FIBER OF KAPOK (*CEIBA PENTANDRA*) AS COMPONENT OF A METAL SENSOR FOR LEAD IN WATER SAMPLES

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Kapok fibers were utilized as component of a metal sensor. The kapok fiber, which contains lignocellulosic materials, was used as the metal-binding substance in a carbon paste electrode and then used in the voltammetric analysis of heavy metals. Such analysis indicates the capacity to detect lead ions. Optimization of different parameters was done for possible application of the kapok metal sensor as a rapid method for lead analysis of water samples. This has immediate application in testing for purity of domestic and industrial waters.

INTRODUCTION

Kapok [*Ceiba pentandra* (L) Gaertn., Family Bombacaceae], the silk cotton tree, is native to the New World and Africa, found widespread in the tropics and in several plantations in Southeast Asia, and is known for its white silky floss. The Java kapok, *Bombax malabarica,* is native to tropical India, has brownish-yellow floss and is less moisture-resistant.

The kapok fibers attached to the seeds are utilized as packing materials for upholstery, mattresses, pillows, quilts and soft toys (Bates 2004). The kapok fiber is excellent material for these because it is soft, flossy and moisture-resistant. The leaves and bark of kapok are used by the Chinese for their medicinal value while the trunk has been tested as sources of pulp for papermaking (Peralta 1982). Kapok seeds contain oil which is similar to cotton oil.

Lignocellulosic materials in plants have been evaluated for their effectiveness in sorption of heavy metal ions and even non-viable plant biomass have been found to effectively bind toxic metals (Seki et al 1998). Since kapok fiber was found to contain lignocellulosic materials (Hori et al 2000), this study was aimed at looking into the possible use of the fiber as a component of a metal sensor to electrochemically detect the presence of heavy metals such as lead.

MATERIALS & METHODS

Kapok fibers were obtained from kapok fruits, which were abundant around the Physical Science building in the summer of 2003. That is because less than 10 m away grows a giant kapok tree on the streambank of Molawin Creek at the UP Los Baños campus. The fiber was separated from the seeds and fruit cover, air-dried at room temperature, and later cut into smaller pieces using a pair of scissors.

The fiber was mixed with carbon powder and mineral oil to form a paste. A portion of the paste was packed into the end of a hard plastic tube (with a thickness of 2 mm diameter) where a copper rod was inserted to establish electrical contact.

The fabricated kapok modified carbon paste electrode (CPE) was then used as the working electrode in a 3-electrode cell connected to a Metrohm 693 VA processor

where all voltammetric measurements were carried out. The processor was interfaced to a personal computer via an RS232 connection, which converts the generated data into ASCII format. The data obtained was processed using Microcal Origin version 5. A platinum auxiliary electrode and Ag/AgCl reference electrodes were used. All potentials were measured against the Ag/AgCl electrodes.

A standard solution containing 1000 mg/L of lead (II) was obtained from JT Baker. Working solutions of lead were prepared just before use by dilution with deionized distilled water obtained from system. All chemicals were analytical grade reagents.

The electrode was immersed in 10 mL of lead (II) standard solution at a precon-centration cell with constant stirring at open circuit. The electrode was then taken out of the preconcentration solution, rinsed with water and transferred to the voltammetric cell containing a supporting electrolyte that includes 0.1 M sodium hydroxide and 0.1 M hydrochloric acid solution.

Cyclic voltammetry was done using the experimental CPE. A potential range of –1000 to 1000mV and a scan rate of 100mV/s were employed. Optimization of parameters like pH of preconcentration solution, accumulation time, deposition time and deposition potential was done using differential pulse adsorptive stripping voltammetry.

RESULTS & DISCUSSION

The electrochemistry of the kapok fiber metal sensor prior to metal accumulation was examined by cyclic voltammetry. This technique is usually employed as a preconditioning mechanism to effectively eliminate any extraneous matter incorporated onto the electrode surface. In this instance, the surface area of the binding sites for the analyte increases. The potential window of the fabricated metal sensor was determined to be within the range of -1000 mV to +1000 mV (Figure 1). From this potential range, the sensor is inert and may be used to detect electroactive species.

Aside from CV, differential pulse anodic stripping voltammetry (DPASV), another electrochemical method was used. A flat region from -1000 mV to 1000 mV was observed (Figure 2). In this case, any metals whose reduction potential are within this region can be detected if peak signal is generated after accumulation of electrode with metal solutions. A distinct peak at about -500 mV appeared when the kapok-modified electrode was accumulated with lead (II) solution in 0.1 M HCl. A peak near the -650 mV region was also observed when 0.1 M NaOH was used.

