Chapter 1
Chemical Oxygen Demand

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1.1 Introduction

Organic pollution in water can be monitored by measuring an important index called chemical oxygen demand (COD).[1] Different countries such as China and Japan set this parameter as a national standard to investigate the organic pollution in water. The conventional method to measure the COD is the determination of excess oxidizing agent such as dichromate or permanganate left in the sample.[2] Thus, COD is defined as the number of oxygen equivalents required to oxidize organic materials in water. In the conventional method, a strong oxidant such as dichromate is added to the water sample to digest the organic matter whereas the remaining oxidant is determined titrimetrically by using $FeSO_4$ as the titrant. However, some drawbacks are associated with this procedure as it requires almost 2–4 h to complete the analysis.[3,4] Thus, rapid as well as automatic analysis is not possible by using this method. Moreover, skilled workers are required to produce reproducible results. In addition, health issues and safety concerns also arise because of the consumption of expensive (Ag_2SO_4), corrosive (concentrated H_2SO_4), and toxic ($Cr_2O_7^{2-}$) chemicals.[5,6]

The problems associated with the conventional method can be prevented by utilizing electrochemical treatment of wastewater having organic pollutants.[7,8] The basic principle of this procedure is to electrochemically oxidize organic matter by

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applying a high potential. This method will degrade organic pollutants into water and carbon dioxide whereas the amount of charge required for electrochemical oxidation is directly proportional to the value of COD. However, this method is practically impossible by using ordinary electrodes because it requires very high potentials to degrade organic pollutants which results in the oxidation of water. In order to shorten the oxidation time, thin-layer electrochemical cells were also fabricated for complete oxidation of organic pollutants.[9,10] In these cells a thin layer of the sample (2–100 μm) was allowed to rest on the electrode surface. This thin-layer electrochemical cell realizes time-effective electrolysis of sample layers with a large ratio of electrode area to solution volume. The coulometric analysis of COD via exhaustive oxidation of organic species is still difficult and requires a long time of about 30 min even in the thin-layer electrochemical cell. In order to overcome these problems, a number of electrodes were designed by coating with electrocatalytic materials which lower the oxidation overpotential as well as shorten the reaction time. The determination of COD in water samples is necessary to evaluate its quality because normally in slightly contaminated water the value of COD is 20–25 mg/L of consumed oxygen[11] and in extremely contaminated industrial wastewater streams its value may increase to 100,000 mg/L.[12]

1.2 Sensors

1.2.1 Pt/PbO_2 Ring-Disc Electrode

The reaction kinetics are very slow when oxidation of the COD pollutants is carried out with oxygen, $K_2Cr_2O_7$, $KMnO_4$, and Ce (IV) which leads to an incomplete or even non-occurring oxidation of some organic compounds even when employing a time-consuming refluxing process in the conventional method. Moreover, inorganic compounds such as (Cl^-, Fe^{2+}) may also be oxidized. Thus, the COD values do not actually reflect the actual concentration of organics present in the sample. In order to overcome these problems, there should be such a species as part of a redox system which should oxidize COD pollutants rapidly and selectively. Moreover, this species should have enough lifetime to react with all the organic species present in the sample. The generation of hydroxyl radicals as an unstable intermediate in the oxygen evolution reaction at the electrode is capable to address all the issues concerning COD values.

A rotating ring-disc electrode (RRDE) was utilized for the determination of chemical oxygen demand (COD).[3] A PbO_2 layer was deposited on the platinum disc surface of the ring-disc electrode because lead oxide is a promising candidate for the direct oxidation of carbohydrates and amino acids. This device was fabricated in such a way to produce a strong oxidant by in situ formation of an aggressive species which oxidizes the compounds that contribute to COD. The aggressive species which are left behind after oxidizing the compounds react with oxygen which is monitored at the ring electrode. In such type of COD sensor, a strong oxidant is electrochemically generated at the disc part of the rotating ring-disc electrode. The COD pollutants are exposed to the RRDE, and some of the pollutants will be directly converted to its elementary components (CO_2 and H_2O) at the disc surface while others will be converted indirectly with the generated oxidant at the disc surface. Thus, organic compounds will be degraded via two different paths. Some organic compounds are directly oxidized at a potential where also the oxygen evolution occurs, and then hydroxyl radicals will be produced as an intermediate. These hydroxyl radicals will consume the rest of the organic compounds and excess of hydroxyl will also be oxidized to oxygen. The generation of a strongly oxidizing agent at the electrode surface has the advantage that it would keep the surface clean by avoiding the adsorption of substances.

