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Chemically modified electrodes

Chemically modified electrodes comprise an approach to electrode system design that finds use in a wide spectrum of basic electrochemical investigations. Chemically modified electrodes are electrodes, which have been deliberately treated with some reagents having desirable properties, so as to take on the properties of the reagent. It is therefore possible to design electrodes for various purposes and applications, providing new vistas for electroanalysis. The application of chemically modified electrodes in electroanalysis holds prominent place compared to other fields. Chemically modified electrodes have received growing interest in the last three decades. The main goal of this kind of electrodes is the improvement of the selectivity and sensitivity of the electrochemical reactions that occur on their surfaces for different purposes, especially analytical [523,524]. Many different strategies have been employed for the electrode surface modification, such as adsorption, covalent
bonding, polymer covering, and self-assembled monolayers. Chemically modified electrodes have wide potential applications as sensors in medical, environmental and industrial fields. They offer advantages including chemical stability, diffusional barriers to interferents, preconcentration of analytes and versatility.

A chemically modified electrode provides one approach to the development of analytical procedures and techniques employing immobilized reagents. The importance of immobilized reagent-based systems lies in minimizing the amount of expensive reagents required for a particular analysis and hence overall costs. Chemically modified electrodes also plays a role in the development of chemical sensors. Although chemically modified electrodes are often referred to as chemical sensors, a sensor requires a counter/reference electrode and associated measurement electronics in addition to an electrode with an attached reagent. The chemically modified electrode is, however, the essential interface between the sample and the measurement electronics; it provides selectivity, enhances sensitivity and the method of chemically modified electrode preparation will influence overall stability.

Some of the researchers who have recently employed the chemically modified electrodes in the drug analysis were Wang et al [214] described a novel method for the determination of trace metoclopramide by anodic stripping voltammetry with nafion modified glassy carbon electrode and also the method was applied for determination in serum samples. A sensitive square wave voltammetric method was developed for the detection of apomorphine using nafion film modified glassy carbon electrode by Cheng et al [215]. Yanez et al [216] described the determination of nitrendipine an antihypertensive drug with β-cyclodextrin modified carbon paste electrode. A differential pulse adsorption voltammetry for the
determination of procaine hydrochloride at a pumice modified carbon paste electrode in pharmaceutical formulations and urine samples have been reported by Wang et al [219]. Carbon paste electrode modified with β-cyclodextrin have been employed by Ferancova et al [221] for the differential pulse voltammetric determination of tricyclic antidepressants – imipramine, trimipramine and thioridazine. Determination of codeine in urine and drug formulations using a clay modified screen printed carbon paste electrode has been reported by Shih et al [223]. Jayarama Reddy et al described electrochemical determination of Sparfloxacin an antibacterial drug in pharmaceutical formulations and urine samples using a β-cyclodextrin modified carbon paste electrode [483] and differential pulse adsorptive stripping voltammetric determination of nifedipine and nimodipine in pharmaceutical formulations, urine and serum samples using a clay modified carbon paste electrode [525].

The continuous interest in chemically modified electrodes arises from the advantages of the combination of conventional techniques with the chemical, structural and other specific properties of the modifiers. In the present investigation, the modifiers such as β-cyclodextrin, clay and nafion were employed.

