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Optimization of Method of Preparing Carbon Paste Electrode

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This work propose the optimization of the preparation of electrode based on carbon paste for application to amperometric biosensor. The method is based on the experimental design of mixtures with graphite, polyaniline and epoxy resin acting as system components and electrical conductivity as the response variable. The materials were characterized such as how much its electrical conductivity and cyclic voltammetry. The experimental design indicated that the higher conductivity electrode was made of a mixture of 25% (wt/wt) graphite 40% (wt/wt) of polyaniline and 35% (wt/wt) of epoxy resin. The addition of silver nanoparticles favoring an increase of 9.71% in the anodic peak current and 32.35% in the peak cathode current.

1. Introduction

The selectivity of an electrochemical biosensor is dependent on the recognition element, the host matrix and the interaction between them (Freire *et al.,* 2003, Mihos *et al.*, 2014). The polymer-metal composite nanoparticles are widely used in biological sensors, since they have suitable characteristics to achieve the stability and sensitivity of these devices (Hong *et al*., 2010; Luo *et al*., 2006). The metal nanoparticles act as a redox mediator biomolecules and polymers act as a selective adsorbent for these devices (Prakash *et al*., 2013).
The manufacture of electrodes chemically modified with AgNPs has increased considerably. Since silver has lower costs than gold, shows excellent catalytic activity, good electrical and thermal conductivity, its application in electroanalysis is very favorable acting as pre-concentrators species of interest and/or mediating redox reactions (Oliveira, 2012). Thus further studies Chairside fabrication transducers as the folder base and the insertion of carbon and silver nanoparticles are relevant in order to obtain transducers that are more sensitive.

2. Materials and Methods

2.1 Experimental design

The experimental design of mixture was developed in order to evaluate the composite components to achieve higher conductivity by using the software Statistica® 8.0. The components used in preparing the composite of graphite powder were biosensor matrix, polyaniline (Aldrich) and epoxy resin and the response variable is the electrical conductivity (S/mm), with a percentages of graphite powder (FlukaChemie AG, USA) mixture ranging from 0 to 30% (wt/wt), polyaniline ranging from 30 to 60% (wt/wt) and epoxy resin ranging from 25 to 55% (wt/wt).

2.2 Preparation of the tablets and conductivity measurements

Once the proportions defined by the planning, the composites were prepared by homogenization with a mortar and pestle and made into tablet form. It were added 0.25g of each mixture on a paper film, and pressed

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manually pastillator. After removed from the mold the pellets were left in an oven at 30°C for 24 h (Southgate, 2011; Santana *et al*., 2014). The conductivity of the shares, consisting of different mixtures was measured using an electrometer (Keithley, model 6517B) by the standard method recommended by the American Society for Testing and Materials - ASTM D257-99, based on the electrical resistance of the material by the two terminals method.

2.3 Preparation of the electrodes and cyclic voltammetry tests

The working electrode was made from PVC support (polyvinyl polychloride) with an inserter sanded iron wire with 1.5 mm in length. The addition of the composite region to have measurements of 3 mm diameter x 3 mm deep. Inserted the carbon paste electrode, it was left in an oven at 30°C for 24 h and there after the extremity electrode was polished with sandpaper 1200. The voltammograms were analyzed in scanning speeds 20, 40, 60, 80, 100, 125 150 mVs^{-1}. Control of the voltammetric parameters and the acquisition of the data were made by the GPES software (General Purpose Electrochemical System) version 4.9.005, Metrohm, Utrecht, Netherlands.

2.4 Incorporation of silver nanoparticles (AgNPs) for composite

The AgNPs incorporated into the carbon paste polyaniline and epoxy resin were synthesized according to the Turkevich method by chemical reduction. In 50 mL of boiling solution of 0.001 $molL^{-1}$ $AgNO_3$ and under stirring was added drop by drop a solution of 1% sodium citrate until that a color change was observed (pale yellow). So, this end solution was poured into 150 mg of graphite. The carbon paste, enriched with silver nanoparticles was homogenized with polyaniline and epoxy resin according to the ratio set by the experimental design. From this mixture tablets were prepared, measured its electrical conductivity and electrochemical behavior using the technique of cyclic voltammetry. All assays were performed in triplicate (Turkevich *et al.*, 1951).

