ELECTROCHEMICAL DETECTION AND CATALYTIC OXIDATION OF PHENOLIC COMPOUNDS OVER NICKEL COMPLEX MODIFIED GRAPHITE ELECTRODE

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(Received 10th Dec 2003; accepted 8th April 2004)

Abstract. A Novel Ni(II) mixed ligand complex modified graphite electrode is developed for detection and oxidation of the phenolic compounds based on simple cyclic voltammetric technique. The Ni(II) mixed ligand complex with thiocyanate and macro cyclic ligand 1, 4, 8, 11 tetraaza cyclotetradecane (cyclam) was synthesised and used for catalytic oxidation of phenolic compounds viz. phenol, nitro-phenol and chloro-phenol etc. The Ni(II)-cyclam-thiocyanate mixed ligand complex was synthesised in typical molar ratio of 1:2:5:: Ni(II):cyclam:thiocyanate and crystallized followed by characterization and catalytic applications. The electrochemical study of the complex mediated graphite electrode revealed its fast electron-transfer property, as formation of higher oxidation state of central Ni(II) metal ion as Ni(III) on applying a positive potential, which catalyses the oxidation of the target species. The Ni(II) complex modified graphite paste electrode enhanced the oxidation current of phenolic compounds many times relatively at lower oxidation potential in comparison to simple graphite paste electrode. It is also found to be sensitive for the detection of various phenolic compounds in the range of 20 mg/L to 0.5mg/L in aqueous solution. The Ni(II)-complex stability at higher potential and ambient condition proved its potential for sensing and detoxification of phenolic compounds released in the ecosystem from polluting industries.

Keywords. *Cyclic voltammetry, chemically modified electrode, mixed ligand complex, phenol oxidation, detoxification.*

Introduction

The determination of phenolic compounds is of great importance due to their toxicity and persistency in the environment [1–2]. Natural waters are ultimately contaminated by inputs from all compartments of the environment. Effluents are discharged into rivers, lakes and seas, while superficial and ground waters receive leachates and run off from the land, which is contaminated by industrial waste compounds [3]. Phenolic compounds are the most common organic pollutants, which are highly soluble in water. Phenols and substituted phenols are important contaminants in medical, food and environmental matrices [4]. Phenolic compounds are a class of polluting chemicals, easily absorbed by animals and humans through the skin and mucous membranes. Their toxicity affects directly a great variety of organs and tissues, primarily lungs, liver, kidneys and genitourinary system [5].

Phenol appears in the effluents of many industries such as explosives, coke ovens, phenolic resins, plastic, rubber reclamation, various chemical and pharmaceutical manufacturing processes and oil refineries [6]. Particularly in the case of coal conversion, phenolic residues are considered an acute environmental problem [7]. Soil and surface water from sites around coal production and processing plants were frequently contaminated by phenols, which may cause considerable pollution of groundwater resources [8]. Many industrial processes generate wastewater flows with a high concentration of phenols and other related compounds. About 26.3% of phenol eventually ends up in air, approximately 73.3% in water and about 0.2% in terrestrial soil and aquatic sediments [1]. Many phenols, especially chlorophenols, are known for their persistency in the environment and propensity for bioconcentration and biomagnification. The estimation and detoxification of phenols from wastewaters is, therefore of great importance. Many methods and techniques are available for the determination of phenolic compounds, including gas chromatography, spectrophotometric analyses [9,10] and sensors/bio-sensors [11,12]. However, these methods suffer from complicated process, sample pre-treatment, unsuitable on-site monitoring and do not having the potential for detoxification.

Conventional processes have proven to be efficient in the detoxification of phenolic compounds. However, these processes have certain disadvantages and limitations. The high cost and disposal of contaminated media are the disadvantages of solvent extraction [13] and activated carbon adsorption while biodegradation has been connected with operational problems and bacterial inhibitions [14]. Chemical and wet air oxidation processes have the limitations such as treament effectiveness, cost (main reason), ease of handling, compatibility with precedent or subsequent treatment steps, oxidising agents and nature of the oxidation operation [15,16].

