

Electroanalysis on Polymer-modified Electrodes

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This study describes the preparation and analytical performance of polymer-modified electrodes with anti-fouling or occluding properties. Permselective coatings such as Nafion and hydrolyzed cellulose acetate (CA) were shown to impart higher selectivity, sensitivity, and stability to electrodes probably by excluding any unwanted matrix constituents from the electrode surface while allowing diffusional transport of the target analyte to the electrode surface. Applications described include the anodic stripping voltammetry of Pb(II) ions in the presence of surface-active non-electroactive compounds, and the analysis of phenol (to represent a surface-fouling electroactive analyte) using flow-injection amperometry.

Keywords: modified electrodes; flow-injection amperometry; phenol; lead; anodic stripping voltammetry

INTRODUCTION

Electrode fouling problems limit the application of direct voltammetric measurements in natural waters containing significantly high concentrations of natural organic matter or inorganic colloids. Chemical literature contains numerous reports of the loss of electrode activity due to strong adsorption of sample contaminants and of the products of electrode reactions on the surfaces of solid electrodes [1]. Environmental samples present a challenge for the development of analytical methodology for the selective and quantitative determination of metal ions and organic contaminants at trace levels.

The most promising way to circumvent electrode fouling is to prevent the diffusion of interfering substances toward the electrode surface by coating the electrode surface with permselective polymer membranes, which possess anti-fouling or occluding properties. This modification of electrodes provides protection, which may also confer selectivity to the electrode. Electrode modification may be accomplished via

different schemes, including: (a) coverage with an appropriate polymer film, prepared by casting a solution containing the dissolved polymer onto the surface and allowing the solvent to evaporate; (b) electropolymerization in the presence of the dissolved monomer; (c) chemical attachment wherein surfaces are designed specially for reacting to and binding target analytes; and, (d) adsorption of the modifier onto the surface [2]. The last method, however, often provides an unstable coating, which decreases rapidly with time.

In this study a glassy carbon electrode (GCE) and thin-mercury film electrode (TMFE) were modified by coating with a thin semipermeable membrane using either CA or Nafion (a non-cross linked perfluorosulfonate cation-exchange resin). The test analytes used were Pb(II) ions, in the presence of a surfactant (Triton X-100) and phenol, an analyte known to cause strong electrode fouling. The analytical performances of both the bare and modified electrodes were tested in static conditions or flowing streams (via flow-injection amperometry).

EXPERIMENTAL

Materials. All reagents used were of analytical grade and all aqueous solutions were prepared with ultrapure water (Barnstead Mega-Pure Series 678).

Samples were collected from different sites of the Marikina River, University of the Philippines (Diliman Campus) Lagoon and groundwater near a Shell petrochemical plant in Pandacan (Metro Manila). Marikina River is located at the heart of a city with manufacturing or food industries such as shoes, softdrinks, and poultry. Moreover, commercial establishments also abound near the river. Bunker oil spills from passenger and cargo boats have been noticed and/or reported. Phenol and its derivatives may be detected in the river, since these chemicals comprise the additives in petrochemicals; they may also come from effluents in manufacturing plants and domestic wastewaters.

Domestic wastewaters from several sources in the UP Diliman Campus could enter the UP Lagoon. Phenols (which are found in many household products) may also be present in these wastewaters.

The Shell petrochemical plant in Pandacan conducts quality control of oil, grease, lubricants, fuels, etc. These products undergo treatment to improve their quality before being sold in the market. Apparently, the treatment chemicals and the petrochemical products themselves contain additives, which include phenol and phenolic derivatives. It is possible that the effluents in this treatment plant could contaminate the groundwater through leaching.

Cyclic voltammetry (CV) of phenol. Electrochemical studies were performed using a Powerlab Electrochemical System (Powerlab/4sp and potentiostat from ADInstruments, North Ryde, NSW, Australia) which is an integrated system of hardware and software designed to record, display and analyze electrochemical experimental data. CV of phenol (JT Baker, 99.9%) in ammonium acetate or phosphate buffer supporting electrolyte (Fluka) was performed with a 3-electrode cell (Metrohm, Herisau, Switzerland), consisting of a GCE (2 mm diameter), Ag/AgCl (in 3 M KCl saturated with AgCl) reference electrode, and a platinum auxiliary electrode.