Optimization of parameters using both 0.1 M HCl and 0.1 M NaOH was done for lead (II) analysis using DPASV. Accumulation time, which is synonymous with time of preconcentration step, was the first parameter to be optimized. Peak current increases with accumulation time because of the increase in the metal ion concentration at the electrode surface (Figure 3). However, it is expected that the increase in current will level off when all the binding sites have been occupied after continuous immersion. This saturation point is the maximum metal ion concentration at the electrode surface.

The next parameter optimized was the effect of pH on the current signal generated by the electrode. The resulting pH profile (Figure 4) showed that pH 4-6 is the optimum pH range for maximum current response. The pH obtained for the optimum response of the kapok modified CPE agrees with the result of an experiment by Gardea-Torresday (1988), which classified lead as among the metals that are tightly and rapidly bound at pH > 5 and stripped at pH< 2. The voltammograms also showed that at pH higher than 6, the peak current decreases. The decrease in the current response of the electrode at higher pH is due to the formation of the hydroxylic lead complexes that inhibit lead accumulation on the electrode. On the other hand, the low peak current at low pH values can be explained by the protonation of the weakly basic coordinating groups at the surface of the modified electrode (Ramos et al 1993). In addition to this, an acidic media is not a good accumulating solution if the mechanism of accumulation of the lead onto the electrode surface is through ion exchange. In acidic media, protons compete with lead for the negative charges of the carboxylic groups. As a result of this, less metal cation will be adsorbed onto the surface of the electrode, resulting in a decreased peak current response.

Figure 2. CV of kapok modified CPE before and after accumulation with lead ions in different supporting electrolytes
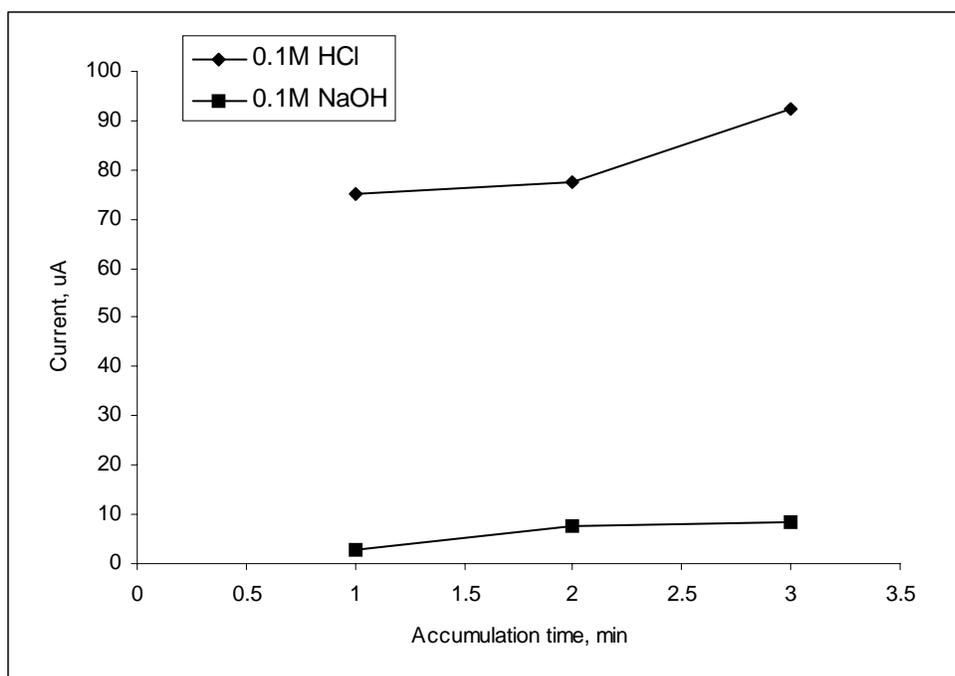