In order to solve this problem, electrochemical techniques have been used [17-19], however, there is still a need to improve the electrode system in order to enhance the sensitivity, simplicity and energy efficiency [20]. Significant attention has been paid for these problems hin the last few years using chemically modified electrodes [21,22]. Although the idea of chemically modified electrodes was first demonstrated systematically in the early 1970’s, this approach has assumed a dominant position in modern electrochemistry [21]. There are different directions by which chemically modified electrodes can benefit analytical applications. These include acceleration of electron transfer reactions (catalytic process), preferential accumulation, or selectivity and stability. Such steps can impart higher selectivity, sensitivity and stability to electrochemical devices [21-24]. Moreover, chemically modified electrodes also offer the possibility of adjustable physical and chemical properties (i.e., charge, polarity, surface area, permeability etc.).

Coordination compounds containing macrocyclic ligands especially “synthetic macrocycles”, viz. phthalocyanines, metalloporphyrins and crown ethers etc., are well known for chemically modified electrodes and development of electrochemical sensors [18,20-24]. However, the stability and electroactivity of the complexes are the major problem in their technological applications. Recently, modified cyclam complexes viz. polymerization or substitution of the cyclam ring or mixed ligand complex have been reported for the construction of chemically modified electrodes in several applications [25-28]. We have recently developed Ni(II)-cyclam-thiocyanate mixed ligand complex and investigated its structure, stability, spectral and electrochemical properties [20].

In the present paper, we report the optimized ratio, construction and application of Ni-cyclam-thiocyanate in the chemically modified graphite paste electrode for catalytic oxidation and low concentration estimation of phenolic compounds using simple cyclic voltammetric technique.

Materials

Materials and Instruments: 1,4,8,11 tetraaza cyclotetradecane (cyclam), graphite powder (2-4 mm) and nujol were obtained from Aldrich Chemicals Company Inc., U.S.A. Potassium thiocyanate and $NiCl_2$ (AR) were obtained from Glaxo Chemicals, Mumbai, India. Tris (hydroxymethyl) aminomethane was obtained from Sisco Research Laboratories, Mumbai, India. All the other chemicals used in this investigation were of analytical extra pure grade.

Electrochemical studies of mixed ligand complex of nickel in solution were performed in a single compartment cell using three-electrode system viz. Glassy carbon (as working electrode), platinum (as auxiliary electrode) and Ag/AgCl (3 M KCl) (as reference electrodes), using Potentiostat/Galvanostat, PG 30, interfaced with a PC, obtained from Autolab, The Netherlands. The Teflon body of graphite electrode or modified graphite electrode was constructed in the laboratory with the help of Electronics Company, ELICO Pvt. Ltd. Hyderabad, India and used for the phenol oxidation and estimation studies.

Methods:

1. Complex Formation: Ni(II)-cyclam complex was prepared in the molar ratios of 1:2 (keeping the concentration of Ni(II) as 20 mM) in 0.2 M tris-buffer, pH 7.2. The

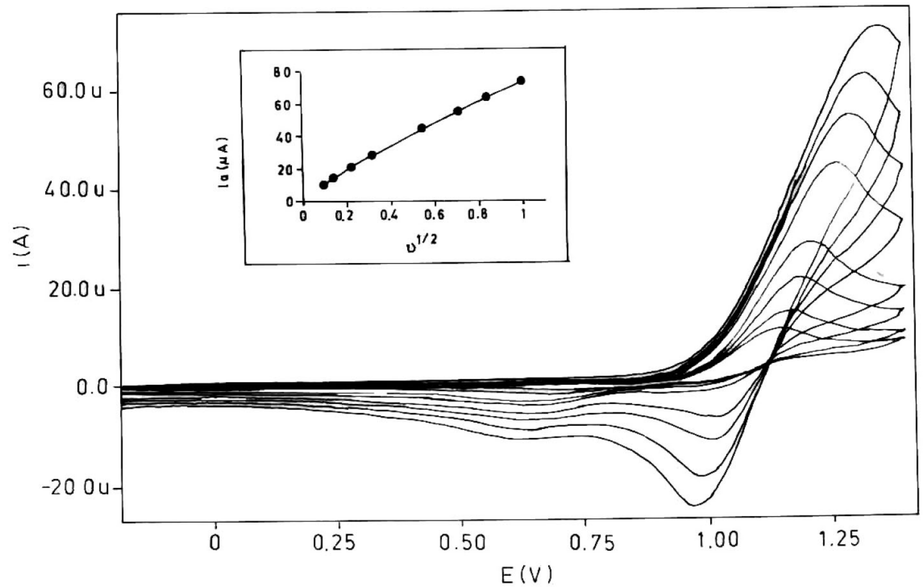

Figure 1. *Cyclic voltammetry of Ni(II)-cyclam-thiocyanate complex in dichloromethane (2 mg/ml) using 0.1 M tetrabutyle ammonium perchlorate as supporting electrolyte at various scan rates from 10 mV/s to 1000 mV/s. Inset: A linear plot for current vs. square root of scan rates.*