All solutions were degassed with nitrogen prior to the electrochemical studies.

Coating the GCE surface with permselective membranes. The electrode was first polished manually with alumina powder (0.05 μ ; Buehler), rinsed with deionized water and allowed to air dry.

The electrode was coated with 20 μ L of 2 w/v % CA (Fluka) solution (in a 1:1 acetone:cyclohexane mixture). The solvents were allowed to evaporate, leaving a uniform film over the

entire surface. The resulting CA film on the GCE was then hydrolyzed in 0.1 M KOH (Merck) for 30 min then rinsed copiously with deionized water and dried before use.

The electrode was coated with Nafion film by applying on the electrode surface 20 μ L of 1% Nafion (Aldrich, 5% by wt. soln.) dissolved in a 1:1 ethanol-water mixture with a micropipette. The solvent was allowed to evaporate and the Nafion film was dried with a hair dryer for 60 sec.

Physical characterization of the electrode coating. The polymeric films used to coat the GCE in this study were coated on a mica sheet (following the same procedure for coating the electrode surface), which was then mounted on the holder of the atomic force microscope (Shimadzu SPM 9500 MODEL SPM), the scanning probe microscope used for this particular analysis. This particular scanning technique involves the use of the contact mode, where the force between the cantilever tips and the contours of the polymeric film produces an image at the desired magnification. The graphical image of the surface as well as depth and contours of the polymeric film being examined was processed by a computer interfaced to the microscope.

Anodic stripping of lead on Nafion-coated (NC) Thin Mercury Film Electrodes (TMFE). Differential pulse anodic stripping voltammetry (DPASV) at both TMFE and NC-TMFE was used in the determination of Pb(II) in simulated surfactant-containing water samples. Increasing amounts of Triton-X100 (Sigma Chemical Co.) were spiked into solutions of Pb(II) (Merck) ions.

The GCE was coated with 20 μ L of 1% Nafion solution by solvent casting as described earlier. Mercury was deposited *in-situ* on the NC-GCE substrate at -800 mV vs. Ag/AgCl for 150 sec, using a solution of 5×10^{-5} M mercury(II) nitrate (Ajax Chemicals) containing the Pb(II) ions in 0.1 M HCl (Merck) supporting electrolyte.

DPASV measurements were performed with a Metrohm system consisting of 693 VA-Processor + 694 VA-stand, GCE (2 mm diameter), platinum auxiliary electrode and Ag/AgCl (3M KCl) reference electrode.

Flow-injection amperometry of phenol. A single line flow-injection amperometric system was set up for phenol detection. A Metrohm flow cell with a wall-tube configuration was used, which contained a Metrohm working GCE (2 mm diameter) and Ag/AgCl (3M KCl) reference electrode; the auxiliary electrode was the stainless steel bolt in the flow cell. The electrochemical flow-cell detector was then connected to the Powerlab electrochemistry system using the shortest possible length of teflon tubing (0.8 mm i.d.) between sample injector and the inlet to the electrochemical flow detector to minimize sample dispersion. Teflon tubings (0.8 mm i.d.) were used for flow channels and sample volume loops. Water samples and phenol standards were injected into the phos-

phate buffer (pH 6.8) supporting electrolyte which served as carrier stream using a Rheodyne Model 7010 sample injection valve. All solutions were propelled into the FIA manifold using a peristaltic pump (Watson Marlow 302 S).

Spectrophotometric analysis of phenol. A standard spectrophotometric procedure for the analysis of phenol [3] was used to validate the results of the flow-injection amperometric method. In this standard method, phenolic compounds are reacted with 4 amino-antipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The intensity of the color produced was measured at a wavelength of 500 nm and is taken as a function of the concentration of phenolic material.

Biological degradation of the phenolic compounds was minimized by the addition of 1 g/L copper sulfate to the sample and acidification to a pH < 4 with phosphoric acid. The sample was kept at 4°C prior to analysis.

