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Environmental Friendly Electrochemistry – a Solution for a Clean Oil Industry

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الكيمياء الكهربائية الصديقة للبيئة- حل لصناعة نفطية نظيفة

بترو الي

تطورت أنظمة المعالجات الفيزيائية والكيميائية والحيوية التقليدية لكي تمنع التلوث وتحافظ على سلامة البيئة البشرية، وتبرز استخدام المعالجة الكهروكيميائية بديلا جذابا لهذه الأنظمة لمقاومة التلوث.

تعتبر الطريقة الكهروكيميائية التقنية نظيفة وأنيقة لأن الالكترونات الناتجة تمدنا على الأقل من هذه الناحية بكواشف متنوعة تستخدم للعديد من تفاعلات الأكسدة والاختزال ، ومن أجل ذلك فان تصميم مفاعل كهروكيميائي يتضمن أقطاب مصنوعة من مواد مناسبة وباستعمال وسائل تحكم هندسي للتفاعل يمكن أن يوفر حلا في الوقت المناسب لتجنب ملوثات محددة ناتجة من تحضير المركبات الكيميائية أو من إعادة استخدام الكواشف أو معالجة المياة أو مراقبة المواد السمية.

تعتبر المركبات العضوية السبب الرئيس لتلوث البيئة في صناعة النفط ، كما تعتبر المعالجة الكهروكيميائية أو تفكيك المركبات العضوية طرقا فعالة للتحكم في التلوث عند درجات حرارة منخفضة كبديل عن المحارق اذ تستطيع العمليات الكهروكيميائية التفكيك الكامل للمركبات العضوية وذلك بأكسدتها عن طريق المهبط أو اختزالها بواسطة المصعد الى مركبات عضوية صغيرة غير ملوثة . ويمكن أيضا بواسطة هذه الطريقة تفكيك الملوثات مباشرة خلال ما يسمى بالتحليل الكهربي وذلك عن طريق تفاعل الالكترونات المنقولة من والى الملوث التي تحدث على سطح القطب الكهربائي. ومن ناحية أخرى يمكن تفكيك الملوثات باستخدام عامل مختزل/مؤكسد مذاب (مثل $H_2O_2,O_3,HC1O,CI_2$) ناتج أو متضمن في المادة الالكتروليتية للتخلص من المادة الملوثة ، كما تتضمن هذه الورقة سلوك بعض العمليات الكهروكيميائية البيئية.

Abstract: *Conventional physical, chemical and biological treatment processes have been developed in order to prevent environmental pollution and to preserve the quality of human habitats. An attractive alternative for these processes are offered by the electrochemical approach of pollutant neutralization. Electrochemical processing is an elegant and clean technology because "electrons", at least from this point of view, may provide a versatile reagent for many redox reactions. Therefore, electrochemical reactor design, incorporating suitable electrode materials and using controlled reaction engineering, can provide a timely solution to avoid certain pollutants via clean synthesis, reagent recycling, water treatment or monitoring of toxic species.*

Organic compounds are the main cause of environment pollution in oil industry. The electrochemical treatment or destruction of organic compounds is potentially a powerful method of pollution control, offering a low temperature alternative to incineration. Electrochemical processes can determine the complete destruction of organic species by anode oxidation to carbon dioxide or cathode reduction to low or non-pollutant organic compounds. The electrochemical destruction of pollutants can be achieved directly through the so called direct electrolysis in which an electron transfer reaction

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to or from the undesired pollutant occurs at the surface of an electrode. On the other hand, with the so called indirect electrolysis, the destruction of pollutants can be achieved with the use of a dissolved redox reagent (e.g. H_2O_2, O_3, $HOC1,C1_2$ *existing in or being generated from the electrolyte in order to neutralize the undesired pollutant. Some performance parameters of environmental electrochemical processes are also presented.*

INTRODUCTION

Environmental pollution has become a considerable problem due to a rapid increase in the global industrialisation. In this context, the continuous rising demand of oil products has brought a rise in the crude oil extraction and processing. This fact has determined the appearance of important related environmental pollution problems.

The extraction leads to crude oil pollution of soil, natural waters and air in those areas. The crude oil components that pollute the environment, especially the soil, are accumulated and inflict negative consequences upon the flora and the fauna in the region. The human population also has a lot to suffer.

The main environment pollutants that originate from the extraction and processing of crude oil are presented in Table 1. As it can be seen, there is a great diversity of substances which will determine specific removal methods. Thus, conventional physical, chemical and biological treatment processes have been developed in order to prevent environmental pollution and to preserve the quality of the environment.

