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Research Article

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Melamine selective electrode based on nanoporous carbon/molecularly imprinted polymer

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ABSTRACT

Potentiometric sensor of melamine based on nanoporous carbon/molecularly imprinted polymer (MIP) have been made and characterized. The purpose of research are to know the optimum conditions in the analysis of melamine and validation method. Molecularly Imprinted Polymer (MIP) is synthesized by mixing 0,2 mmol of melamine as a template, 0,8 mmol of methacrylic acid as monomer, 2,4 mmol of ethylen glycol dimethacrylate as crosslinker end 1 mmol benzoyl peroxide as initiator. Electrode is made by mixing nanoporous carbon, MIP and paraffin in the ratio of 45:20:35. From this research it is obtained optimum pH of melamine solution is 3,0-4,0, the Nernst factor is 54 mV/decade and range of measurement is 10^{-6}M–10^{-2}M. The limit of detection that can be measured by nanoporous carbon/MIP is 8,86x10^{-7} M.. The selectivity coefficient of electrode for Na^+, K^+, Ca^{2+} end Mg^{2+} ions are 2,904x10^{-6}, 6,072x10^{-8}, 2,632x10^{-9}, and 2,566x10^{-9} which means that the ion do not interfere in measurement. This electrodes coefficient is variated it is 1,06% for concentration 10^{-2}M and 2,34% for concentration 10^{-4}M while % recovery is 104,35% for concentration 10^{-4}M.

Keywords: melamine, molecularly imprinted polymer, potensiometry, nanoporous carbon

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INTRODUCTION

At the end of 2008, the world was startled by the news that the milk in People Republic of China (PRC) resulted in thousands of babies suffered kidney damage and kidney failure, four of them died. The cause of this occurrence is the presence of melamine in milk products in PRC[1]. Determination of melamine levels is mostly by liquid chromatography and tandem techniques (combined) LC-MS-MS [2,3]. This method required a very large investment and high operating costs.

A simple analysis of the potentiometric method requires an electrode as a sensor to recognize the target analyte. Electrode surface is a sensor that should contain components that react chemically with the analyte and reversible [4]. Currently, the molecularly imprinted polymer (MIP) has been developed to melamine sensor by potentiometric using modified MIP electrodes membranous PVC type of tubes [5]. However, this type of electrode needs a special skill in its manufacture and prone to leakage.

Modification of electrodes with the MIP sensor can result in a selective and sensitive to the target analytes [6]. Molecularly imprinted polymer with a analyte target as template is a technique that has grown as a sensor that is specific to a particular compound, analogs, or for the enantiomer [7]. This polymer has the advantage of being very stable in organic solvents, extreme pH, and extreme temperature [8]. The advantage of MIP is ideal as an electrochemical sensor. Development of MIP to the type of potentiometric transducer still has not much studied [9].

Molecularly imprinted polymer is known as polymerization technique which is formed by reacting a functional monomer, crosslinker, and initiator molecules that surrounding the template (the analyte). Then the template is removed in several ways, such as by the extraction process, thereby forming a polymer that has been printed in accordance with the analyte molecules. Imprinted polymer is specific to the analyte in the sample [10]. In this study, MIP was mixed in nanoporous carbon as a support attached to surface of electrode body using copper wire as a conductor. This electrode is used as a potentiometric sensor of melamine. Molecularly imprinted polymer is prepared using methacrylic acid as monomer, ethylene glycol dimethacrylate (EDMA) as cross linker and benzoyl peroxide as an initiator. Nanoporous carbon as support material because it is inert and has high conductivity [11].

EXPERIMENT SECTION

The materials used in this study include melamine, methacrylic acid, chloroform, ethylene glycol dimethacrylate (EDMA), benzoyl peroxide (BPO), solid paraffin, ultra high pure water, methanol, glacial acetic acid, and copper wire. All chemicals are used in degree of purity pro analysis. Carbon nanoporous is obtained from forest products research center, Bogor with specification are surface area of 867.5 m^2/g, the degree of crystalline 50.02%, 7.5 Ω resistances, and particle size 100 nm-30 μm. Instruments used in this study include a set of potentiometric CyberScan 510, the reference electrode Ag/AgCl, FT-IR Perkin-Elmer and glassware commonly used in analytical chemistry.