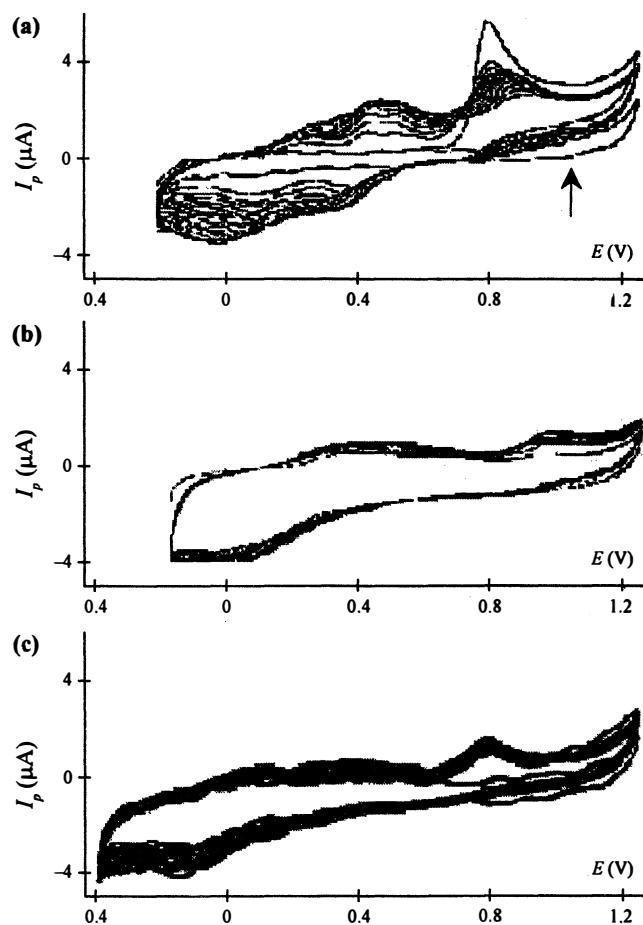


Fig. 1. CV of 1×10^{-4} M Phenol in 0.1 M NH_4OAc buffer, 100 mV/s, 20 cycles at: (a) bare GCE; (b) CA-coated GCE (CA-coating hydrolyzed for 30 min); and, (c) NC-GCE. The percentage decreases in the anodic peak current from the first to the 20th scan: (a) 54; (b) 19; and, (c) 0.4.

RESULTS AND DISCUSSION

CV of phenol on bare and modified GCE. Figure 1a shows the repetitive CV scans of 10^{-4} M phenol on bare GCE in 0.1 M ammonium acetate (NH_4OAc) supporting electrolyte (pH 6.9). The CV response at the bare GCE consisted of a broad irreversible oxidation peak, with the peak potential occurring initially at ~ 0.75 V, and shifting to more positive values with subsequent scans. Electrode fouling may be discerned from the dramatic decrease in current response with subsequent scans. The repetitive scans on the CA and NC electrodes (Fig. 1b and c) show that measured currents were