3. Results and Discussion

3.1 Determination of mixture composition transducer matrix

The evaluation of the conductivity of the shares was conducted taking into account its dimensions, in according to equation (1).

$$\text{Conductivity (S/mm)} = \text{thickness (mm)} / [\text{area (mm}^2) \times \text{resistance } (\Omega)] \quad (1)$$

Table 1 shows the average sizes of the inserts and the average values of the resistance electrometer obtained by calculating the conductivity.

Table 1: Average sizes from each sample and the average values of the resistance of tablets

Sample	Diameter (mm)	Thickness (mm)	Area (mm^2)	Resistance (Ω)
1	12.94	1.21	131.51	82.163
2	13.98	1.37	153.50	1690.755
3	13.03	1.65	133.28	65.577
4	12.87	1.43	130.02	141.025
5	12.99	1.70	132.53	107.809
6	13.01	1.47	132.87	51.220
7	12.88	1.38	130.25	101.063
8	13.98	1.10	153.57	437.905
9	13.98	1.53	153.39	705.435
10	12.98	1.78	132.32	66.972
11	12.95	1.38	131.78	373.359

The following table gives the compositions of the pellets and their average analytical response.

Table 2: Percentage of components of prepared pellets and the mean of the response variable

Sample	Graphite (%)	Polyaniline (%)	Epoxi (%)	Conductivity (S/mm)	Variance	Standard Deviation
1	30.0	30.0	40.0	$1.120.10^{-04}$	$4.176.10^{-08}$	$5.719.10^{-05}$
2	0.0	45.0	55.0	$5.425.10^{-06}$	$6.511.10^{-13}$	$8.069.10^{-07}$
3	30.0	45.0	25.0	$2.312.10^{-04}$	$1.843.10^{-08}$	$1.358.10^{-04}$
4	15.0	45.0	40.0	$8.498.10^{-05}$	$8.572.10^{-10}$	$2.928.10^{-05}$
5	15.0	60.0	25.0	$1.405.10^{-04}$	$7.313.10^{-09}$	$8.551.10^{-05}$
6	30.0	37.5	32.5	$2.170.10^{-04}$	$6.850.10^{-10}$	$2.617.10^{-05}$
7	22.5	30.0	47.5	$1.071.10^{-04}$	$4.434.10^{-10}$	$2.106.10^{-05}$
8	15.0	30.0	55.0	$1.714.10^{-05}$	$2.226.10^{-11}$	$4.718.10^{-06}$
9	7.5	37.5	55.0	$1.489.10^{-05}$	$2.224.10^{-11}$	$4.716.10^{-06}$
10	22.5	52.5	25.0	$2.011.10^{-04}$	$9.519.10^{-12}$	$3.085.10^{-06}$
11	0.0	60.0	40.0	$2.807.10^{-05}$	$1.730.10^{-12}$	$1.315.10^{-06}$

3.2 Statistical analysis of the data

Among the mathematical models that have obtained statistical significance, the full cubic model was the one that had the highest coefficient of determination adjusted (0.87), while the quadratic and the special cubic models did not achieve statistical significance. The complete mathematical model is cubic statistically significant, indicating interaction between the components of third order. This model fully describes the electric conductivity (S/mm) by the composite, as shown in Figure 1a, by means of the graph of predicted vs. observed values of the electrical conductivity having a poor dispersion of the points on the line.
The Pareto diagram on the basis of the test statistic values Student t test, Figure 1b shows that the epoxy component, the quadratic interaction between graphite and polyaniline and the cubic interaction between the graphite, polyaniline and epoxy are not statistically significant because the p-level value of each coefficient is greater than 0.05, i.e., the probability of error is not relevant, and need not be considered in the mathematical model.