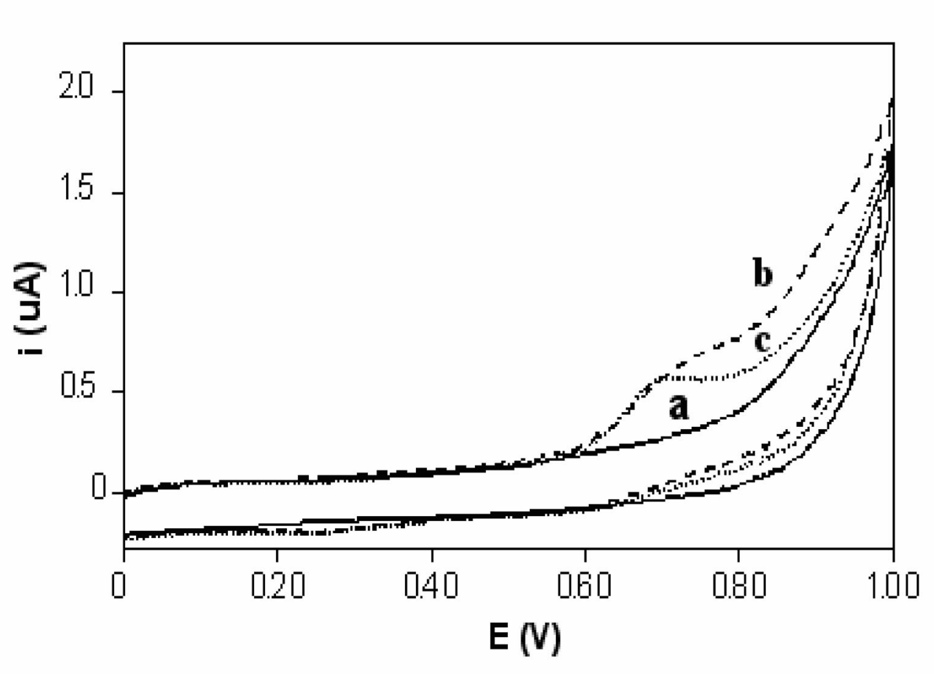

Figure 2. *Cyclic voltammogram in 100 mg/l phenol solution (in 0.2 M Tris-HCl buffer at pH 7.2) for potential range 0.0 V to 1.0 V over (a) 0.0 % (b) 0.5 % and (c) 0.25% Ni(II)-cyclam-thiocyanate complex modified graphite paste electrode.*

