklessly burning fossil fuels which in turn results in environmental pollution like generation of undesired gases. Thus 'Green House Effect" or thinning of ozone layer results leading to climatic calamities. At present the world's energy demand is met by fossil fuels like petroleum and natural gas. Their extraction and processing have harmful impact on the environment. The global awareness to the growing energy demand, depletion of fossil fuels and alarming rate of environmental pollution had drawn to explore the alternate energy systems, preferably from renewable energy sources.

Apart from electrochemical power sources like primary and secondary cells, fuel cells, which store a limited extent of electrical energy, there are other sources which can be produced in large quantities. With depletion of fossil fuels, it is necessary to explore energy from renewable energy sources like solar, wind, geothermal, tidal etc. But since transportation is not possible with all these energy sources, finding an intermediately or synthetic form of energy which can be more economical to produce, easily storable, transportable and pollution free becomes essential. It is hopefully expected that the hydrogen energy system can form good link between the new energy source and the user and also solving the environmental pollution. Production of hydrogen by electrolysis of water offers several advantages over the present large scale hydrogen production methods, which are based on hydrocarbons, in so far it eliminates raw material supply, pollution etc. It is believed that for distances greater than 700-800 km, transporting hydrogen through pipelines would be cheaper than electrical transmission lines. Hydrogen can be substituted for petroleum in almost all industrial process and can be converted to a variety of fuel forms such as methanol, ammonia etc. Hydrogen is able to serve both the electrical energy demands by the use of either fuel cell or more conventional and safe method for the storage and transmission of hydrogen.

For the removal of pollutants, there are four very powerful tools based on principles of electrochemistry:

- electrodialysis
- electro -flotation and -floculation
- cathodic reduction
- anodic oxidation

Electro-dialysis: This process involves the removal of ionized solutes from a solution and removal of electrolytes from non-electrolytes based on electromigration through ion-exchange membranes. These anion and cation exchange membranes are positioned alternatively between two end electrodes. When a potential is applied, ions are allowed to permeate by the concerned membrane, leading to enriching of concentration in alternate compartments and dilution in other alternate compartments. A widespread example is the desalination of brackish water in which half of the compartments carry water of depleted salts and other half carry water of increased salt content. The same principle is also applied in getting concentrated NaCl by electrolysis using univalent permselective membrane. Waste recovery is also possible by electrodialysis. As an example, sodium sulphate waste from chemical industries can be converted into caustic soda and sulfuric acid by electrodialysis using suitable ion exchange membranes,

$$Na_2SO_4 + H_2O \rightarrow H_2SO_4 + 2\ NaOH \qquad (1)$$

Electro -flotation and –flocculation: Gases like H_2 and O_2 evolved during aqueous solution electrolysis can be effectively used for the removal of pollutants (especially oil in water emulsion like fats from food and dairy industries). Since the gas bubbles carry them out to the solution, they can be easily collected and removed. Irrespective of the solution conditions, optimum sized bubbles can be produced. If H_2 gas is produced at the cathode and metals like Fe and Al are used as sacrificial anodes, the insoluble metal hydroxides and hydrates well be getting precipitated along with pollutants and this sort of settling is reported to be more convenient than chemical methods. An electrochemical method for the removal of fluoride based on the principle of electrofloculation has been described wherein the fluoride content can be brought down to less than 0.5 ppm from water containing even up to 100 ppm fluoride. Al plate electrodes are employed, where aluminum anode is used as sacrificial anode. In the proposed electrolytic treatment of sewage, aluminum anode is electrolytically dissolved to precipitate the phosphate present from detergents. It is also possible to decolorize dye containing solution by electrocoagulation with iron or aluminum electrodes.

Cathodic reduction: By this method, removal of toxic metal ions present in the industrial effluents or drinking water (in lower quantities) can be effectively carried out to meet the permissible concentration of metal ions in water. The electrochemical process involves in the reduction of metal ions to its elemental or easily removable from. Since the metal ion concentration is very low, the mass transport can be accelerated by different techniques like rotation of cathode, forced electrolyte flow, fluidized bed, packed bed etc. One of the applications of this phenomenon is the removal of iron from pickle liquor from steel industries, where the reduction takes place in the form of metal:

$$Fe^{3+} + 3^{e-} \rightarrow Fe \quad (2)$$

Dilute solution of metal ions especially Cu and Ni from plating industries can be made to undergo this process and metals can be effectively recovered. Chlorinated organic compounds also can be possibly reduced either in acidic or basic solutions by a replacement mechanism to yield comparatively less toxic compounds. Nitrate can be converted to environmentally friendly nitrogen by cathodic reduction.