2.1 Preparation and characterization of molecularly imprinted polymer

Molecularly imprinted polymer prepared according to the procedure of Liang et al [5]. Control polymer synthesized in the same way without addition of melamine. For characterization of the MIP and control polymer used FT-IR.

2.2 Preparation of carbon nanoporous/MIP electrode

Carbon nanoporous/MIP electrode is prepared by mixing MIP, carbon nanoporous and paraffin through heating. Mixture which is still hot inserted into the electrode body of a micropipette tip placed where in the copper wire. Further, pressure is applied on the electrode surface to obtain a solid electrode. Electrode surface is smoothed by rubbing it on HVS paper.

RESULTS AND DISCUSSION

Molecularly imprinted polymer is composed of methacrylic acid as monomer, melamine as a template and ethylene glycol dimethacrylate as a cross linker with a mole ratio of 4:1:12. MIP in order to obtain the template is extracted by hot water. Type of bonding that occurs between the template (melamine) and monomer (methacrylic acid) is a non-covalent bond that is more specific hydrogen bonds. MIP which was extracted with hot water will form a mold specific to melamine molecules. Furthermore, polymers were characterized by FTIR

Figure 1 shows that the existence of two absorption bands at 3332 cm-1 and 3419 cm^{-1} which is the absorption band of N-H stretching in primary amines [11]. In the MIP spectrum, after washing it by methanol:acetic acid it is discovered that there is no absorption band at wavenumber around 3350 cm^{-1}, it indicates the absence of the primary amine N-H in MIP. This is due to the melamine -NH_2 groups formed hydrogen bonds with the-COOH group of methacrylic acid. Whereas after washed MIP with water 70 °C, the spectrum there is no absorption band at wavenumber around 3350 cm-1 band but there is widen absorption at 3431 cm^{-1} indicating the presence of the OH group of methacrylic acid. In the MIP which is only washed by methanol:acetic acid there is no-OH groups due to hydrogen bonding with the amine group on the melamine.

Table 1 The effect of nanoporous carbon and MIP composition to potential of melamine

Electrode	Nanopore carbon (%wt)	MIP (%wt)	Paraffin (%wt)	Nernst factor (mV/decade)	Range of measurement (M)	Correlation Coefficient (r)
E1	65	0	35	25,2	10^{-5}-10^{-3}	0,920
E2	50	Control Polymer	35	32,0	10^{-4}-10^{-2}	0,631
E3	45	20	35	54,0	10^{-6}-10^{-2}	0,996
E4	40	25	35	15,3	10^{-6}-10^{-2}	0,949

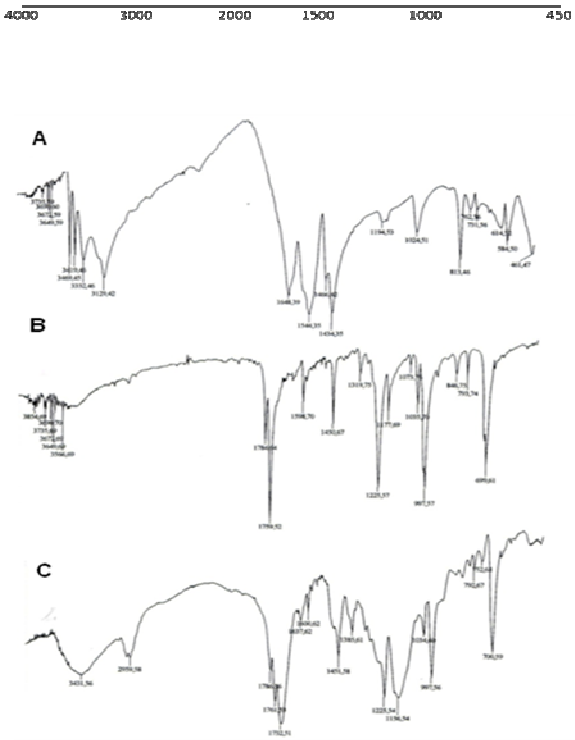

Figure 1 FT-IR spectra of (A) melamine, (B) MIP after washing by methanol: acetic acid, (C) MIP after washing with water 70 ºC