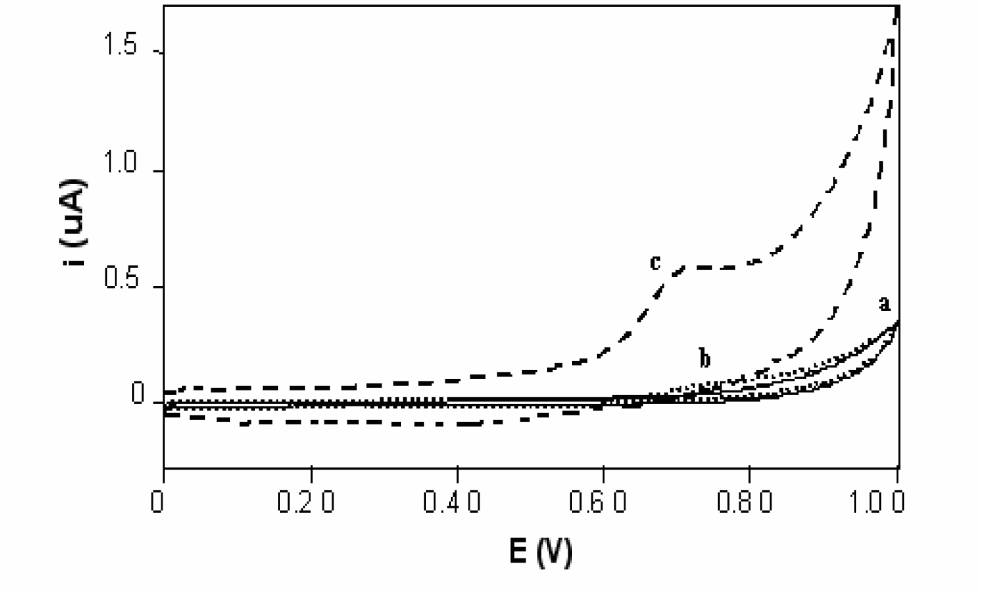

Figure 3. *Cyclic voltammogram in (a) 0.2 M Tris-HCl buffer at pH 7.2 in the potential range 0.0 V to 1.0 V, (b) 100 mg/l phenol solution over graphite paste electrode and (c) 100 mg/l phenol solution over 0.25% Ni(II)-cyclam-thiocyanate complex modified graphite paste electrode.*

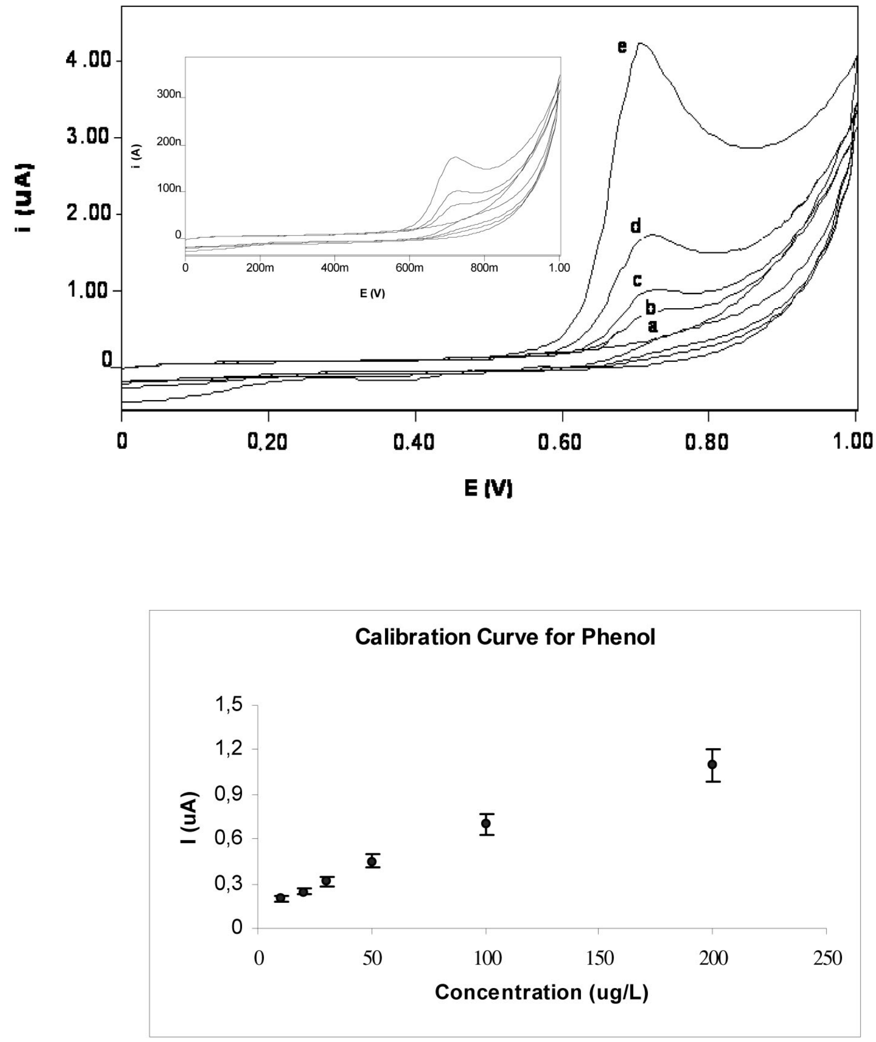

Figure 4. *(a) Cyclic voltammogram (100 mV/s scan rate) over 0.25% Ni(II)-cyclam-thiocyanate complex modified graphite electrode for 0, 50, 100, 200, 500 mg/l and in Inset for 0, 10, 20 and 30 mg/l phenol concentration of phenol in 0.2 M Tris-HCl buffer at pH 7.2 (b) calibration curve for phenol from 10 mg/l to 200 mg/l.*

complex formation was monitored by change in the absorption spectra (in the range of 300-800 nm) and electrochemical behaviour. Mixed ligand complex formation of nickel was carried out by adding thiocyanate solution in 0.2M tris buffer (pH 7.2) to the Ni(II)-cyclam complex in the molar ratios of 1:2:5 and crystalline product was characterized by spectral and electrochemical behaviour as described earlier [20].