Anodic oxidation: Two types (direct and indirect) of reaction can be applied in regard to anodic oxidation processes. In the direct processes the destruction of noxious spices can be accomplished by the electrochemical reduction at the anode. For example in the cyanide removal it is oxidized at the anode at high temp (~80°C) for several days, thereby converting to obtain carbon dioxide and nitrogen according to following reaction:

$$2CN^- + 8OH^- \rightarrow 2CO_2 + N_2 + 4H_2O + 10e^- \quad (3)$$

In the indirect method where the generated oxygen or ozone or hyphochlorite or free chlorine by electrochemical means can be used as oxidant to destroy the pollutants or sterilize the noxious materials is more advantageous than the direct method, since apart from the complete cyanide destruction, metal ion constituents of the wastes can also be removed. Here cyanide is oxidized to nitrogen and carbon dioxide by electrolyzing the waste alone with steel cathode, the current density being 2-13 A/dm^2. The hypochlorite generated electrolytically oxidizes cyanide to carbon dioxide and nitrogen. Ozone is also used for the destruction of cyanide which involves two separate chemical steps, oxidation of cyanide to cyanate and further oxidation or hydrolysis of cyanide to nitrogen or ammonia.

Destruction of organics is carried now by the process known as “silver bullet”, it employes a divided parallel plate reactor to generate Ag (111) species anodic alloy by oxidation of Ag(I) in concentrated nitric acid. This is a powerful oxidizing agent and can be used to treat organics (eg. phenols, chlorinated hydrocarbons etc.) at a low temperature (30-60 ºC) in a batch recycle processes.

Electrokinetic remediation

Electrokinetic technique has been widely used to remove inorganic and organic contaminants from wet solid matrix viz., soils and sludge. This process involves the application of direct current across the contaminated soil or sludge through anode and cathode in the subsurface. The main electrode reactions are generally oxygen evolution at the anode and hydrogen evolution at the cathode. In this process the contaminants are removed by the combination of electroosmotic flow of the pollutant, electromigration of contaminants carrying ionic charges in the liquid phase and electrophoresis of the charged particles carrying contaminant on their surfaces. During electrokinetic process, the hydrogen and hydroxyl ions are transported into soil by the applied direct-current resulting in a low pH environment near the anode and a high pH environment near the cathode. The acid solution will release heavy metals and other cations that are sorbed on negatively charged clay surfaces, the cations migrating towards the cathode. The alkaline environment causes precipitation of most heavy metals and radionuclides unless they form negatively charged complexes. These complexes migrate towards the anode and will form free metal ions again, when they meet the acid environment. In this way species are concentrated in the region where the two pH-environments meet and pH changes abruptly.

Electrochemical removal of gaseous pollutants

Gaseous pollutants may also be removed electrochemically, provided that they are first dissolved into an electrolyte. The overall process will then generally consist of at least two steps: absorption of the gaseous species in a liquid and the subsequent electrochemical conversion of them to less harmful products.

(i) Removal of SO_2 by electrochemical methods: For controlling problem of acid rains resulting from sulphur dioxide emissions from flue stacks, especially in coal-fired thermal stations for power production, two methods are available. In the first process, molten salt electrolysis of potassium pyro sulphate is envisaged and the second process utilizes Br_2.

In the first process, the cell comprises of an immobilized molten salt electrolyte viz. potassium pyropsulphate and porous gas diffusion electrodes formed by perovskite type. The temperature of operation is 350-400°C at a current density of $5A/dm^2$. The cell voltage is < 0.5V with an energy consumption of 420 KWh/T of sulphur dioxide. The sulphur dioxide removal efficiency is 99%. However SO_3 is the byproduct gas at the cathode chamber. This is a continuous one step operation with the following advantages:

1. Salable by product with no waste production.
2. On-line temperature operation with no cooling or reheating of the flue gas.
3. Electricity is the only added reagent.

The second process, for removing sulphur dioxide from the flue gases uses anodically generated bromine from the electrolysis of hydrogen bromide in an undivided filter press reactor. The overall reaction of the process in the conversion of SO_2 and water to form H_2SO_4 is:

$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + HBr$ (4)

The intermediate Br_2 is electrolytically regenerated in the membrane cell from HBr:

$2HBr \rightarrow H_2 + Br_2$ (5)

Thus the advantage of this process is the production of the hydrogen as a byproduct in addition to value added H_2SO_4, the pilot facility treat flue gas having minimum SO_2 content of 0.016% by volume.