1.2.2 F-Doped PbO_2-Modified Electrode

In another approach the electrocatalytic activity of lead oxide was enhanced with fluoride doping. The F-doped lead oxide-modified electrode leads to the fabrication of an electrochemical detection system for flow injection analysis to detect the chemical oxygen demand (COD) in water samples.[13] The combination of flow injection analysis with electrochemical detection of COD results in the development of a low-cost, rapid, and easily automated detection system with minimum reagent consumption. The basic principle of the F-doped lead oxide electrode is the generation of hydroxyl radicals which are subsequently utilized for the oxidation of COD pollutants in order to determine the COD value. It is a multistep process: at first, hydroxyl radicals will be produced at the surface of the F-PbO_2 electrode by the anodic discharge of water:

$$S[] + H_2O \rightarrow S[OH] + H^+ + e^-$$

These hydroxyl radicals will be adsorbed on the unoccupied surface sites (S[]) forming S[OH] which represents the adsorbed hydroxyl radicals. The electrocatalytic activity of lead oxide is amplified with the doping with F^- because it increases the number of unoccupied surface sites.[14] If the reverse discharging reaction is ignored then the O-transfer step can be represented by the following equation:

$$S[OH] + R \rightarrow S[] + RO + H^+ + e^-$$

The COD pollutants are electrocatalytically oxidized by the surface sites and output current signals are produced which are proportional to the COD value. R represents the organic pollutants which are oxidized to RO by the hydroxyl radical. However, the current efficiency of the O-transfer reaction will be decreased by the consumption of hydroxyl radicals which results in the evolution of oxygen by the following reaction:

$$S[OH] + H_2O \rightarrow S[\,] + O_2 + 3H^+ + e^-$$

The higher the overpotential of materials for oxygen evolution, the better the reaction compels the physisorbed hydroxyl radicals to oxidize the organics rather than to turn into oxygen.

1.2.3 Rhodium Oxide–Titania Electrode

Dimensionally stable anodes (DSAs) are usually fabricated by depositing metallic oxides on a metal substrate such as titanium. In order to synthesize DSAs, a precursor such as metallic chloride is decomposed in an oven or by electromagnetic induction heating. However, this procedure is very complex and requires a lot of time to complete. These problems can be solved by using the laser as a heat source for developing DSAs via calcination. The designed DSA possesses very unique properties of high corrosion resistance, robustness, and electrocatalytic abilities. The electrocatalytic activity of DSAs is attributed to the formation of hydroxyl radicals at the electrode surface. These physisorbed species, generated by the oxygen evolution reaction, has the ability to oxidize organic pollutants electrochemically. However, a severe side reaction occurs simultaneously which consumes hydroxyl radicals and results in the evolution of oxygen. Thus, this side reaction competes with the oxidative degradation of organic pollutants and lowers the current efficiency. The problem can be solved by using higher overpotential metal oxides for oxygen evolution which preferentially compel hydroxyl radicals to electrocatalytically oxidize organic compounds rather than to release oxygen. A Rh_2O_3/Ti electrode was prepared by laser calcination to develop an amperometric sensor for the determination of COD.[15] Electrocatalytic oxidation of organic compounds could be monitored with this electrode in flow injection analysis. The current responses from the oxidation of the organic contaminants at the electrode surface were proportional to the COD values.

1.2.4 Boron-Doped Diamond Electrode

Boron-doped diamond (BDD) possesses unique properties such as a wide-range working potential, low background current, stable responses, environmental friendliness, and robustness.[16,17] Thus, boron-doped diamond is an excellent material to design a sensing electrode for electrochemical water treatment.[18,19] A BDD film can be deposited on a support electrode by microwave plasma chemical vapor deposition.