3.1 Optimization of electrode composition

The four electrodes that have been made are used to measure the melamine solution with a concentration of 10^{-8} – 10^{-2}M. By considering the Nernst factor, correlation coefficient and the measurement range of the obtained optimum composition ratio of carbon electrodes with nanoporous and MIP at 45:20 is E3 to the Nernst factor is 54.0 mV/ decade, the measurement range of 10^{-6}M–10^{-2} M and the correlation coefficient is 0.996 (Table 1).

The amount of MIP which is added will affect the amount of the active recognition of melamine molecules and thereby increasing the selectivity of the electrodes. However, the addition of MIP 25% will not show a good response is possible because the membrane becomes rigid.

3.2 Optimization of pH

Measurements were made the concentrations of 10^{-3} M melamine solution. Figure 2 shows that at pH 3-4the potential value the constant, so selected as the optimum pH. At this pH, melamine is in the form of molecules that fit the print, so that they can give better response and stable. At pH <3 melamine will hydrolyze and change the structure into amelina, amelida and cyanuric acid (Bozzi et al., 2004). While at pH> 4 the amine group on the melamine is likely to react with OH that is gradually forming other compounds that are less stable. Melamine structure changes into amelina, cyanuric acid and amelida which is caused by hydrolysis can be seen in Figure 3.

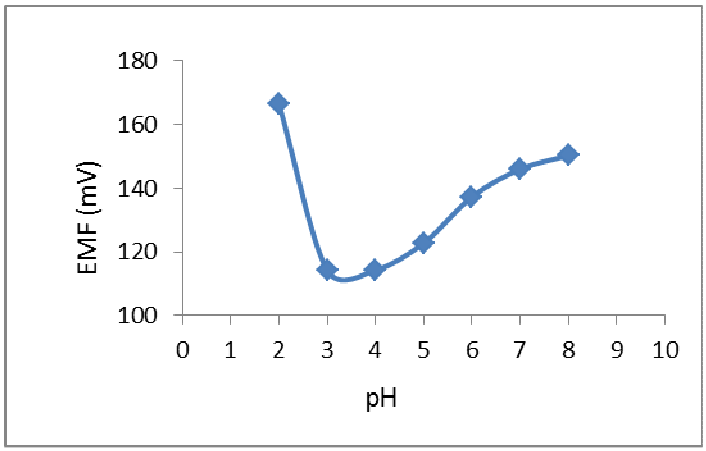

Figure 2 The effect of pH on the potential solution of melamine 10^{-3} M

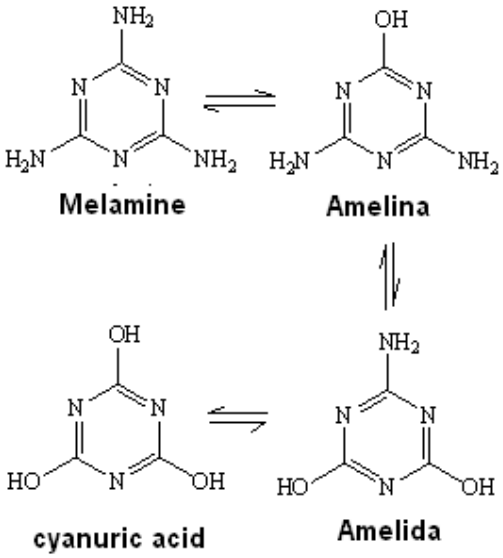

Figure 3 Hydrolysis of melamine (Bozzi, 2004)

3.3 Calibration curve of melamine

Potentiometric calibration curve is a curve relationship between log concentrations of the solution to EMF according to the Nernst equation. Using the E3 as the working electrode and Ag/AgCl as reference electrode, a calibration curve obtained the concentration of melamine who gave a linear relationship is 10^{-6}- 10^{-2} M as can be seen in Figure 4.

