

ANALYSIS OF CREATININE BY POTENTIOMETRIC USING ELECTRODE CARBON PASTE MODIFIED BY MOLECULARLY IMPRINTED POLYMER AS SENSOR

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ABSTRACT

This research aims to develop an electrode carbon paste-molecularly imprinted polymer (MIP) as sensor for the analysis of creatinine by potentiometric. The preparation of non-imprinted polymer (NIP) is done by mixing aniline, creatinine and potassium peroxodisulfate with mole ratio of 2:0.1:1. Creatinine is extracted from the polymer using hot water to form mold creatinine, this so-called MIP. In this study, the optimum electrode having composition made of activated carbon, paraffin, and MIP of 40:35:25 (mass ratio) and response time for 91-192 seconds. Nernst factor obtained from this study was 23.2 mV/decade, the measuring range of 10^{-6} - 10^{-3} M, lower detection limit of 5.49×10^{-6} M and the upper detection limit of 1.07×10^{-3} M. The accuracy of methods for concentration of 10^{-6} - 10^{-3} M was 76.40% - 165.80% and the precision is expressed by the coefficient of variation for the concentration is 0.05% - 0.32%. The electrodes are still well used up to 83 times of usage. Urea does not interfere with the performance of the electrode carbon paste-MIP on the analysis of creatinine.

Keywords: Creatinine, Molecularly imprinted polymer, Carbon paste, Potentiometric

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INTRODUCTION

Creatinine is a metabolic waste product of the breakdown of muscle creatine. The creatinine levels in the blood serum indicate an equilibrium between production and excretion by the kidney and is an indicator of kidney function.¹ Normal concentrations of creatinine in the blood serum for adult males is 0.62 to 1.10 mg/dL and 0.45 to 0.75 mg/dL for adult women.² Increased serum creatinine levels, comparable to the decline in the quality of the kidneys, so that the analysis of creatinine levels in the blood is very important to know the quality of work the kidneys.

Creatinine analysis methods that are generally used in the medical field is the Jaffe method. Analysis of creatinine using the Jaffe method has a principle, namely by forming a colored complex solution which can be analyzed by UV-Vis spectrophotometer. The advantages of this method is an analytical process is easy and simple, while the drawback is the low selectivity. Other common methods used for the analysis of creatinine is the enzymatic method. Analysis of creatinine with this method is hardly bothered by another matrix, but it takes a long time for the analysis and the cost is quite expensive.³

Another method that has been used for the analysis of creatinine is potentiometric method. In the potentiometric method used two electrodes, the working electrode and reference electrode.⁴⁻⁸ The function of the working electrode is censoring the analyte in the solution being analyzed, so that the working electrode must be selective and sensitive to analyte. Electrodes used for potentiometric analysis can be modified with the aim to increase the selectivity and sensitivity to analyte. Therefore in this research the analysis of creatinine by potentiometric conducted using carbon paste electrodes modified with MIP made from aniline as monomer.

EXPERIMENTAL

Materials and Chemicals

The chemicals used in this study were creatinine ($C_4H_7N_3O$), aniline ($C_6H_5NH_2$), potassium peroxydisulfate ($K_2S_2O_8$), hydrochloric acid (HCl), acetic acid (CH_3COOH), sodium acetate (CH_3COONa), urea ($CO(NH_2)_2$), activated carbon, solid paraffin, and Ag wire. Chemicals used have degree of purity of pro analysis. The water used is distilled water.

Preparation of Polyaniline

Polyaniline made with pipette 0.3 mL of aniline, mixed with 7.5 mL of HCl 1 M. Then the solution was stirred with magnetic stirrer and heated for 30 minutes at $50^\circ C$. After 30 minutes was added potassium peroxydisulfate solution are made 0.5000 g of potassium peroxydisulfate and dissolved in 2.5 mL of distilled water. The addition of potassium peroxydisulfate done slowly and stirring is slowed. Then the solution is allowed to stand at room temperature for 12 hours. The solids that formed were washed using HCl 1 M and dried in oven.

Preparation of Non-molecularly Imprinted Polymer (NIP)

The preparation of non-molecularly imprinted polymer (NIP) done by mixing the monomer, initiator, and templates (analyte) with mole ratio of 2:1:0.1. Monomers used in this study is aniline, initiator is potassium peroxydisulfate, and as template is creatinine. Aniline pipette 0.3 mL, mixed with 7.5 mL of HCl 1 M and added as much as 0.0183 g of creatinine. The mixture is stirred with magnetic stirrer and heated at $50^\circ C$ for 30 minutes. Then added potassium peroxydisulfate solution (made of 0.5000 g of potassium peroxydisulfate in 2.5 mL of distilled water) done dropwise with stirring slowed. The solution was allowed to stand at room temperature for 12 hours and washed using HCl 1 M. Then the solid was heated in oven to obtain dry powder.