(ii) Removal of H_2S by electrolysis: Direct electrochemical oxidation creates blocking of electrodes by sulphur. Hence the new process developed consists in dissolving hydrogen sulfide in sodium hydroxide and oxidizing electrochemically in two compartment cell with Nafion membrane and carbon electrodes (C.D 10 A/dm^2) to get sulphur and hydrogen. The voltage of cell is 0.5 V and a current efficiency of 94% is achieved.

(iii) Electrochemical treatment of carbon dioxide: Green house effect due to increase in the carbon dioxide content of the atmosphere may cause irreversible damage to the environment. The electroreduction of carbon dioxide at various metal electrodes yields many kinds of organic substances, namely CO, CH_4, C_2H_6, EtOH, other alcohols etc., four classes of metallic electrodes in aqueous electrolytes and three classes for nonaqueous media can be distinguished. Thus in aqueous solutions:

- Metallic In, Sn, Hg and Pb are selective for the production of formic acid.
- Metallic Zn, Au and Ag produce carbon monoxide.
- Metallic Cu exhibits a high electrocatalytic activity for the formation of hydrocarbons, aldehydes and alcohols.
- Metallic Al, Ga and Group VIII elements (except Pd) show electrocatalytic activity in carbon dioxide reduction.

In non aqueous electrolytes:

- On Pb, Tl and Hg the main product is oxalic acid.
- On Cu, Ag, Au, In, Zn and Sn CO and carbonate ions are obtained.
- On Ni, Pd and Pt are selective for CO formation.
- On Al, Ga and Group VIII elements (except Ni, Pd and Pt) form both CO and oxalic acid.

The ultimate goal appears for a new energy utilization system in which CO_2 may be used as energy storage medium. An alternative route is the electrochemical fixation of CO_2 in organic compounds. For example 2,5 –dihydro benzoic acid is obtained by the electrolysis of 1,4 benzoquinone in the presence of CO_2.

Electrochemical Ion Exchange (EIX)

An important trend in pollution abatement is a combination of electrochemical technique with other physical or separation process known as Electrochemical Ion Exchange (EIX). In EIX, a weak acidic or basic ion exchanger is bonded for the removal of cations or anions respectively. Adsorption of ions into an EIX electrode is controlled by an externally applied potential. The passage of current can enhance the rates of metal ion removal to achieve high volume retention. Ellution is achieved by simple polarity reversal to give high volume decontamination and no elluant chemical are required. Trace levels (100 ppb) of metal contaminants could be removed using EIX. In practice, this method is also employed for the removal of Cl^-, SO_4^{2--}, Ca^{++}, Mg^{++}, Pb^{++}, Cd^{++} and mercury from industrial effluents.

Aerogel and electrochemistry for cleaning contaminated water: Recently, Capacitive DeIonization (CDI) has been used as a water treatment technology due to the simple principle and low operating potential (consumes only 16-32 Wh/gallon), without the need for chemicals. Therefore, it is considered as an environmentally-friendly and economical system. A CDI system operation consists of adsorption and desorption periods for obtaining purified water and concentrated water respectively. When an electric potential is applied to CDI cells, charged ions in contaminant water are adsorbed onto the surface of charged electrodes and formed an electric double layer due to the charged electrode and adsorbed ions, producing purified water. After the adsorption of ions, the saturated electrode undergoes regeneration by desorption of the adsorbed ions under zero electrical potential or reversed electric field.

Photo-electrochemical Methods: In recent years, photo-electrochemistry has led to a new and interesting possibility for treatment of pollutants from wastewater. In this case, suspensions of semiconductor particles can be used to harness the light with production of electrons and holes in the solid which can destroy pollutants by means of reduction and oxidation, respectively. In this way, water containing organic, inorganic or microbiological pollutants can be effectively treated.

The number of application areas and the scale of operation for environmental chemistry are found to increase as process experience is gained. However, electrochemical techniques must be integrated with other treatment procedure. More often the amount of pollutants available or after conversion may be in small quantities. Hence proper techniques for analysis are of prime importance. Again here the use of the electrochemical techniques using ion- selective electrode for different ions, sensors and anodic stripping voltammetry makes electro-chemistry as an indispensable subject in the environmental pollution abatement and production. CSIR-CECRI has developed different technologies for green and clean environment viz., PEM based hydrogen generator, De-floridation, De-arsenator, Hypochlorinator, Electrochemical nitrate removal unit for drinking water treatment.

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