Table 1. Types of environmental pollutants from oil industry (after Sadiq[1], Kalabokas[2], and Obiajunwa[3]).

Organic pollutants	Inorganic pollutants
Alkanes Aromatic hydrocarbons Phenols Ketones Halogenated hydrocarbons Nitrated hydrocarbons Sulfonated hydrocarbons	Heavy and transitional metals NO_x, SO_x

Conventional chemical treatment processes are based on the usage of reagents. The products of their reaction often pose recycling problems or even pollution problems on a smaller scale than the original problem. Biochemical treatment processes are used very often but in certain situations, the high toxicity of the waste blocks the activity of the used biological species. An attractive alternative to the conventional treatment processes, which gain more and more interest, is electrochemical treatment. Electrochemical methods are of great diversity which can deal with a large number of pollutants related to the extraction and processing of crude oil.

This paper is an overview on electrochemical applications with regard to pollution problems in the oil industry. Research results obtained in the "Babes-Bolyai" University, Laboratory of Electrochemical Researches, Cluj-Napoca (Romania) on the in-situ electrosynthesis of hydrogen peroxide by cathodic reduction of dissolved oxygen in alkaline solution are mentioned.

GENERAL THEORETICAL ASPECTS ON ENVIRONMENTAL ELECTROCHEMICAL PROCESSES

Electrolysis for the production of useful chemicals and materials, energy producing electrochemical reactions and electrochemical methods for destruction of toxic or hazardous materials are environmental - friendly processes.

Electrochemical Technologies (ET) have definite advantages over the traditionally used physical or chemical processes. The inherent advantage of ET is the environmental compatibility, due to the fact that the main reagent, the electron, is a "clean reagent". The removal of pollutant species by oxidation/ reduction processes can be carried out directly in an electrochemical cell without the addition of redox chemicals. The high selectivity of many of these processes helps to prevent the production of unused by-products, which in some cases have to be treated as wastes. Other advantages of ET are (Rajeshwar[4], Juttner[5]): versatility (i) – direct or indirect oxidation and reduction, phase separation, concentration or dilution, ET can deal with a variety of pollutants, *e.g.* gases, liquids, and solids, and can treat small volumes of microlitres as well as large volumes of millions of litres; energy efficiency (ii) – ET generally have lower temperature requirements than their equivalent non-electrochemical methods *e.g.* thermal incineration; processes are easily monitored and automated via electrical signals (iii) and cost effectiveness (iv) electrochemical reactor and peripheral equipment are generally simple and, if properly designed, also inexpensive.

Considering electrochemical measures regarding environment protection, three alternative concepts must be pointed out:

(i) Electrochemical processes for treating wastes- this includes all techniques where toxic compounds are removed from gases, liquids or even solids;
(ii) Process-integrated environmental protection – these include recycling of valuable material and substitution of waste-producing processes by cleaner ET with little or no waste production;
(iii) Electrochemical methods for environment monitoring, which will not be discussed here.

The main purposes of the environmental electrochemistry can be illustrated by considering examples from the following areas:

(a) Metal ion removal and recovery (*e.g.* Pt, Au, Ag, Cu, Sn, Zn, Ni, Cd, Hg).
(b) Regeneration of redox reagents (*e.g.* Cr (VI), Ce (IV), Ti (III), Fe (III) Ag (II)).
(c) Purification of water via disinfection using Cl_2, OCl^-, H_2O_2, O_3, $OH^{*\cdot}$
(d) Concentration and separation of streams via membrane processes such as electrodialysis, electrochemical ion exchange.
(e) Sensing and monitoring of species via ion selective electrodes, gas sensors, microelectrodes.
(f) Removal of noxious gases, such as H_2S, SO_x, $NO_{x.}$
(g) Degradation and destruction of organic compounds such as phenols, chlorinated hydrocarbons, cyanides.

The basic parameters for an electrochemical process in the removal of impurities, but generally also for ET, are the current density, i – current per unit electrode area, the current efficiency, ϕ, and the space-time yield. The rate of an electrode reaction per unit of time is given by Faraday's law of electrolysis:

$$m = \frac{\phi\, i\, A}{z\, F}\ [\mathrm{mol\ s^{-1}}]$$

where A is the electrode area, z number of electrons and F is the Faraday constant. The current efficiency ϕ represents the ratio between the theoretical value of the current quantity given by Faraday's law and the real current quantity which is higher than the former due to possible secondary electrode reactions. The rate per unit reactor volume, V_R is:

$$\frac{1}{V_R}\cdot\frac{dm}{dt} = \frac{\phi\, i\, A}{z\, F\, V_R}\ [\mathrm{mol\ s^{-1}\ m^{-3}}]$$

which is the space-time yield.