A cyclodextrin is a cyclic carbohydrate consisting of glucose units that associate with other organic compounds. The unique property of cyclodextrin is that it forms the inclusion complex with the guest compounds in the cavity. Guest compounds incorporated in the cyclodextrin cavity include various organic species of appropriate size, especially aromatic compounds. The compounds namely Sparfloxacin, Ofloxacin, Norfloxacin, Gatifloxacin and Lomefloxacin, which are analyzed at β-cyclodextrin modified carbon paste electrode,
exhibited significantly improved sensitivity compared with bare carbon paste electrode. This improved sensitivity at modified electrode is due to the formation of complex between β-cyclodextrin and quinolone group present in the drugs. The compounds under investigation are strongly adsorbed on the surface of modified electrode, which is indicated by the cross over point in the reverse sweep of cyclic voltammograms and these cross over point is called the nucleation loop. The sensitivity at modified electrode is twice higher in comparison with a bare carbon paste electrode. The shift of the reduction potentials to more negative values at modified electrode clearly indicates that the preconcentration was possibly due to the formation of the complex between β-cyclodextrin and quinolone group. The preconcentration time at β-cyclodextrin modified carbon paste electrode has been reduced nearly to half the value in comparison with bare carbon paste electrode with significant improvement in the peak currents. It was observed that when β-cyclodextrin modified carbon paste electrode is employed, improved linearity ranges and limit of detection (L.O.D) were obtained in comparison with bare carbon paste electrode. Better recoveries were obtained for the compounds under investigation in pharmaceutical formulations and spiked urine samples. The results indicate that the electrode modified with β-cyclodextrin manifests a maximum attainable voltammetric response and significantly higher than the bare carbon paste electrode. The described procedure with β-cyclodextrin modified carbon paste electrode offers to have good stability, accuracy and low cost, due these reasons it offers a good possibility as a substitute for the previous approaches used in routine analysis.
Clays are aluminosilicates, which present a number of interesting properties such as cation exchange capacity, intercalation, swelling, porosity, catalytic activity and sorption. These clay materials are able to adsorb and incorporate electroactive species for the determination of the analyte. Clays allow efficient preconcentration of the compounds on the electrode surface in some matrices. The compounds namely Nifedipine and Nimodipine, which were analyzed at clay, modified carbon paste electrode exhibited remarkable enhancement in the peak current in comparison with bare carbon paste electrode. The voltammetric currents obtained at clay modified carbon paste electrode is about 2.5 times higher than that observed at bare carbon paste electrode, suggesting that the clay modified carbon paste electrode has better efficiency for accumulating Nifedipine and Nimodipine. The increase in the peak currents at clay modified carbon paste electrode may be due to the fact that the clays are complex microporous media, which have an appreciable surface area and unusual intercalation properties towards organic molecules. Moreover in electroanalysis, accumulation of the analyte in the chemical modifier leads to the higher sensitivity and may also provide improved selectivity. By employing clay modified carbon paste electrode significant improvement in peak currents and decrease in the accumulation time by nearly half (180s) were obtained in comparison with bare carbon paste electrode. Improved linearity ranges, limit of detection (L.O.D), promising recoveries of Nifedipine and Nimodipine in pharmaceutical formulations, spiked urine and serum samples were obtained with a clay modified carbon paste electrode. The method described with clay modified carbon paste electrode is a sensitive, simple, rapid and inexpensive. The method was proved to be suitable...
for the selective measurements of Nifedipine and Nimodipine in pharmaceutical formulations, urine and serum samples with out any preliminary treatment.

Nafion, a perfluorinated sulfonated ion-exchange polymer, has been receiving attention as a modifier for polymer-coated electrode because of its highly stable nature in aqueous solution both thermodynamically and chemically. The hydrophilic charged sulfonate group in nafion enables it selectively to preconcentrate cations by electrostatic interaction, and the hydrophobic fluorocarbon network of the polymer gives it ionic selectivity for hydrophobic organic cations by hydrophobic interaction. These two factors give nafion selectivity for cations and especially high selectivity for hydrophobic organic cations. The local anesthetics drugs Benzocaine and Butacaine which were analyzed at nafion modified glassy carbon electrode exhibited nearly two and half times greater peak currents than at bare glassy carbon electrode. The electrochemical oxidation of the investigation compounds at nafion modified glassy carbon electrode is easier, since the peak potential is reduced by 0.150 and 0.110 V less positive than the one obtained at bare glassy carbon electrode. The enhancement of peak current at nafion modified glassy carbon electrode is due to the preconcentration of Benzocaine and Butacaine in to the nafion film. Improved linearity ranges and limit of detection (L.O.D) are achieved by employing modified electrode. The nafion modified glassy carbon electrode is less susceptible to the peak depression than the bare glassy carbon electrode in the presence of surfactants Triton X-100 or SDS. Besides, improved resistance to interference from ascorbic acid at nafion modified glassy carbon electrode indicates that the modification of the electrode surface by nafion film increases the resistance of the electrode against the surface active substances.