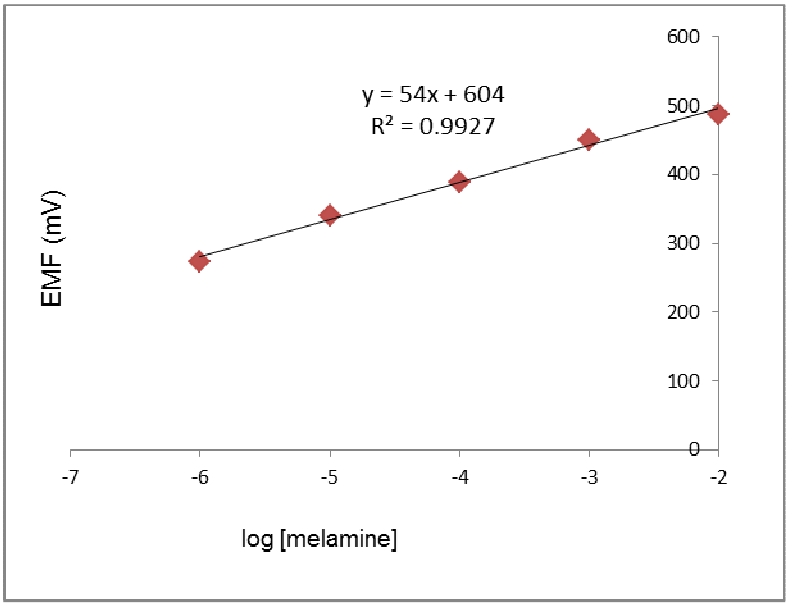

Figure 4 Calibration curve of melamine

3.4 Detection limit

The detection limit of the electrode can be obtained by making two lines of the function is non-linear function of the line to the curve of potential (mV) versus log [melamine]. Both functions are then defined lines of intersection points. If two lines are intersection extrapolated to the abscissa, will be obtained log concentration of melamine detection limit of the electrode. In this study, the detection limits obtained from the electrodes at the concentration 8.86 x10^{-7}M. The results of this study is better than study conducted by Liang, et al [6] which used a tube type membrane electrode with detection limit of 6x10^{-6} M.

3.5 Accuracy

Accuracy which is the magnitude of percent recovery represented by the value of the ratio between the concentration of standard solution recovered by the actual concentration of standard solutions. Determination of melamine

recovery of the solution concentration 10^{-4} and 10^{-2} M are 104 356 and 71 097% respectively. In this case did not measure repeated (Table 2). In this study, nanoporous carbon/MIP electrode has good accuracy for the concentration of 10^{-4} M because it still come into the allowed range are 90-107% [14].

Table 2 Measurement accuracy of melamine with carbon nanoporous/MIP electrode

Actual contentration (M)	Concentration measured (M)	Accuracy (%)
10^{-4}	$1.04x10^{-4}$	104.356
10^{-2}	$7.1x10^{-3}$	71.097

3.6 Precision

Determination of precision used in the solution of melamine with a concentration 10^{-2}M and 1 measured 3 times. Precision value is indicated by the value of the coefficient of variation (CV). In the analytical measurement, a good precision is <3%. [15] Based on the data, coefficients of variation obtained with a good precision, which is 1.06% and 2.34% (Table 3).