The effectiveness of electrolysis for dilute solutions is strongly determined by the mass transfer of the species to be removed, the electrode surface area and the occurrence of electrode site reactions.

The current density represents the actual rate of an electrode reaction. Its maximum value, called the limiting current density, i_L, is defined by the following expression:

$$i_L = zFk_mc,$$

where k_m represents the mass transfer coefficient and c represents the bulk concentration of the species reacting at the electrode (the species which needs to be removed). In order to increase the value of the limiting current, two alternatives must be considered. Firstly, the mass transfer must be improved in order to have a higher value for k_m. This can be achieved by setting the electrodes in motion or by increasing the flow rate of the electrolyte solution. Secondly, the electrode area must be increased. To accommodate this, electrodes with a large active specific area are needed. Different types of electrodes with a large specific area are employed nowadays (*e.g.* porous electrodes, packed-bed electrodes, moving-bed electrodes). These electrodes are generally called three-dimensional electrodes and have a specific area ranging from 10^3 to 10^4 m^2/m^3.

ANODIC TREATMENT OF AQUEOUS EFFLUENTS AND ORGANIC WASTE

A partial or complete decomposition of pollutants can be achieved by anodic treatment. The organic material can be completely decomposed to carbon dioxide.

The decomposition of waste through anodic oxidation can be achieved directly on the anode surface or, indirectly, using appropriate anodically formed oxidants (*e.g.* Cl_2, hypochlorite, peroxide, ozone, Fenton's reagent, Cr^{6+}, Ag^{2+}).

Direct electrochemical oxidation methods are industrially of very little or no interest (Janssen[6]). The reasons for this are: (i) the rate of the electrochemical process is very small, (ii) the available electrode material is not inert (*e.g.* Pb corrodes slowly) and is expensive (*e.g.* borium-dopped diamond electrodes are very inert, but expensive).

Using chlorine-based compounds (anodically generated) as oxidation reagents are not recommended due to a high risk of forming chlorinated organic compounds.

Oxidants like hydrogen peroxide and ozone can be used in open-end circuits because an excess of these compounds can be easily destroyed. These oxidants can be produced either on-site in special electrochemical cells (see below) or directly in the process liquids.

In order to obtain high efficiencies in the indirect oxidation process there are a few important requirements (Rajeshwar [4]). The potential at which the intermediate species is produced must be far from the value of oxygen generation. Next, the generation rate of the intermediate species must be large. Also, the reaction rate of the intermediate species with the pollutant must be higher than the rate of any competing reactions. Finally, the adsorption of the pollutant (or any other species) must be minimized.

Many anodic O-transfer processes occur with considerable overvoltage in the potential region for the anodic production of oxygen. The rate of the O-transfer process has been maximized without excessive oxygen evolution through the development of a doped metal oxide electrode material (e.g. Bi(V) doped – PbO_2).

Fenton's reagent, Cr^{6+}, Ag^{2+} and other such oxidants must be used in closed liquid circuits of the process in order to prevent metal losses.

Fenton's reagent is produced by the simultaneous cathodic reduction of Fe^{3+} and O_2 and subsequent reaction to the hydroxide radicals (Scott[7], Saracoo[8]):

$$O_2 + 2H^+ + 2e^- = H_2O_2$$
$$Fe^{3+} + e^- = Fe^{2+}$$
$$Fe^{2+} + H_2O_2 = Fe^{3+} + HO^- + HO^*$$
$$Fe^{2+} + HO^- = Fe^{3+} + HO^*$$

This species are very efficient in the oxidation of polycyclic aromatics, tarry and oily wastes, chlorinated aromatics and so on.

For a total oxidation only redox couples with high oxidation potential are suitable (*e.g.* Co^{3+} / Co^{2+} +1.82 V / NHE and especially Ag^{2+} / Ag^+ +1.98 V / NHE). Ag^{2+} is generated at the anode from Ag^+ in an aqueous nitric solution using an electrochemical cell divided by a membrane.

Phenols are considered one of the primary pollutant components in waste water due to their high toxicity (the limit for phenol concentration in water is 0.05 mg dm^{-3} and lower concentration limits are in discussion (Comninellis [9])), high oxygen demand (theoretically, 2.4 mg O_2 mg^{-1} phenol) and low biodegradability (Bahadir [10]).

