

ELECTROCHEMICAL METHODS OF PURIFYING WASTE WATER

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The electrochemical methods of purifying industrial waste water have a number of advantages over chemical methods. Unlike chemical methods, they do not increase mineralization.

The electrochemical purification methods can be divided according to the purpose for which electrical energy is used: for generation of gas bubbles in the flotation of impurities (electroflotation), for formation in the liquid bulk of metal hydroxides with a highly developed surface (electrocoagulation), or for electrochemical transformation of substances, resulting in formation of low toxicity, or readily removable compounds (electrochemical decomposition).

An important feature of electroflotation is small size of floating bubbles, which is responsible for its high efficiency, especially in the case of finely dispersed impurities. Presently, electroflotation is suggested for purification of waste water of widely different nature, in particular for removal of solids and slime formed in electrochemical treatment of metals, in separation of proteins from starch-like substances at sugar refineries, in purification of waste water of pig-breeding farms and in manganese recovery from ores. Particularly effective is electroflotation in the case of water purification from oil products.

The most popular purification method is electrocoagulation, which combines to the utmost the advantages of electroflotation and electrochemical decomposition. Electrocoagulation is a method in which the prevailing process is adsorption of impurities by metal hydroxides formed upon anodic polarisation. As anodic materials, iron and aluminium are almost exclusively used. The range of applicability of the electrocoagulation method is very wide. Excellent results are obtained by the use of electrocoagulation in conjunction with destruction of dyes.

Phenols, alcohols, aldehydes and organic acids are oxidized to low toxicity substances by the use of electrochemical decomposition method.

Electrodialysis is based on ion transport across selective ion-exchange membranes under the action of direct current. At present two tendencies in the application of electrodialysis are beginning to show. The first is associated with demineralisation of water containing salts in the amount 0.5-10 per cent. The process yields fresh water containing no more than 0.05 per cent salt and relatively concentrated brine. Electrodialysis units for water demineralisation are presently produced on a commercial scale. The productivity of the most powerful electrodialyzers is 10,000m³ and more a day. The second trend being intensively developed in recent years is electrodialysis of solutions to obtain substances not contained in the original salts, such as acids, alkalis etc.

The use of electrochemical methods of environmental protection holds great promise. To-date only demineralization by electro dialysis is in current use in industry. The application of other electrochemical methods will solve a number of vital problems of environmental protection.

Keywords: Electrochemical Methods; Purification of Waste Water; Electroflo-tation; Electrocoagulation; Electrochemical Decomposition; Electro-dialysis

INTRODUCTION

THE electrochemical methods of purifying industrial waste water are specific in that, unlike chemical methods, they do not increase mineralization. This advantage is of particular importance on account of increasing power consumption for demineralization of waste water.

The electrochemical purification methods can be provisionally divided according to the purpose for which electrical energy is used: for generation of gas bubbles flotating impurities (electroflotation), for formation in the liquid bulk of metal hydroxides with a highly developed surface (electrocoagulation), or for electrochemical transformation of substances, resulting information of low toxicity, or readily removable, compounds (electrochemical decomposition). This classification is arbitrary since electroflotation may involve partial dissolution of anodes to form hydroxides, or coagulation of colloids present in the waste water, which may lead to additional water purification due to adsorptive capacity of the gel being formed in the process. It is also possible that during flotation, organic impurities can undergo oxidation or reduction. On the other hand, decomposition of organic compounds is always accompanied by strong gas evolution, which leads to partial transfer of impurities into the surface layer. Electrocoagulation is also always attended by flotation and quite frequently by reduction or oxidation of impurities. During electro dialysis, substances may undergo electrochemical transformations.

ELECTROFLOTATION

Electroflotation is based on molecular adhesion of impurity particles present in waste water and finely-dispersed gases evolved in the course of electrochemical water decomposition. Just as in the case of pressure flotation, the aggregates formed are transferred from liquid bulk to the surface.