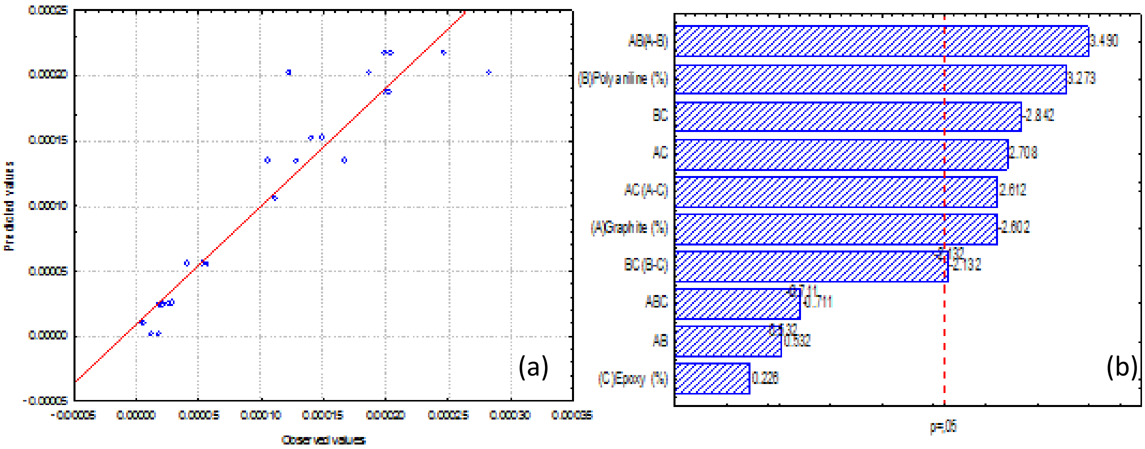

Figure 1: a) Predicted values vs observed values of electrical conductivity. b) Pareto diagram for the electrical conductivity presented by the composite according of the Student's t-test.(A:graphite, B: epoxy and C: polyaniline).

Once the statistic value of the t test of Student graphite is negative, it indicates that it alone provides a decrease in electrical conductivity presented by the composite, but some test statistic values Student t of their interactions of second order with the other components are positive, providing an electrode with higher conductivity. In sum, despite the graphite isolation provide a decrease in electrical conductivity, which is no reason to ignore it because their interaction with other components is essential to increase the electrical conductivity presented by composite.
The statistic value of the t Student test of polyaniline is the highest among the other components, so it appears that this component will determine the electrical conductivity of the composite, but the statistic value of the t Student test of the interaction between the graphite polyaniline and [AB (A-B)] is the largest, making this interaction the responsible for producing a composite with higher electrical conductivity. From the Pareto chart

can also be noticed that the graphite, polyaniline and some second-order interactions {graphite interacting with epoxy [AC and AC (A-C)], polyaniline interacting with epoxy [BC and BC (B-C)] and graphite interacting with polyaniline [AB (A-B)]} are statistically significant since their p-level of values are less than 0.05.

By Pareto diagram it is noticeable that the combination of polyaniline with epoxy form an antagonistic mixture because the statistic values of the Student t test of their interactions are negative, and the other combinations form synergistic mixtures. It is recommended to bypass some interactions that are not significant to reduce the number of terms of the proposed mathematical model. Ignoring the interaction between the three components (ABC), the R^2_{fit} and remained virtually the same and the p-level of the model had decreased from 0.01 to 0.009, making it slightly more statistically meaningful model. Thus, the mathematical model is obtained to describe the electrical conductivity presented by composite as Equation (2).

$$\begin{aligned} \textit{Electrical Conductivity} = & -0.041830A + 0.9105B - 0.03224C + 0.057378AB + 0.063282AC - 0.012BC + 0.060381A^2B \\ & + 0.060381A^2B + 0.060381AB^2 + 0.035185A^2C + 0.035AC^2 - 0.026401B^2C - 0.02640BC^2 \end{aligned} \quad (2)$$

The response surface is used to obtain high, intermediate and low ranges of electrical conductivity presented by the composite due to the graphite, the polyaniline and epoxy. The contour lines provide a simpler view of the tendency of the response variable, where each ton has the same value of electrical conductivity presented by composite as shown in second Figure. The contour lines are obtained by folding the response surface on a plan. Both the level curves and the response surface take into account the design constraints, or pseudo-components, therefore it is not noticeable the ideal composition to provide a composite having higher conductivity as a percentage of the original components.