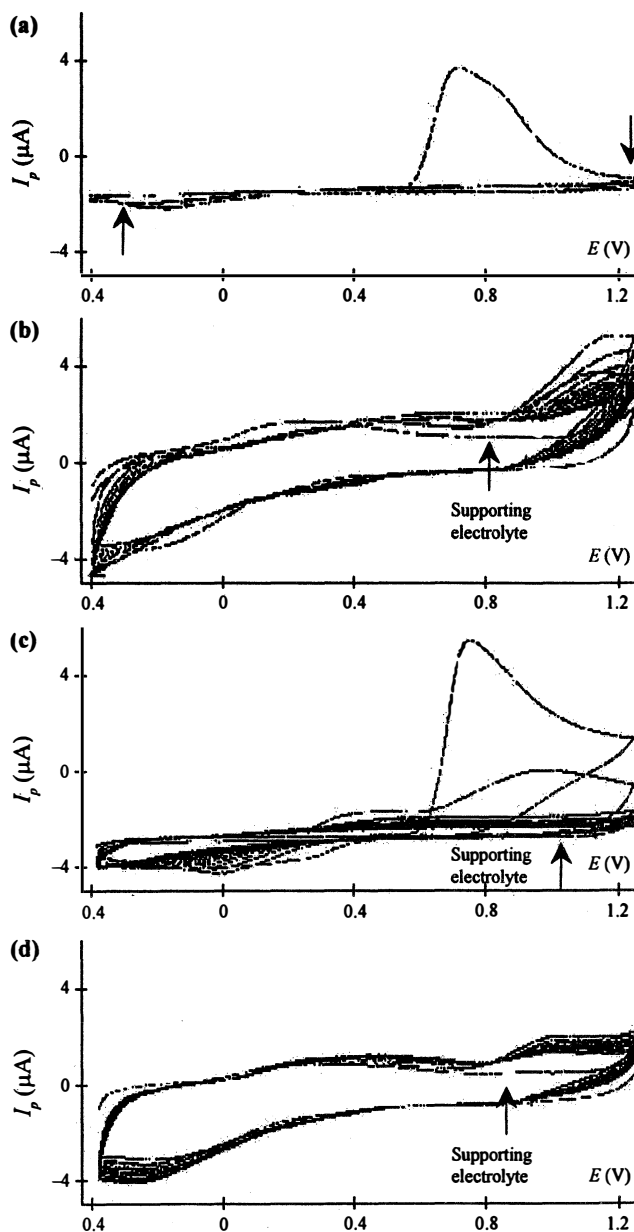


Fig. 2. CV of phenol 0.1 M NH_4OAc buffer; 100 mV/s, 20 cycles. Phenol concentration was 10^{-3} M (a, b) or 10^{-2} M (c, d) using bare GCE (a, c) or CA-coated GCE (b, d). The percentage decreases in the anodic peak current from the first to the 20th scan: (a) 95%; (b) 28%; (c) 96%; and, (d) 49%.

much smaller at the coated electrode than at the bare electrode, indicating a reduced active area. The currents also decreased with repeated scanning, although somewhat more gradually and appeared to achieve a limiting value (see for example Fig. 1b).

The electrode coating apparently slowed down the rate of electrode fouling by phenol and/or its oxidation product(s), and maintained electrode activity even after 20 scans. Figure 1 indicates that the relative decrease in the magnitude of the anodic peak current (i_p) from the 1st to the 20th scan at coated electrodes was much smaller than at the bare electrode.

The peak oxidation potential also occurred at a more positive value for the coated electrode compared to the bare GCE, suggesting that the oxidation process was more difficult on the coated electrode. At phenol concentrations greater than 10^{-4} M, the observed anodic currents decreased very rapidly at the bare electrode, but at much reduced rates at the coated electrodes, as seen in Fig. 2, which shows CV scans for 10^{-3} M and 10^{-2} M phenol.

Several workers [4–6] have reported similar observations on other electrode surfaces. Bejerano *et al.* [4] have studied the electrode fouling effect of phenol on platinum using CV. They concluded that the primary reaction in the oxidation of phenol at platinum electrodes was a one-electron oxidation, which

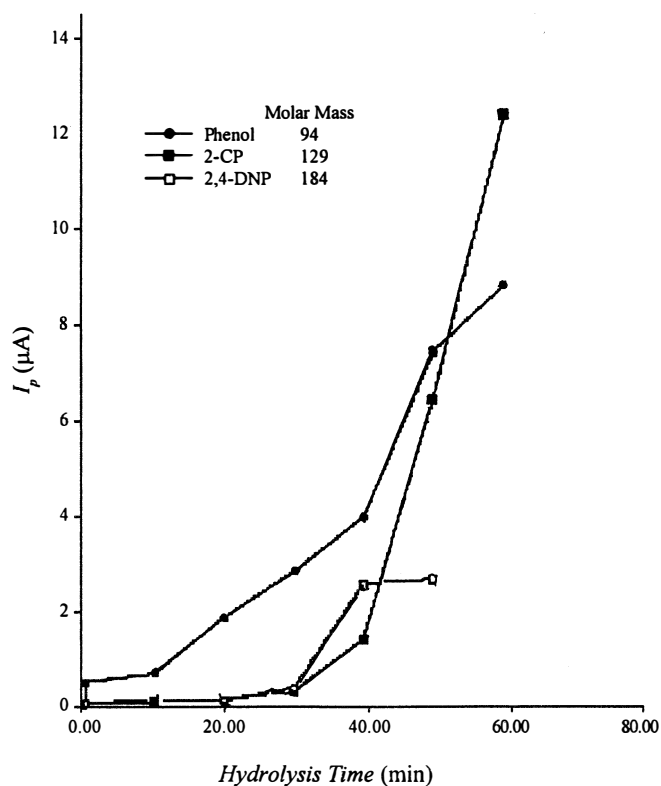


Fig. 3. Observed peak anodic current (1st CV scan) as a function of hydrolysis time of the CA film. Other compounds used: 2-CP = 2-chlorophenol; 2,4-DNP = 2,4 dinitrophenol.