An important feature of electroflotation is the small size of flotating bubbles, which is responsible for its high efficiency, especially in the case of finely dispersed impurities. As hydrogen bubbles are smaller than oxygen bubbles, cathodic gases are more effective than anodic. At present, electroflotation is suggested for purification of waste water of a widely different nature, in particular for removal of solids and slime formed in electrochemical treatment of metals, in separation of proteins from starch-like substances at sugar refineries, in purification of waste water of pig-breeding farms, in manganese recovery from ores. Particularly effective is electroflotation in the case of water purification from oil products. There is some evidence in literature that by electroflotation it is possible to get

diamonds of much smaller size than by conventional methods. Frequently electroflotation is used as a supplementary treatment to biological purification in order to decrease the impurity content.

As has been already pointed out, an important application of electroflotation is purification of water, sea-water in particular, from hydrocarbons. As we know, each decade the amount of oil transported by tankers is trebled. This leads to increasing pollution of sea-water by hydrocarbons either from ballast water (in this case the oil content may be as high as 4kg/m^3), or from water used for washing tankers. The oil losses in these operations and due to wrecks reach 1 per cent of the total amount of transported oil. For example, in 1974 these losses amounted to 22 million tonnes. The International Convention adopted in London at the end of 1973 sets very rigid limits on the content of oil products in used sea-water. However, the methods now in use: settling, filtration, centrifuging, various chemical and physico-chemical methods (extraction, sorption, flotation) have a number of disadvantages and are expensive.

In this situation, electroflotation shows some advantages, in particular in that it allows more uniform saturation of waste water with gas bubbles having a high dispersion degree. Experiments have shown that oil globules which are over 5microns in size are completely removed by electroflotation.

It is clear from the above examples that application of electroflotation to purification of waste water in various industries holds great promise. However, not all problems involved in the use of insoluble anodes have been fully solved. It is known that most anodes disintegrate when used in treating waste water containing chlorides. Disintegration of graphite, for instance, leads to additional pollution of the water undergoing purification. Evidently, solution of this problem is associated with the use of new durable anodes.

ELECTROCOAGULATION

At present, the most popular purification method is electrocoagulation, which combines to the utmost the advantages of electroflotation and destructive treatment. Electrocoagulation is a method in which the prevailing process is the adsorption of impurities by hydroxides formed upon anodic polarization of some metals. As anodic materials, iron and aluminium are almost exclusively used.

Electrocoagulation is used in several cases involving electrochemical purification.

The design of an electrocoagulator, just as that of an electroflotator, is exceedingly simple: It is a box of insulating material in which is located a row of horizontally or vertically arranged electrode plates. The range of applicability of the electrocoagulation method is very wide. It covers purification of waste water from suspended and emulgated matter, from heavy metal cations, from bichromate anion, from dyes of different structure, from various organic substances, including those involved in sulphate-cellulose industry, from waste water containing animal

vital activity products, not to mention a few other problems solved by means of electrocoagulation.

The electrocoagulation method has a further advantage—it disinfects waste water. The disinfection is achieved mainly due to adhesion of negatively charged microorganisms to positively charged ferric and aluminium hydroxides and their coflotation. This enables a sufficiently thorough disinfection of waste water of large pig-breeding farms.

Excellent results are obtained by the use of electrocoagulation in conjunction with the destruction of dyes. The electrochemical reduction of dyes can occur along the azo-group, the azo- and nitrocompounds being reduced to respective amines, which in their turn can be oxidized at the anode to CO_2 and ammonia. Undestructed dyes are adsorbed on electrochemically generated hydroxides. Under these conditions, the electrical energy consumption is less and the purification of waste water more thorough, being 90–100 per cent for dyes and 60–80 per cent for other organic compounds. Phenols, alcohols, aldehydes and organic acids are oxidized to low-toxicity substances.

The electrocoagulation method yields good results in the case of waste water containing organic compounds or heavy ions as impurities. If thorough desalinization is required, electrodialysis is preferable.