Figure 2. DPASV of kapok modified CPE before and after accumulation with lead ions in different supporting electrolytes
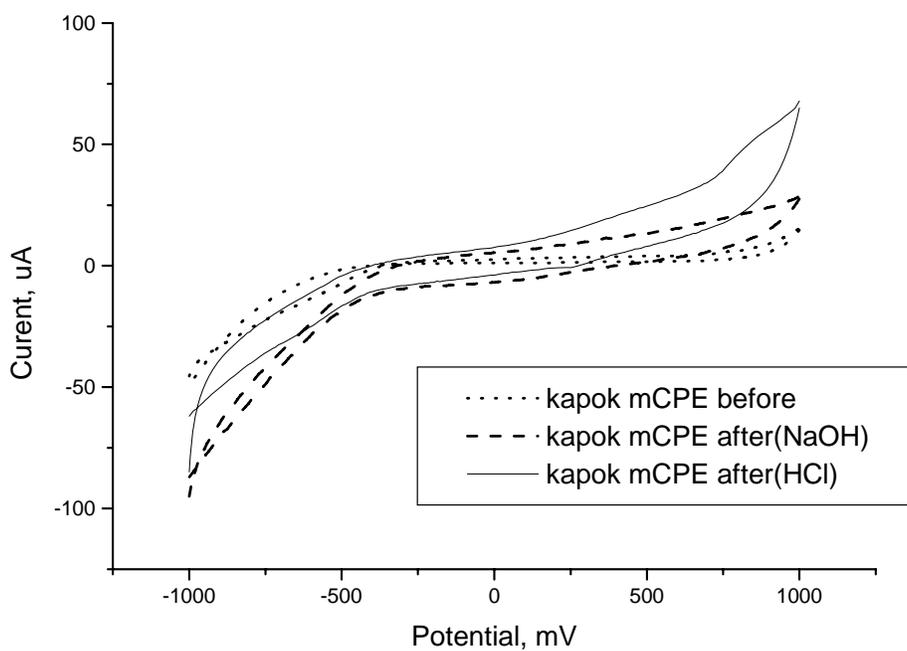
Figure 4. Current generated by different accumulation times of kapok modified CPE in 0.1 M HCl and 0.1 M NaOH
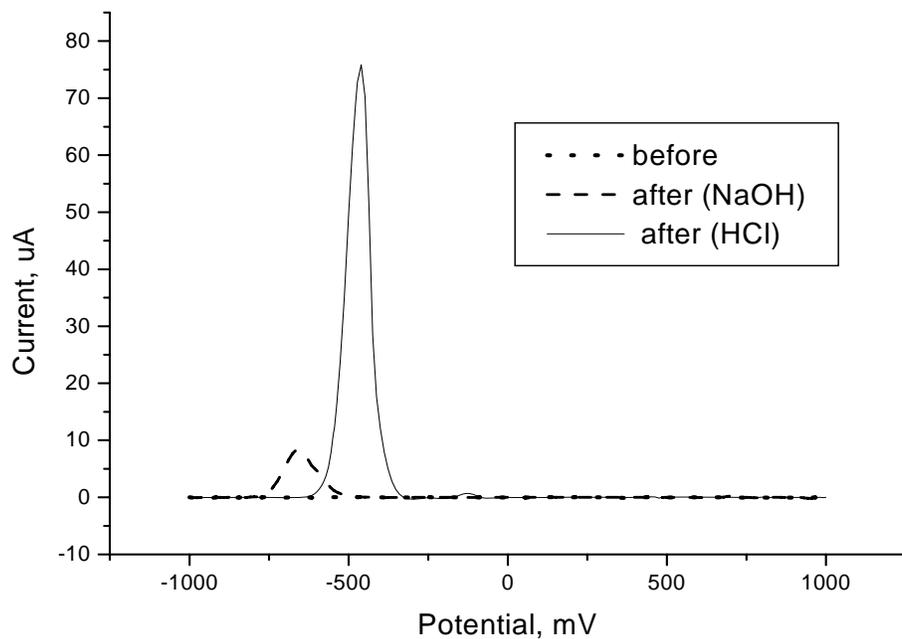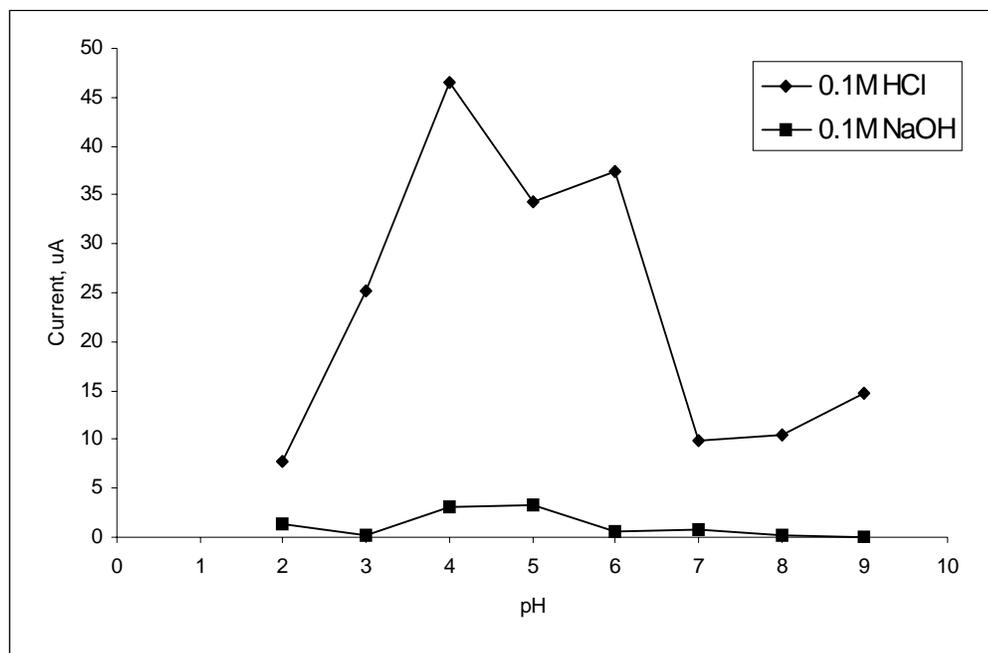