For proper visualization of the ideal composition of the composite in order to achieve higher conductivity it is used the ternary diagram with restriction shown in Figure 2b.

The planning region is bounded by the hexagon found (Figure 2b) and the region that provides the highest electrical conductivity is indicated by the area of darker color. The delimited region indicates that the higher conductivity is promoted by the mixture of about 25% graphite, 40% of polyaniline and 35% epoxy. In accordance with the level curves, there is a region that provides an even higher conductivity located in the lower right corner of Figure 2a, however this region is not within the hexagon of Figure 2b, being outside the experimental range design, disregarded for analysis.

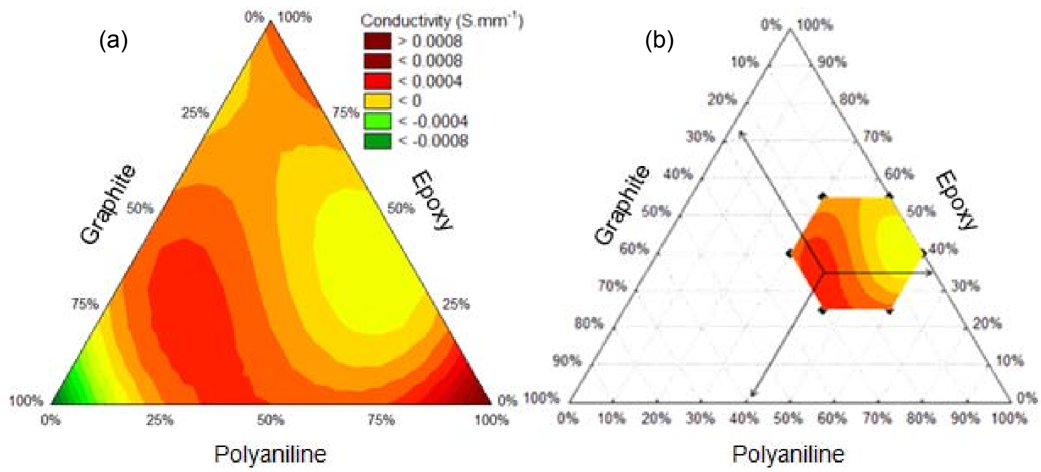

Figure 2: a) Level curves for the composite electrical conductivity shown as a function of pseudo-components of the mixture; b) Ternary diagram with restriction for electrical conductivity presented by composite depending on the components: graphite, epoxy and polyaniline

According to the proposed mathematical model, a composite made from 25% graphite, 40% and 35% of polyaniline epoxy provides a conductivity of 2.53×10^{-4} S.mm^{-1}. The selection of the percentages for the estimated conductivity electrical presented by composite was based from the observations of the diagram.

3.3 Electrochemical characterization of the working electrodes by cyclic voltammetry

For the electrodes with absence and with presence of silver nanoparticles, the scan rates wereof 40 and 80 mVs^{-1}, respectively. Showing a module ratio of the anodic peak current (Ipa) and the cathodic peak current (Ipc) nearest of 1, therefore a higher character of reversibility (Table 3).

Table 3: Comparation between the peak currents of the electrodes with and without AgNPs

Electrode	v (mVs^{-1})	Ipa (A)	Ipc (A)	|Ipa/Ipc|
WithoutAgNPs	80	$-1.75.10^{-04}$	$1.36.10^{-04}$	1.28
WithAgNPs	40	$-1.92.10^{-04}$	$1.80.10^{-04}$	1.07

The highest current values were provided by the electrode comprised of 25% (w/w) graphite 40% (m/m) of polyaniline and 35% (m/m) of epoxy resin composition according to the experimental planning estimated. Thus, this ratio was maintained fixed and evaluated the influence of silver nanoparticles on carbon paste. The results can be observed by voltammograms for the two electrodes as shown in Figure 3.