The BDD electrode was employed as a detecting element for determining COD in combination with flow injection analysis (FIA).[20] This continuous flow method led to the development of an online amperometric COD monitoring system which reduced the analysis time significantly. The BDD electrode was deactivated if the applied voltage was very low because of the electropolymerization of some organics such as phenol on the surface of the electrode. This inhibition of electrode could be overcome if a high voltage was applied to hinder the polymerization of organic compounds. The COD values monitored by this rapid online system were closely related to the conventional method. The electrode with BDD acts as a generator for hydroxyl radicals due to its wide electrochemical potential window, and high oxygen evolution potential.[21] The electrochemical oxidation of organic pollutants in water samples by employing BDD electrode is a direct or a hydroxyl radical-mediated process. However, oxidative degradation of organics is mainly dominated by indirect hydroxyl radicals at high potential. Moreover, the oxidative potential of hydroxyl radicals decreases with an increase in pH. At the same time, the overpotential for oxygen evolution will be lowered when the solution becomes more alkaline which leads to oxygen bubbles at the electrode. The excellent correlation of the BDD-detecting element with the conventional method supports the suitability of the proposed sensor for COD detection.

1.2.5 Nano Copper-Modified Electrode

The electrochemical deposition of Cu nanoparticles on a Cu disc electrode led to the fabrication of a sensor device for chemical oxygen demand (COD).[22] The modification of the Cu disc electrode with Cu nanoparticles by using controlled-potential reduction greatly increased the oxidation current signals in comparison to the simple Cu disc electrode. The increase in sensitivity was attributed to the large surface area, and enhanced active sites of nanomaterials in comparison to bulk materials. Thus, nano-Cu exhibited high catalytic activity which resulted in a decrease of the oxidation overpotential and an enhancement of the current signals of the oxidation of organic compounds present in water. In this way, a very sensitive and stable amperometric sensor was developed for the detection of COD.

1.2.6 Activated Glassy Carbon Electrode

A special carbon material called glassy carbon is widely used as electrode material in the field of electrochemistry. The responsive behavior of a glassy carbon electrode (GCE) can be greatly enhanced by means of electrochemical treatment. The GCE can be activated by cyclic sweeps[23] or constant potential oxidation.[24] The activation of glassy carbon electrode (GCE) by applying constant potential oxidation tailors its surface morphology, functional groups, and electrochemical activity.

The oxidative activation method introduces thornlike nanostructures as well as hydroxyl groups on the surface of a GCE which will enhance its electrochemical activity.[25] This strategy develops a very sensitive, low-cost, and simply fabricated amperometric COD detection system having better practical applicability and accuracy.

1.2.7 Cobalt Oxide-Modified Glassy Carbon Electrode

The modification of a glassy carbon electrode with cobalt oxide led to an excellent sensor for chemical oxygen demand.[26] The sensing film of cobalt oxide was prepared on the surface of a glassy carbon electrode via constant potential oxidation. $Co(NO_3)_2$ was used as a precursor for the electrochemical deposition of a thin and homogeneous layer. The electrocatalytic ability of the cobalt oxide film was directly related to the potential applied to the electrochemical film deposition. The sensing film which was prepared at an optimized potential (1.3 V vs. SCE) had a high surface roughness, which enhanced its response area and the number of active sites. The high valence cobalt in the sensing film had the capability to catalytically oxidize reduced organic compounds which led to a decrease of the current signal at 0.8 V vs. SCE. The cobalt oxide film was highly useful for COD determinations and the results were reproducible as the response signal decreased sharply after the addition of the wastewater.

1.2.8 Nickel Nanoparticles

The physical and chemical properties of metal nanoparticles greatly differ from their bulk materials because of their morphology. Nanoparticles show excellent catalytic activity and selectivity towards different analytes if their shape and sizes are properly controlled.[27] The convenient and most suitable way for synthesizing metal nanoparticles is electrochemical deposition. Nickel nanoparticles can be deposited on the electrode surface via galvanic or potentiostatic deposition. A process of constant potential reduction was employed for electrochemically depositing nickel nanoparticles on the surface of a glassy carbon electrode by utilizing $NiSO_4$ as precursor. The sensitive surface fabricated in this way exhibited high electrochemical activity to oxidize reduced organic compounds which resulted in an increase of the oxidation current signals. The catalytic activity of Ni nanoparticles could be enhanced by optimizing the preparation parameters such as reduction potential, deposition time, pH value, and concentration of nickel ions. By optimizing these parameters the shape and sizes of particles were controlled which lead to the fabrication of a sensitive detection tool for the chemical oxygen demand but with poor reproducibility.[28]