2. Preparation of Graphite Paste Electrode and Modified Graphite Paste Electrode: Graphite paste electrode (GPE) was prepared by filling the paste of graphite powder (80 mg) mixed thoroughly with mineral oil (20 ml) into the bottom hole of Teflon body (hole diameter 2 mm and depth 2.5 mm) electrode. This electrode was used for the analysis

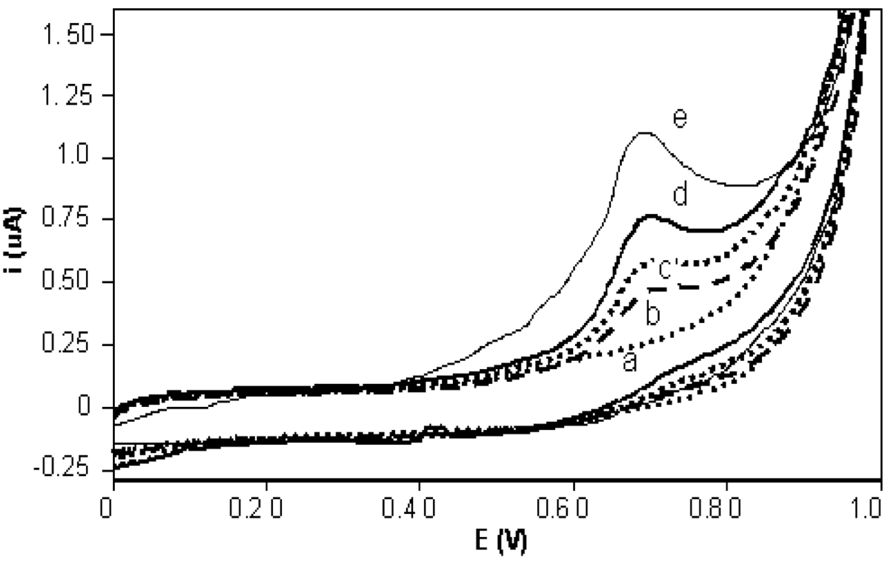

Figure 5. *Cyclic voltammogram (100 mV/s scan rate) over 0.25% Ni(II)-cyclam-thiocyanate complex modified graphite electrode for 0, 50, 100, 200 and 500 mg/l concentration of 2,4-dichloro phenol in 0.2 M Tris-HCl buffer at pH 7.2.*

and oxidation of the phenolic compounds. The catalytic effect of the Ni(II)-cyclam-thiocyanate complex on the electrochemical oxidation of phenol was studied by incorporating the complex in the graphite paste electrode. This is now termed as Modified Graphite Paste Electrode (MGPE). MGPE was prepared by taking various amounts of complex mixed thoroughly with graphite paste and an optimum amount of 0.25% of the complex in graphite paste (by weight) was found to be optimum for the study.

3. Electrochemical Studies: Cyclic voltammetry of GPE and MGPE was performed in the wide range of potential –0.2 V to 2 V vs. Ag/AgCl (3 M KCl) in 0.1M tris buffer, pH 7.6 at room temperature (25°C ± 1°C) and also in the chloroform solution (2 mg/ml) using tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte at various scan rates.

The cyclic voltammetric estimation of phenolic compounds was also done along with the platinum counter electrode and Ag/AgCl (3 M KCl) reference electrode in 0.1 M tris HCl buffer in the range of 0 V to 1 V. The data was recorded on the computer in the software provided with the Potentiostat.