Preparation of Molecularly Imprinted Polymer (MIP)

Half of the NIP is used to make molecularly imprinted polymer (MIP). MIP is made by extracting creatinine from synthesis result of NIP using hot water ($50^\circ C$) through the centrifugation technique for 20 min. Extraction performed 10 times. The solid was subsequently dried in oven.

Preparation of Carbon

Preparation of carbon is done by chemical and physical activation. The chemical activation is done by soaking carbon in solution of HCl 4 N for 24 hours and then soaked in n-hexane. Physical activation is done by heating the carbon at temperature of $500^\circ C$ in furnace.

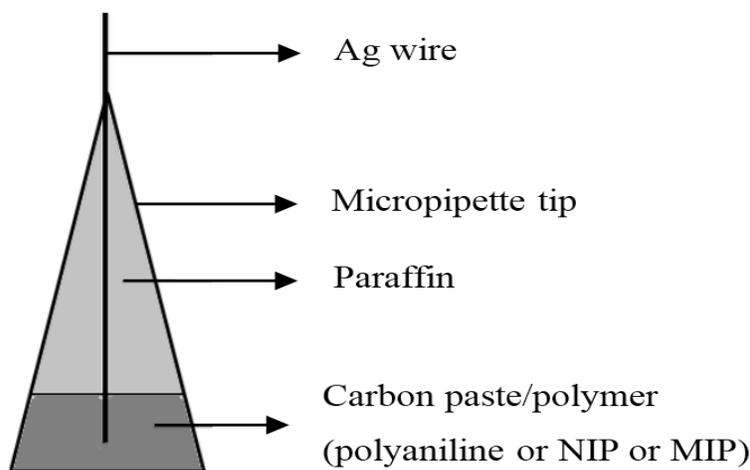


Fig.-1: The construction of electrode carbon paste-polymer (polyaniline or NIP or MIP)

Preparation of Electrode Carbon Paste-Polymer (Polyaniline or NIP or MIP)

The electrode carbon paste-polymer (polyaniline or NIP or MIP) made with set Ag wire in 1 ml micropipette tip. The function of Ag wire is as liaison between the electrodes with potentiometer. Then micropipette tip filled with solid paraffin up to three-quarters. The remaining parts are still empty micropipette tip is filled with mixture of activated carbon, paraffin, and polymer (polyaniline or NIP or MIP). The mixture of activated carbon, paraffin, and polymer (polyaniline or NIP or MIP) added with certain ratio (40 : 35 : 25 (% w/w)). Before placing the micropipette tip, solid paraffin is heated in watch glass at 60°C using hotplate. Filling the mixture into micropipette tip is done by way of emphasis. The surface of electrode carbon paste-polymer (polyaniline or NIP or MIP) scrubbed using the HVS to be smooth. The construction of electrode carbon paste-polymer (polyaniline or NIP or MIP) shown in Figure-1.

RESULTS AND DISCUSSION

Comparison of the performance electrode carbon paste-polyaniline, electrode carbon paste-NIP, and electrode carbon paste-MIP

This study compared the performance electrode carbon paste-polyaniline, electrode carbon paste-NIP, and electrode carbon paste-MIP. These electrodes are made with the same composition and are used to measure the potential of the creatinine solution with concentrations of 10^{-6} - 10^{-3} M at pH 6. From the measurements results can be made the curve with relationship between potential against log concentration. The curve with relationship between log concentration against potential of electrode carbon paste-polyaniline, electrode carbon paste-NIP, and electrode carbon paste-MIP can be seen in Figure-2.

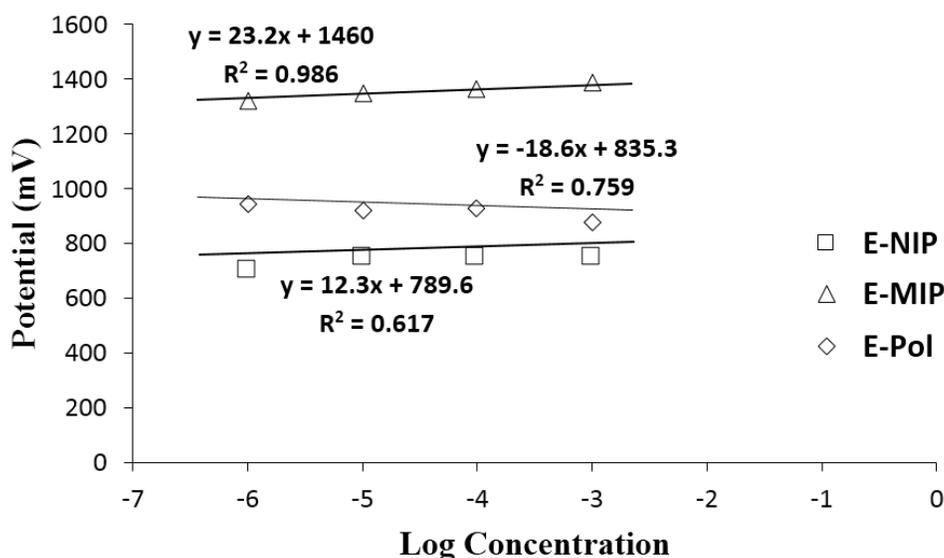


Fig.-2: The curve with relationship between log concentration against potential of electrode carbon paste-polyaniline, electrode carbon paste-NIP, and electrode carbon paste-MIP

Figure-2 shows that the measurement result using electrode carbon paste-MIP has better Nernst factors and linearity compared to the others. That is because the MIP has active specific site to the analyte, so that performance is more optimal than the electrode carbon paste-polyaniline and electrode carbon paste-NIP.