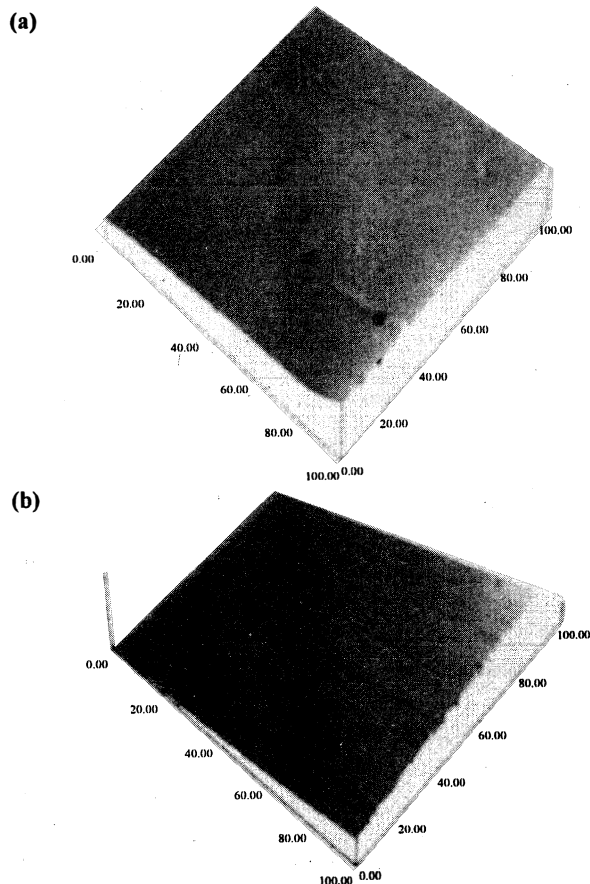


Fig. 4. Atomic force microscopy profiles of CA casted on a mica sheet (100.00×100.00 [mM]); Hydrolysis times: (a) 15 min. (b) 30 min.

produced a very stable phenoxy radical that was adsorbed on the electrode surface. The radicals then polymerized, building up surface layers on the electrode, which caused the loss of electrode activity. The same processes may be assumed to occur during the oxidation of phenol on a bare GCE, as previously described.

Studies on the CA film. The CA film may be hydrolyzed for varying length of time to provide different permeabilities, which impart size-selectivity on the film. Figure 3 shows the dependence of the anodic response of different phenolic compounds at the GCE, which was coated with CA that was hydrolyzed for different lengths of times. The plot suggests a dependence of the films' permeability on the molecular mass and size of the three phenolic compounds tested: phenol (MW = 94), 2-chlorophenol (MW = 128.56) and 2, 4-dinitrophenol (MW = 184.11). At 0 to 20 min hydrolysis time, only the small phenol molecules penetrated the membrane and gave well-defined peak currents. At hydrolysis times greater than 20 min, the permeability of the membrane increased allowing the diffusion to the electrode surface and detection of the heavier and larger molecules (2-chlorophenol and 2,4-dinitrophenol).

Table 1. Anodic stripping voltammetry of Pb on TMFE.

Pb Concentration (mg/L)	TMFE		NC-TMFE	
	E_p , mV	i_p , μ A	E_p , mV	i_p , μ A
0.1	-467 ± 8	32 ± 2	-494 ± 5	21 ± 4
0.2	-469 ± 6	64 ± 1	-480 ± 10	59.5 ± 0.2
0.3	-466 ± 4	84 ± 2	-471 ± 4	93 ± 4
0.4	-466 ± 1	111 ± 6	-471 ± 2	119 ± 3
0.5	-462 ± 1	138 ± 4	-465 ± 0	165 ± 4

Notes:

1. E_p , i_p are the potential and stripping current of the anodic peak.
2. All results are based on three replicate trials.
3. Experimental conditions: Supporting electrolyte: 0.1 M HCl; purging time: 90 s; deposition potential: -800 mV vs. Ag/AgCl; deposition time: 150 s; sweep rate: 120 mV/s

Table 2. Effect of Surfactants on the ASV Peak Stripping Currents.^a

Triton-X Concentration (mg/L)	i_p (μ A)	
	TMFE	NC-TMFE
0	119 ± 1	121 ± 6
1	71 ± 35^b	85 ± 6
2	99 ± 13	66 ± 1
4	~ 0 (blank reading)	60 ± 1
8	~ 0 (blank reading)	51 ± 2
10	c	46 ± 2
15	c	37 ± 5

^a Pb(II) concentration = 0.5 mg/L; other conditions as Table 1.