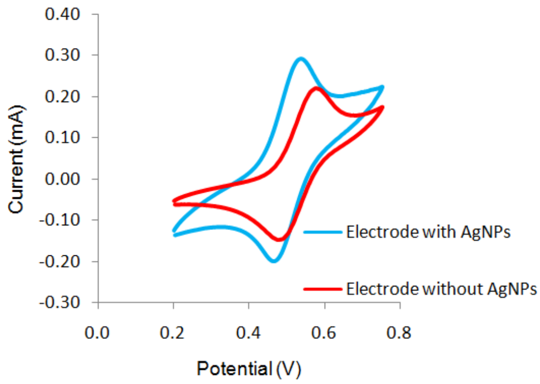

Figure 3: Cyclic voltammograms obtained with the electrodes with and without AgNPs solution containing 10mM $K_4Fe(CN)_6$in 3 M KCl vs.Ag/AgCl

The insertion of AgNPs resulted in an increase of 9.71% in the anodic peak current and 32.35% of the cathode peakcurrent as well as increasing the reversibility of the electrode, due to the ratio |Ipa/Ipc| become closer of one.

4. Conclusions

The higher values and well-defined peak current shapes were obtained with the electrode whose experimental design exhibit higher conductivity, *i. e*. 25% graphite, 40% of polyaniline and 35% of epoxy resin.
The AgNPs insertion resulted in an increase of 9.71% in the peak anodic peak current and 32.35% at cathodic peak current of the electrodes.
The system showed reversibility character; demonstrating that the graphite mixture, polyaniline, epoxy resin and AgNPs do not affect the reading, relating to the proper functioning of the electrode.
The development of graphite paste electrodes base for application to amperometric biosensor becomes efficient and practical to apply the experimental design of mixtures, being an essential method for optimizing the fabrication of electrodes.
The statistical data showed that the percentages of the mixture corroborate the values of cyclic voltammetry, with the addition of silver nanoparticles favoring the sensitivity of current measurement

Acknowledgements

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References

Santana A.C.O., Southgate E.F., Mendes J.P.B.G., Dweck J., Alhadeff E.M., Bojorge Ramirez N.I., 2014, Characterization of an HRP-AOX-polyaniline-graphite composite biosensor, Journal of Electrochemical Science and Engineering 4, 165-175.

Freire R.S., Pessoa C.A., Mello L.D., Kubota L.T., 2003, Direct electron transfer: an approach for electrochemical biosensors with higher selectivity and sensitivity, Journal of the Brazilian Chemical Society 14, 230-243.

Hong W., Bai H., Xu Y., Yao Z., Gu Z., Shi G., 2010, Preparation of gold nanoparticle/graphene composites with controlled weight contents and their application in biosensors, The Journal of Physical Chemistry C 114, 1822-1826.

Luo X., Morrin A., Killard A.J., Smyth M.R., 2006, Application of nanoparticles in electrochemical sensors and biosensors, Electroanalysis 18, 319-326.

Mihos F.D.C.S.S., Silva L.M., Salgado A.M., Maggesissi M.R., 2014, Application and Construction of a Biosensor Using Graphite Rod and Bean, *Phaseolus Vulgaris L*., for Phenol Detection, Chemical Engineering Transactions 38, 439-444. DOI: 10.3303/CET1438074

Oliveira P.R., 2012, Construção e avaliação de eletrodos modificados com hexacianoferrato de prata para a determinação amperométrica de isoniazida, Dissertação, Mestrado em Química Analítica, Universidade Federal do Paraná, Curitiba, Brazil, 20-124.

Prusak-Sochaczewski E., Luong J., Guilbault G., 1990, Development of a piezoelectric immunosensor for the detection of *Salmonella typhimurium*, Enzyme and Microbial Technology 12, 173-177.

Southgate E.F., 2011, Desenvolvimento de biossensor eletroquímico para detecção de etanol, Monografia, Bacharelado em Química Industrial, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, 33.

Turkevich J., Stevenson P.C., Hillier J.A., 1951, Study of the nucleation and growth processes in the synthesis of colloidal gold, Discussions of the Faraday Society 11, 55-75.