Table 3 Coefficient of variation of measurement

Concentration of melamine (M)	Potential (mV)			CV (%)
	1	2	3	
10^{-4}	389	396	378	2.34
10^{-2}	488	478	485	1.06

3.7 Selectivity

The Selectivity of an electrode is indicated by the value of selectivity coefficient *Ki,j*. To prove the selectivity of the carbon nanoporous/MIP electrode, solution is measured by Na^+, K^+, Ca^{2+} and Mg^{2+} ion as interfering with each concentration 10^{-1} M. If $K_{i,,j}$ <1, the electrode is selective to the *i* ion (primary ion) than the *j* ion (interfering ion). If the value of $K_{i,j}$ > 1, the electrode is more selective toward the ion interfering than the primary ion. [16] The Selectivity coefficient values are shown in Table 4. Based on data obtained by the electrode is highly selective for melamine because of the selectivity coefficient has a value smaller than 10^{-3}.

Table 4 The coefficient of selectivity of the carbon nanoporous/MIP electrode as a sensor of melamine in potentiometric

Concentration of melamine (M)	Potential (mV)			CV (%)
	1	2	3	
10^{-4}	389	396	378	2.34
10^{-2}	488	478	485	1.06

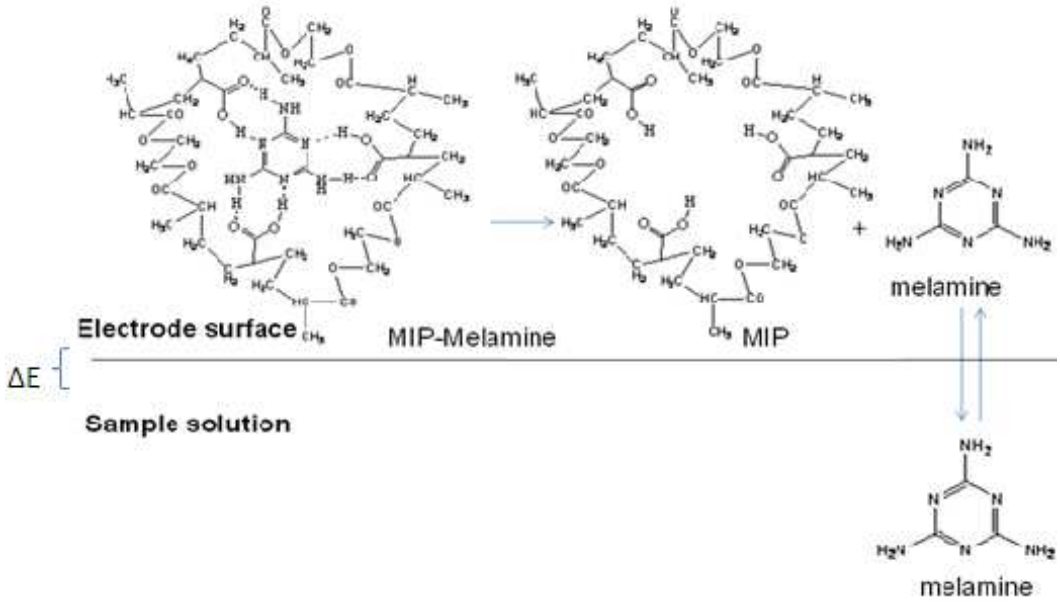

Figure 5 The mechanism that produces potential difference at interface the membrane nanoporous carbon/MIP surface electrode and a solution containing the analyte. The structure of the MIP and MIP-Melamine adopted from Liang, 2009

3.7 Potential Response Mechanism

The mechanism of occurrence of the potential difference is shown in Figure 5. In the nanopore carbon/MIP electrode there is equilibrium between the MIP-melamine become MIP and melamine. The presence of melamine in the sample solution will disturb the equilibrium of MIP-melamine in the nanopore carbon/MIP electrode. This led to

disruption of the equilibrium potential difference which then responded by potentiometer.

CONCLUSION

The optimum composition of the carbon nanoporous/MIP electrode are nanoporous carbon 45%, MIP 20 % and paraffin 35%. The optimum pH measurements melamine solution are at pH 3-4. These electrodes have Nernst factor, measuring range, detection limit and selectivity coefficient for Na^+, K^+, Ca^{2+}, and Mg^{2+} ions are 54.0 mV/decade, 10^{-6} M─10^{-2} M, and $<10^{-3}$ respectively.

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