Petrochemical refineries are one of the main sources of phenol pollution. In the past years, numerous treatment technologies have been proposed for phenol removal from wastewater (*e.g.* Comninellis[9]), Bahadir[10]). Thus, under suitable circumstances and in concentrations above 2-4 g/L, phenols can be economically recovered from waste waters (Canizares[11]). Below these concentrations, phenol destruction is always the best method for treating phenolic wastes. Among the existing processes, photochemical degradation, chemical oxidation, wet oxidation and electrochemical direct or indirect oxidations are of interest.

The direct anodic oxidation is characterised by a low reaction rate or low current efficiency. Phenol is well known for its ability to foul electrodes and the tarry deposit forming on electrodes during phenol oxidation is attributed to phenol polymerization products (Zareie [12]). Due to these circumstances, the indirect electrochemical oxidation, using redox couples with high oxidation potential, is the more preferable path.

CATHODIC TREATMENT OF AQUEOUS EFFLUENTS AND ORGANIC WASTE

The most important application of cathodic treatment is the removal of toxic metal ions from waste-water and organic waste. There is a considerable number of papers and some reviews in the literature referring to this topic (Rajeshwar [4], Jüttner [5], Janssen [6]). Also, most of the industrial applications are of this particular nature.

The recovery of metals from aqueous effluents by electrodeposition depends on the ion concentrations in the wastewater. If metal ion concentrations in the feed-solution are in the range of 1-3 g/dm^3 then two-dimensional cathodes should be used in order to achieve concentration levels of 0.1 – 0.5 g/dm^3 at the outlet (Scott [7]). Thus, the removal of a metal ion from a process stream to a pre-determined concentration enables the recycling of either solution or metal to be processed. If concentration levels of 0.001 g/dm^3 in the effluent are required, in order to process a feed solution with concentrations levels of 0.1 g/dm^3 of metal ions, three-dimensional electrodes are preferably used.

Our research was focused on the Cu removal from waste water and Cr^{6+} regeneration (Ilea [13, 14]).

The electrochemical reactor can operate continuously or in a batch mode and can produce either compact metal for re-use, powdered or flake metal, or concentrates for recycling.

Chlorinated organic compounds comprise another important category of substances that are amenable to cathodic reduction (Rajeshwar [4], Sequeira [15], Scott [7] , Rajeshwar [16]). These compounds can be reduced in acidic or basic solutions by a replacement mechanism to yield the less toxic aromatic parent compounds plus chloride ions.

Hydrogen peroxide can also be electrosynthesised by cathodic reduction of oxygen and used for the removal of low concentrations of organics. Also, hydrogen peroxide is a much more attractive mediator since the reactant can be oxygen from the air and any excess hydrogen peroxide eventually decomposes only to oxygen and water, therefore leaving no residual chemicals in the environment (Alvares-Gallegos [17]). However, in order to electrogenerate hydrogen peroxide directly in the wastewater, it is necessary to reduce the oxygen to hydrogen peroxide under quite different conditions in comparison with those used in commercial manufacturing processes.

The synthesize of hydrogen peroxide by partial reduction of oxygen has been carried out in alkaline media (Ilea [18, 19], Rosca [20]). The main advantage of this electrosynthesis is the low energy consumption because the reaction:

$$O_2 + H_2O + 2e^- \Leftrightarrow HO_2^- + HO^- \qquad \varepsilon^0 = -0.065V$$

(Kinoshita [21])

can be conducted at low cathodic polarisation.

The hydrogen peroxide electrosynthesis (HPE) was studied using classic linear voltammetry and wall-jet ring disk electrode techniques. The specific parameters of HPE were determined. Thus, the quasi-reversible character of the process, the average number of electrons transferred in the electroreduction of oxygen at carbonaceus materials electrodes, the current efficiency of HPE and the heterogeneous rate constant were established.

CONCLUSIONS

Electrochemical technologies can and will contribute to environment protection by means of waste purification processes. Some of these methods have been presented and briefly discussed here. Methods like the recovery of metals from aqueous effluents by electrodeposition are already frequently used, while other electrochemical techniques (*e.g.* direct and indirect anodic incineration of pollutants) are in competition with classic procedures.

Electrochemical methods can deal with a large number of pollutants related to the extraction and processing of crude oil. The possibility of using these methods on a large scale in the near future is related to the availability of some effective electrode materials. It is also related to the fact that through electrochemical technologies the recovered substance may have a significant resale value or it might be internally recovered in the process.

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