^b Peaks appeared distorted.

^c Experiment was discontinued.

The microscopic images of some of the CA films at various hydrolysis times are shown in Fig. 4, which confirm that longer film hydrolysis times increased the pore size of the CA film. These observation suggest CA-coating of the required permselectivity may be prepared through proper control of the hydrolysis time of the fresh film.

Anodic stripping voltammetry of Pb on bare and NC-TMFE.

One of the most common problems in anodic stripping voltammetry when applied to the direct analysis of metal ions in polluted waters is the presence of interfering organic components of the sample matrix. Adsorption of surface-active compounds onto the working electrode tends to hinder the diffusional transport of the analyte, leading to depressed anodic stripping peaks. Table 1 shows the response of TMFE and NC-TMFE in varying concentrations of Pb(II) ions in the absence of any organic surface-active compounds. Peak current enhancement and improved precision in current measurements were observed for lead at the NC-TMFE at Pb(II) concentrations of 0.1–0.5 mg/L. The linearity of the peak stripping current responses at both electrodes was comparable, with correlation coefficients (r^2) of 0.9965 and 0.9932 for the TMFE and NC-TMFE, respectively.

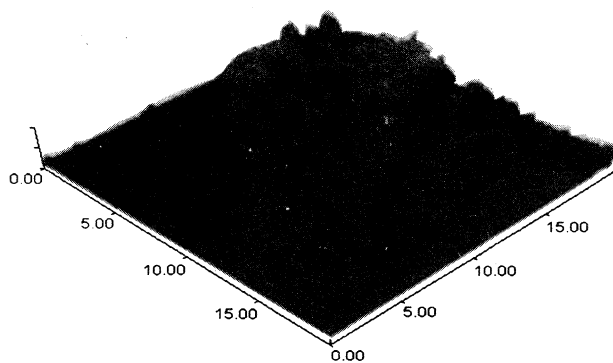


Fig. 5. Atomic force microscopy profiles of Nafion film casted on a mica sheet (20.00 × 20.00 [mm]).

The effect of increasing amounts of Triton X-100 (a non-ionic surfactant) on the stripping voltammetry of Pb on the TMFE and NC-TMFE is shown in Table 2. The stripping peak current of lead (at 0.5 mg/L) decreased with increasing surfactant concentration at both electrodes. At surfactant concentration greater than 2 mg/L, no lead anodic peak current could be observed at the TMFE, suggesting that the surfactant inhibited the diffusion of lead into the electrode by being adsorbed at the mercury surface and preventing the deposition of Pb. The same decrease in the peak current response with increasing surfactant concentration was observed at the NC-TMFE; however, anodic stripping currents were measured even at surfactant concentrations of 15 mg/L. Thus the NC effectively inhibited the surfactant from causing electrode fouling of the TMFE, while allowing the diffusion of Pb(II) ions to the electrode.

Characterization of the Nafion film. Nafion is a non-cross-linked perfluorosulfonate cation-exchange resin. It has hydrophobic ($\text{CF}_2\text{-CF}_2$) and hydrophilic (SO_3H) regions in its polymeric structure [6]. Nafion is chemically inert, non-electroactive and insoluble in water. Visual inspection of the surface of a NC-GCE showed that the coating was transparent and appeared as a duller surface than the bare GCE. Also, tilting the coated electrode at different angles under light showed a highly refractive center zone, which reflected light of a myriad of colors. This pattern probably resulted from the gradual evaporation of the Nafion solution during the preparation of the coating.

The AFM micrograph of the Nafion membrane is shown in Fig. 5. The image suggests that the refractive center zone possessed small finger-like projections at the surface. These protruding fragments could be the anionic regions of the polymer, which may be capable of preconcentrating positively-charged species, such as the Pb^{2+} , present in the solution, leading to the enhancement of the lead stripping peak current response observed at the NC-TMFE.

Table 3. Comparison of flow-injection amperometry at bare and NC- GCE with the standard spectrophotometric method.