Figure 3. Current generated at different pH of kapok modified CPE in 0.1 M HCl and 0.1 M NaOH

Deposition time and deposition potential were the other parameters optimized. The deposition time is referred to as the time required for the reduction of mercury (II) to its metallic state which happens on the surface of the electrode. For the analysis done using 0.1 M NaOH, peak current increases as the deposition time increases. In comparison with analysis done in 0.1 M HCl, deposition time of 60 sec gave the maximum response. Lastly, the different deposition potential applied in the analysis gave contrasting results in the two supporting electrolytes used. A more negative potential (mV) decreases the current generated for analysis done using 0.1 M HCl while the reverse was observed for analysis done using 0.1 M NaOH.

In all the optimization experiments using the two supporting electrolytes, higher peak response was observed using 0.1 M HCl. It meant that it has a higher sensitivity for the determination of lead compared to 0.1 M NaOH. HCl gave the optimum current response because it is an acid. An increase in the peak current was observed when acid was used as the stripping solution because of its protons' ability to displace lead from the binding positions (Ramos et al 1993). Since acid aids in the stripping of the metal cations on the electrode surface, it enhances the peak current response of the CPE. Moreover, the lead (II) ions readily react with chloride in the HCl. The chloride group of the media complexes lead (II) ions from the electrode into the solution, thus aiding in the stripping of the metal. In addition to that, the chloride ion promotes the oxidation of lead because it is a better leaving group than the other ions.

After optimization, the relationship between different concentrations of lead ions and current generated was tested. Results showed a linear relationship between the lead ion concentration and current signal generated. Thus, the higher the concentration of lead ions, the greater the current peak generated.

Current can be generated for as low as 1.0 mg/L of lead ion concentration. This means that the fabricated CPE sensor when used in optimized conditions can detect lead ions in water samples at a concentration as low as 1.0 mg/L

The ability of the fabricated metal sensor to detect lead is probably due to the affinity of the lead ions with the functional groups present in kapok fibers. Kapok from the Philippines has been found to contain 21% lignin (Hori 2000). Lignins and their derivatives are well known for their ability to bind heavy metal ions (Varma et al 1990, Volchek et al 2000). Lignins are a group of phenolic polymers (Lignin Institute 2001) and their derivatives contain an abundance of oxygen-containing functional groups such as phenolic, alcoholic and carboxylic structures (-OH, -SO$_3$H, C-O-C, C=O), which could possibly form lignin-metal macromolecular complexes with high stability through ionic, hydrogen and coordinate covalent bonding. Peat moss is a very good example of a complex material containing lignins as major constituents that contain polar functionalities such as alcohols, aldehydes, ketones and acids, which can be involved in chemical bonding of cations like heavy metals (Couillard 1994).

Aside from lignin, it is possible that the other materials like cellulose present in kapok can bind with the lead ions. The sorption capacity of lignocellulosics for metal ions is generally described as adsorption. The cations are attracted to negatively charged active sites throughout the lignocellulosic materials. The exact location of the active sites has yet to be determined, but it is believed that hydroxyl and carbonyl groups are the main suppliers of active sites. Other possible mechanisms for the lead affinity of kapok are by chelation and ion exchange of metal ions with the functional groups present in kapok fiber.

It will be noted that untreated kapok fibers were successfully used as metal binding component of the experimental detector for lead ions in water samples. With this result, it is also possible to utilize kapok fibers as remediating materials to remove metal ions present in wastewater effluents and other liquid materials. These abundant materials that otherwise would be wasted could then be turned into high-value materials with high economic value.

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