Comparison of potentiometric methods using electrode carbon paste-MIP with previous method for analysis of creatinine

In this study conducted comparison analysis of creatinine using the potentiometric method with previous methods, such as HPLC⁹ and stripping voltammetry¹⁰. The comparison results of these methods showed that each method has advantages and disadvantages. Potentiometric method has wider measuring range and

better response time compared with HPLC method. But voltammetry method has lower detection limits and better accuracy than the potentiometric method. The comparison of analysis methods of creatinine can be seen in Table-1.

Table-1: The comparison of analysis methods of creatinine

Methods	HPLC ⁴	Voltammetry ⁵	Potentiometric (this study)
Detection limit	$0.0083 \times 10^{-3} \text{ M}$	$1.30 \times 10^{-9} \text{ M}$	$5.49 \times 10^{-6} \text{ M}$
Measurement range	$4.40 \times 10^{-6} - 3.52 \times 10^{-4} \text{ M}$	$2.20 \times 10^{-8} - 7.40 \times 10^{-4} \text{ M}$	$10^{-6} - 10^{-3} \text{ M}$
Response time	252 sec	-	91-192 sec
Accuracy	94-104%	99-105%	76.40% - 165.80%
Selectivity	-	Selective in the creatinine matrix rather than NaCl, creatine, urea, glucose, phenylalanine, tyrosine, histidine, and cytosine	Selective in the creatinine matrix rather than urea
Life time	-	-	83 times

CONCLUSION

From the research that has been done it can be seen that the analysis of creatinine by potentiometric can be done use electrode carbon paste-MIP with composition of activated carbon, paraffin, and MIP was 40 : 35 : 25 (% , w/w). The electrode carbon paste modified with MIP made from aniline as monomer to the analysis of creatinine by potentiometric has response times for 91-192 seconds. The electrode measurement range is $10^{-6} - 10^{-3} \text{ M}$, the obtained Nernst factor is 23.2 mV/decade, the lower detection limit of $5.49 \times 10^{-6} \text{ M}$ and the upper detection limit of $1.07 \times 10^{-3} \text{ M}$. Accuracy of methods for concentration of $10^{-6} - 10^{-3} \text{ M}$ is 76.40% - 165.80%, and the obtained coefficient of variation is 0.05% - 0.32%. Based on selectivity test can be known that urea did not interfere on the analysis results of creatinine. In addition it can be seen that the electrode carbon paste modified with MIP can be used up to 83 times.

REFERENCES

1. M.M. Horne and P.L. Swearingen, *Fluids, Electrolytes and Acid-Base Balance*, 2nd ed., Mosby, St Louis (1993).
2. A. Skurup, T. Kristensen and G. Wennecke, *Clinical Chemistry and Laboratory Medicine*, **46**(1), 3 (2008).
3. M.D. Guo and H.X. Guo, *Journal of Electroanalytical Chemistry*, **585**, 28 (2005).
4. H. Darmokoesoemo, N. Widayanti, M. Khasanah and H.S. Kusuma, *Rasayan Journal of Chemistry*, **10**(1), 54 (2017).
5. H. Darmokoesoemo, L. Kustyarini, M. Khasanah and H.S. Kusuma, *Rasayan Journal of Chemistry*, **10**(1), 64 (2017).
6. H. Darmokoesoemo, N.M. Sari, Y. Kadmi, M. Khasanah and H.S. Kusuma, *Results in Physics*, In Press (2017). DOI: 10.1016/j.rinp.2017.05.012
7. H. Darmokoesoemo, N. Widayanti, Y. Kadmi, M. Khasanah, H.S. Kusuma and H. Elmsellem, *Results in Physics*, In Press (2017). DOI: 10.1016/j.rinp.2017.05.013
8. H. Darmokoesoemo, L. Kustyarini, Y. Kadmi, M. Khasanah, H.S. Kusuma and H. Elmsellem, *Results in Physics*, In Press (2017). DOI: 10.1016/j.rinp.2017.05.015
9. S.K. George, M.T. Dipu, U.R. Mehra, P. Singh, A.K. Verma and J.S. Ramgaokar, *Journal of Chromatography B*, **832**(1), 134 (2006).
10. D. Lakshmi, B.B. Prasad and P.S. Sharma, *Talanta*, **70**(2), 272 (2006).

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