Sample No.	Phenol Concentration (μM)			Ratio of Response	
	Standard Spectrophotometric Method	Bare GCE	NC-GCE	Standard to Bare GCE	Standard to NC-GCE
s1	11	4.6	11	2.4	1
s2	11	4.9	11	2.2	1
s3	12	3.6	12	3.3	1
s4	9.9	3.0	7.8	3.3	1.3
Limit of detection	0.2	0.5	0.1		

See Fig. 6 for description of samples.

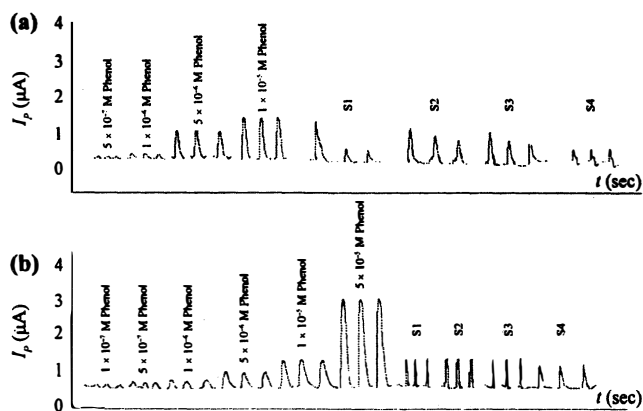


Fig. 6. Flow injection amperometry of phenol at bare GCE (a) and (b) NC-GCE (b). See text for experimental conditions. Samples: S1 = Marikina River water sample—near floating restaurant; S2 = Marikina River water sample—near grotto; S3 = UP (Diliman Campus) Lagoon water sample; S4 = Shell Petrochemical Plant in Pandacan, Metro Manila.

Flow injection amperometry at a NC-GCE. The potential application of coated electrodes in routine flow-injection analysis of phenol in water samples was tested. Water samples were taken from different locations and analyzed for phenol using both bare and coated GCE in a single line flow-injection amperometric system (applied potential of +800 mV). A 0.1 M phosphate buffer (pH 6.8) carrier solution at an optimum flow rate of 1.5 mL/min was used.

Figure 6 shows the typical diagrams of triplicate 500 μL injections of phenol standards, followed by triplicate 500 μL injections of the water samples.

The precision of FIA responses at phenol standard concentrations of 0.1–10 μM at the bare and NC electrodes were comparable: between 1–3% RSD for triplicate injections of each phenol concentration level. However, the FIA responses for the sample gave better precision at the NC electrode (0.2–

0.4% RSD) than at the bare electrode (18–61% RSD). Moreover, the linear concentration range of the bare electrode was narrower (1–10 μM , $r^2 = 0.9974$) than that at the Nafion-coated electrode (0.1–50 μM , $r^2 = 0.9958$). At 50 μM phenol, electrode fouling was evident from the irreproducibility of FIA responses at the bare GCE. The limits of detection at the bare GCE and NC-GCE were estimated as 0.5 μM and 0.1 μM , respectively.

The results of the water sample analyses for phenol content by FIA at bare and coated electrodes were validated against the standard spectrophotometric method for phenol analysis. The results are shown in Table 3. The data show that the results of FIA on NC-GCE gave a better correlation with the spectrophotometric method than FIA on bare GCE: spectrophotometric results were 2.2–3.3 and 1–1.3 times those at the bare GCE and NC-GCE, respectively.

CONCLUSION

Permselective coatings such as Nafion and hydrolyzed CA offer improved sensitivity, selectivity, and stability to electrodes. This is probably achieved by exclusion from the electrode surface of unwanted matrix constituents while allowing diffusional transport of the target analyte to the electrode surface. The CA coating exhibited permselectivity based on pore size (*i.e.*, the membrane hindered the transport of larger analytes to the electrode surface). Obviously a compromise between exclusion of unwanted matrix constituents and the unhindered transport of the target analyte must be sought. The NC, on the other hand, brought stability and sensitivity as reflected by the enhanced stripping peak current of lead using ASV on the NC-TMFE. The NC electrode's enhanced performance appears to be consistent with a charge exclusion mechanism. Finally, the applicability of the NC electrode for routine FIA-amperometry of phenol (a compound which strongly fouls bare electrodes) in water samples gave results which agreed reasonably well with the standard spectrophotometric method.

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