ELECTRODIALYSIS

Electrodialysis is based on ion transport across selective ion-exchange membranes under the action of direct current. At present, two tendencies in the application of electrodialysis are beginning to show. The first is associated with demineralization of water containing salts in the amounts 0.5–10 per cent. The process yields fresh water containing no more than 0.5 per cent salt and a relatively concentrated brine. At salt concentrations in the starting solution beyond these limits, demineralization by electrodialysis is uneconomical. At the present time, electrodialysis units for water demineralization are produced on a commercial scale. The productivity of the most powerful electrodialyzers is $10,000\text{m}^3$ and more (a day). The energy consumption for demineralization of water with the initial salt concentration 0.5 per cent is about $8\text{kW}/\text{m}^3$. Introduction into industry of new ion-exchange membranes greatly enhanced the competitiveness of electrodialysis. A new trend of complex application of electrodialysis made its appearance, namely for extraction of valuable substances from sea-water in the process of its demineralization. The concentration of salts in brine in these cases can be increased upto $200\text{g}/\text{l}$.

To-day desalinization or concentrating of solution free of hardening salts presents no difficulties. But the use of electrodialysis for demineralization of hard water is complicated by the possibility of precipitation of salts in concentrating chambers and in membrane pores. The precipitate has a low conductivity and increases the system resistance, which may result in overheating and even in melting of the ionite membrane. However, in the concentration of these salts less than $2\text{mg}/\text{l}$, electrodialysis ensures softening of water. In addition, electrodialysis allows a

sufficiently complete purification of water containing cyanides, wash water of galvanic workshops as well as concentration of sulphuric acid.

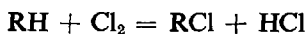
The second trend being intensively developed in recent years is electro dialysis of solutions to obtain substances not contained in the original salts, such as acids, alkalis, etc. This possibility appeared when dipolar membranes had been developed.

By using electro dialyzers with dipolar membranes it is easy to obtain hydrochloric acid and alkali from sodium chloride; to obtain nitric acid and alkali or ammonium hydroxide from corresponding nitrates, polluting the waste waters of nitrogenous fertilizer plants. This offers a possibility of reducing the energy consumption and decreasing significantly the waste water amounts from industrial plants.

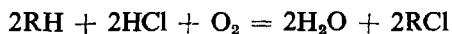
OTHER METHODS

In spite of great advances in water purification by electrochemical and other methods, some problems remain unsolved as yet, in particular, purification of water from waste hydrochloric acid.

Hydrochloric acid is a nonutilizable waste product of many large plants, mainly those producing chloro-organic compounds by substitution chlorination reaction:



To-day, nearly half the world production of chlorine is used for chloro-organic products. Thus about 20 per cent of the total amount of chlorine obtained goes into production of waste hydrogen chloride. The utilization of such product is hindered by its containing significant amounts of chloro-organic compounds as impurities. This precludes its processing to obtain chlorine by electrolysis without previous thorough purification, which increases the cost of produced chlorine. The matter is further complicated by the fact that during electrolysis of hydrochloric acid, hydrogen is formed in the cathodic compartment, which is a much cheaper product than the alkali obtained in electrolysis of sodium chloride. Another difficulty is the high aggressivity of the electrolyte, hydrochloric acid, in which chlorine is dissolved, which imposes high requirements upon the corrosion resistance of the equipment, particularly, diaphragms. Due to all these difficulties, the volume of industrial processing of hydrochloric acid into chlorine by electrolysis is much less than that of the hydrochloric acid produced. Another large consumer of hydrochloric acid is the oxychlorination process, i.e., the catalytic chlorination of hydrocarbons:



which also necessitates thorough purification of hydrogen chloride due to the high sensitivity of catalyst to impurities.

Our Institute together with the institutes of the Azerbaijan Academy of Sciences has developed a new method of utilizing the hydrochloric acid produced as waste

product. This method consists in chlorination or hypochlorination of hydrocarbons by chlorine generated during electrolysis of hydrochloric acid.