1.2.9 Nickel-Copper Alloy Electrode

An environmentally friendly sensor was developed by fabricating a nickel-copper (NiCu) alloy electrode to determine the chemical oxygen demand.[29] The NiCu alloy film was applied to modify the surface of a glassy carbon electrode which led to a very stable detecting element. The surface morphology of NiCu alloy was investigated by atomic force microscopy which confirmed its continuity and uniform thickness over the entire electrode. The chemical composition of the developed NiCu film was evaluated by energy-dispersive X-ray spectrometry which revealed 69 % presence of Ni in the alloy.

Nickel is widely used as an electrode material for electrochemical water treatment as well as in many electrochemical analyses. Moreover, it is an excellent electrocatalyst for oxidizing different organic compounds on the basis of the Ni $(OH)_2$/NiOOH redox couple. Mixing of Ni with Cu enhances the electrocatalytic activity as well as provides long-term stability to the structure. In addition, a wide range of composition of NiCu alloys is possible because both metals have similar face-centered cubic structure.[30] The addition of Cu to the $Ni(OH)_2$/NiOOH redox couple suppresses the formation of γ-NiOOH and enhances the formation of β-NiOOH which is an excellent electroactive substance. The electrochemical activity of NiCu alloy was evaluated by cyclic voltammetry where the electrochemically relevant reactions were attributed to the Ni(II)/Ni(III) redox couple[31]:

$$\mathrm{Ni} + 2\mathrm{OH}^- - 2\mathrm{e}^- \rightarrow \mathrm{Ni(OH)_2}$$

$$\mathrm{Ni(OH)_2} + \mathrm{OH}^- - \mathrm{e}^- \leftrightarrow \mathrm{NiOOH} + \mathrm{H_2O}$$

The formation of $Ni(OH)_2$ at the electrode leaves behind a Cu-enriched surface which can be also oxidized to Cu_2O and finally to $Cu(OH)_2$. At the end, the surface film will be a mixture of NiOOH and $Cu(OH)_2$ where the counterions are mobile enough to maintain electroneutrality at the electrode surface during the redox process. When a NiCu alloy-modified electrode comes in contact with organic pollutants present in the sample the Ni(III) species rapidly oxidize them and form Ni(II) species, as follows:

$$\mathrm{Ni(OH)_2} + \mathrm{OH}^- \rightarrow \mathrm{NiOOH} + \mathrm{H_2O} + \mathrm{e}^-$$

$$\mathrm{NiOOH} + \mathrm{organics}_{(\mathrm{reduced})} + \mathrm{H_2O} \rightarrow \mathrm{Ni(OH)_2} + \mathrm{organics}_{(\mathrm{oxidized})} + \mathrm{OH}^-$$

The electrocatalytic activity of the NiCu alloy electrode is higher than of a Ni electrode because the $Cu(OH)_2$ species enhance the formation of the β-NiOOH phase and suppress the formation of γ-NiOOH. The proposed sensor device based on NiCu alloy is a promising tool for the determination of COD in water quality control and pollution evaluation.

1.3 Total Organic Carbon (TOC)

Total organic carbon is considered as a parameter to assess the organic pollution of a sample.[32] In order to measure the TOC in aqueous solutions two digestion procedures[33] are employed such as high-temperature combustion[34] and photo-oxidation[35] to degrade organics. The basic principle of the abovementioned methods is the complete conversion of organic compounds to carbon dioxide. Then, the evolved carbon dioxide is detected by following traditional analytical techniques such as infrared spectrometry, coulometry, conductivity, flame ionization, or ion chromatography. Both methods demand certain protocols, as oxidation via combustion requires high temperature as well as expensive thermal catalysts. The second method needs UV light of shorter wavelengths in the presence of peroxodisulfate in the sample to completely oxidize organic compounds at moderate temperature. The inexpensive photo-oxidation method has an advantage of measuring lower TOC concentrations in comparison to the combustion method.

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