Results and Discussion:

Cyclic Voltammetry (CV) of Ni(II):Cyclam complex (in solution phase) did not reveal any defined redox peak in –0.2 to 2.0 V vs Ag/AgCl range in 0.1 M tris-buffer, pH 7.6, however, the Ni(II)-cyclam-thiocyanate crystalline complex dissolved in chloroform using 0.1 M TBAP as supporting electrolyte exhibited two well defined oxidation peak at 1.15 V along with reduction peak at 1.1 V vs. Ag/AgCl and an irreversible oxidation peak at 1.65 V vs. Ag/AgCl. The CV of Ni(II)-cyclam-thiocyanate complex in chloroform recorded at various scan rates further reveals a pseudo reversible redox

Ni(II) → Ni(III) system with high stability of the complex as shown in Figure 1. A linear plot was observed for the current vs. square root of scan rates (Fig. 1-inset). Indeed, the formation of Ni(II) → Ni(III) are reported in several systems viz. Ni(II)-peptide [28] and Ni(II)-porphyrin [29]. The CV studies for several cycles and at higher potential provided the information regarding reversible redox system and stability of the complex.

The effect of the Ni(II)-cyclam-thiocyanate complex on electrochemical oxidation of the phenol was studied over carbon paste electrode by incorporating with various amounts of complex. The variation of the complex percentage in the carbon paste was studied with the change in the peak height and peak sharpness for 100 mg/l phenol oxidation in 0.1 M Tris-HCl buffer at pH 7.6 in the potential range 0.0 V to 1.0 V vs. Ag/AgCl. A comparison of the CV of MGPE with 0.5% and 0.25% (by weight) Ni(II)-cyclam-thiocyanate complex is shown in the Figure 2. A relatively sharp and at lower oxidation potential (0.7 V vs. Ag/AgCl) peak was observed with 0.25% complex, which was found to be optimum and used for the phenol analysis and oxidation studies.

A comparison of GPE alone and MGPE was done for the oxidation of 100 mg/l phenol in 0.1 M Tris-HCl buffer at pH 7.6 using cyclic voltammetry in the potential range 0.0 V to 1.0 V vs. Ag/AgCl and the data was recorded as shown in Figure 3. A very large difference of oxidation peak current (more than 10 times), relatively at lower potential (0.2 V) was observed for 100 mg/l phenol over MGPE in comparison with simple GPE. The large enhancement of the oxidation current revealed the catalytic effect of the complex, which is probably due to the reversible Ni(II) to Ni(III) conversion at low potential, which serves as a fast electron-transfer mediator for the oxidation process. It has been already reported that electrochemically formed nickel porphyrin coated electrodes exhibit good electrocatalytic activity for the oxidation of carbohydrates and benzyl alcohol [29].

The cyclic voltammogram were recorded over same MGPE for 0 mg/l to 1000 mg/l phenol solution in 0.1 M Tris-HCl buffer at pH 7.6 in the potential range 0.0 V to 1.0 V and a well defined oxidation peak at 0.7 V vs. Ag/AgCl (3M KCl) were observed as shown in Figure 4 (inset for lower concentration of phenol). The calibration curve was plotted with peak current vs. phenol concentration showed a linear response with detection limit of 20 mg/l phenol, which saturated over 200 mg/l. The detection of phenol was also done over simple graphite electrode or graphite paste electrode and no any defined relation were found below 500 ppb of phenol using cyclic voltammetry.

The other phenols viz. chloro or nitro phenols were also studied over MGPE and nearly the same results were observed with 50mg/l detection limit. A typical voltammogram of 2,4-dichloro phenol of 0, 50, 100, 200 and 500 mg/l concentration is shown in Figure 5. The complex modified graphite electrode exhibits the potentiality for the catalytic oxidation for organic materials especially for phenolic compounds.

Conclusion

The reversible Ni(II) to Ni(III) conversion at low potential and fast electron-transfer mediator property of the Ni(II)-cyclam-thiocyanate complex is demonstrated and the property was used for the catalytic application. The enhanced oxidation for phenolic compounds was observed over the complex modified graphite electrode. Thus, nickel complex based electrodes offer an indisputable advantage for developing new electrode materials in the field oxidation of phenolic compounds and also for other organic derivatives. The use of simple cyclic voltammetry makes the technique simple and easy to be used for the application of sensing and detoxification of phenolic compounds and construct the portable devices. These descriptive results constitute the first step in our studies that are under investigation to evaluate this complex in the field of analysis and detoxification of organic pollutants in the industries.

Acknowledgement. The technical assistance of Mr. Ramesh Chandra and Dr. S. K. Hasan is gratefully acknowledged.

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