An example of this process is chlorination of ethylene by electrochemically generated chlorine. The electrolyser used for this purpose has graphite electrodes and no diaphragm. Ethylene is passed into the anode compartment and the hydrochloric acid produced as waste substance is used without previous purification as electrolyte. Electrolysis is carried out at high current densities (over 1 Amp/cm²). In the course of electrolysis, chlorine is formed, which is adsorbed on the anode and reacts with ethylene also adsorbed on the anode :



It was shown by special experiments that it is the chemical step rate which limits the overall chlorination process rate.

It is known that the transition process to more efficient reactors is a most complex process, requiring long adjustment. In the process under consideration this difficulty is absent since the process rate is determined not by hydrodynamic factors but by the surface reaction. Therefore, keeping the current density constant, it is not difficult to pass from low-productivity to high-productivity reactors. In practice, transition from a laboratory plant with the load 5Amp to a semi-industrial electrolyser with the load 500 and then 5000Amp did not necessitate any correcting of the process parameters. The absence of diaphragm simplifies and reduces the maintenance cost of electrolyser, while the high anodic current densities (ten times as high as in a chlorine electrolyser with a solid electrode) decrease significantly the outlay expenses, as compared to chlorine production by electrolysis of sodium chloride. For this reason, the method under consideration can compete with the chemical method in wide use at present, for which chlorine is produced by electrolysis of sodium chloride. Of considerable importance in this case is also the fact that the current efficiency and the dichloroethane yield in relation to the ethylene used is close to 100 per cent, and the obtained product is of high purity and can be used for processing into vinyl chloride reaches half a million tonnes per year. Therefore, by the method described it is possible to solve to a large degree the problem of utilizing HCl obtained as a waste gas.

By the above method it is also possible to decrease the initial hydrochloric acid concentration from 27 to 10 per cent. With greater solution depletion, the amount of ethylene chlorohydrin formed rises sharply.

The problem of utilizing of diluted hydrochloric acid can be solved by using in an electrochemical synthesis of propylene chlorohydrine and glycerol dichlorohydrine. Both of them are initial compounds for commercially important products—propylene oxide and epichlorohydrine, are widely used in polymer production. We have found that propylene chlorohydrine and glycerol dichlorohydrine obtained by using chlorine generated during electrolysis of diluted (4–10) hydrochloric acid and propylene or allyl chloride, have purity sufficient for further processing. The reaction of electrochemical production of substances above mentioned goes at a

high rate and with adequate selectivity. Thus with the introduction of the electrochemical method into industry, instead of being producers of waste HCl polluting the environment, the propylene chlorohydrine and glycerol dichlorohydrine production process will become its consumers.

It is evident from the foregoing that the use of electrochemical methods of environmental protection holds great promise. To-day, only demineralization by electro-dialysis is in current use in industry. The application of other electrochemical methods will solve a number of vital problems of environmental protection.

Discussion

S. GURUSWAMY (*Central Electrochemical Research Institute, Karaikudi*): 1. What is the mechanism involved in electro-coagulation from aqueous systems? 2. Is AC or DC employed for electro-coagulation? Is it necessary to add suitable additives to bring about electro-coagulation? 3. What are the current densities involved?

G. A. TEDORADZE (*Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow*): 1. Fe- or Al- hydroxides adsorb impurities because such hydroxides have very high developed surface. 2. Mostly DC is used. 3. The usual value of current density is 0.5–2Amp/cm². The limiting factor is passivation of anodes. In the chloride containing solutions, current densities are usually higher because passivation is weaker.

S. KRISHNAMURTHY (*Formerly Chief Chemical Technologist, Indian Telephone Industries Ltd. Bangalore*): Is there any possibility of cyanide bearing wastes being destroyed by electrochemical methods?

G. A. TEDORADZE: Electrolysis of such wastes with some chloride ion addition—active chlorine destroys cyanides is the most effective.