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Synthesis of Graphene Oxide-Nanozeolite Composite Electrode for Aspirin Analysis by Cyclic Voltammetry

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A graphene oxide-nanozeolite composite was prepared and empolyed as electrode for cyclic voltammetric analysis of aspirin. Graphene oxide was synthesized with the improved Hummer method, while nanozeolite synthesized using a mechanical ball milling method. Cyclic voltammetric analysis of aspirin was influenced by several factors *viz*. the composition of working electrode, pH, deposition time and scan rate. The optimized parameters of graphene oxide-nanozeolite composite electrode has the best composition at a ratio of 3:2:5 at pH of solution 4, deposition time at 5 s and scan rate at 100 mV s^{-1}. A recovery percentage of 99.61% having limit detection of electrode was 0.0611 ppm (0.002 mM).

Keywords: Graphene Oxide, Aspirin, Nanozeolite, Cyclic voltammetry.

INTRODUCTION

Aspirin or acetylsalicylic acid is widely used in the treatment of mild to moderate pain and its pharmacological effects of aspirin include analgesics, antipyretics and anti-inflammatory [1,2]. Usage of aspirin in different pharmaceutical drugs touches 35,000 per annum, however overdosage of aspirin can cause an acute and chronic poisioning. Death in acute overdoses reaches 2% and in chronic overdoses reaches 25%. The effects of aspirin overdose are hallucinatory pain, kidney failure, seizures, coma and death [3]. Thus, determination of aspirin levels in pharmaceuticals is essential to test the product quality before and during the production process, because as an overdose of aspirin might cause death. Some of the reported methods for the analysis of aspirin are UV-visible spectrophotometry [4], mass spectroscopy [5] and HPLC [6] and voltammetry [7]. However, voltammetry was chosen due to its easy sample preparation in analysis, high selectivity, low detection limits on the ppb scale and easy to operate.

The working electrodes commonly used in the voltammetry process are the carbon paste [8] and glass carbon electrodes [9-11]. The conductivity of carbon can still be improved in the process of electron transfer at the working electrode. Increased conductivity can be done with a material that has better conductivity than carbon such as graphene oxide by oxidizing carbon allotropic derivatives, namely graphite to graphene oxide.

Graphene oxide has the advantages of good electron mobility, good thermal conductivity, chemical stability and good mechanical properties, in terms of the conductivity, stability and sensitivity of graphene oxide can be increased with a composite material [12,13]. Zeolite as a composite was chosen because it can improve electrode performance by working as an adsorbent [14,15]. Beside from being an adsorbent, zeolites are also able to separate molecules based on their size. To increase pores and enlarge the surface area of zeolite, the size of zeolite is reduced to nano, which can increase the electron transfer to the working electrodes with wider surface area. In this study, cyclic voltammetric analysis of aspirin is carried out using graphene oxide as working electrodes, which are composited with nano-zeolite to increase the sensitivity of the electrodes.

EXPERIMENTAL

Zinc powder, potassium permanganate, hydrochloric acid 37 %, hydrogen peroxide 30 %, sulfuric acid 96 % v/v, phosphoric acid 85 % v/v, ethanol 96 % v/v p.a, sodium hydroxide, sodium citrate dihydrate, citric acid dihydrate and potassium chloride were of analytical grade (Merck), while asprin was of pharma-

ceutical grade and procured from the local medical shop. Graphite pencil faber-castel 2B and paraffin oil (Merck) were used to prepare graphene oxide.

Synthesis of graphene oxide: Graphene oxide was synthesized with improved Hummer's method. In brief, graphite (1 g, 300 mesh) was oxidized by adding it in a mixture of sulfuric acid, phosphoric acid and potassium permanganate. Then graphite oxide and water (1:1) was added with 0.6 g of Zn dust and HCl to reduce graphite oxide to graphene oxide. Stirred the mixture for 1 h and neutralized to pH 7 by washing with deionized water and dried at 60 °C for 24 h.

Synthesis of zeolite: Natural zeolite (20 g, 300 mesh) was washed thoroughly with deionized water and then heated in oven at 120 °C for 4 h. Zeolite was then activated with HCl and NaOH and stirred for 1 h at 50 °C. Decanted the solution and dried the residue at 80 °C in a oven. The activated zeolite were neutralized to pH 7 by deionized water, dried at 120 °C and then calcined for 3 h at 600 °C. Zeolite (5 g) from the activation and calcination were taken into a planetary tube, which was thoroughly washed with 96% ethanol. Zeolite was milled for 4 h at a speed of 500 rpm with planetary ball milling PM 400 in a ratio of of 1:10.

Preparation of electrodes: Graphene oxide-nanozeolite composite work electrodes were prepared in a different ratio of 3:2:5; 3:3:4; 3:4:3; and 3:5:2 consisted of graphene oxide: paraffin:nanozeolite. The composition of each electode was blended homogeneously.

RESULTS AND DISCUSSION

Optimization of composition of graphene oxide-nanozeolite composite: In order to obtain the best response for aspirin by cyclic voltammetric method, it is necessary to optimize the best composition for electrodes by analyzing the highest peak current. The best working electrode of graphene oxide-nano zeolite was carried out by inserting 10 mL of 50 ppm aspirin solution, 10 mL of 5000 ppm KCl solution and 5 mL of pH 3 citrate buffer solutions into the voltammetry cell. Furthermore, electrodes with variations in the composition of graphene oxide: paraffin:nanozeolite (3:2:5; 3:3:4; 3:4:3; 3:5:2) were applied with a current measurement in the range of -2 V to 1 V with a deposition time of 5 s and a scan rate of 100 m/s. As shown in Fig. 1, a compostion having 3:2:5 exhibited the highest peak of cathodic current (I_{pc}), the reason is attributed due to the greater the amount of nanozeolite, which resulted in the faster electron transfer.

Determination of optimum pH: The suitable pH conditions were expected to make more samples absorbed on the surface of the electrodes so that voltammogram with high anodic and cathodic peak currents can be obtained. Determination of optimum pH is performed using graphene oxide-nanozeolite composite electrodes, the best composition in a ratio of 3: 2:5, and other conditions same as mentioned above. A voltammogram with the highest peak of cathodic current (I_{pc}) in the variation of citrate buffer was obtained with pH 4. As the pH increased from 2 to pH 4, an increased in the peak current has been observed (Fig. 2). However, further increase in the pH value led to a decrease in peak current.

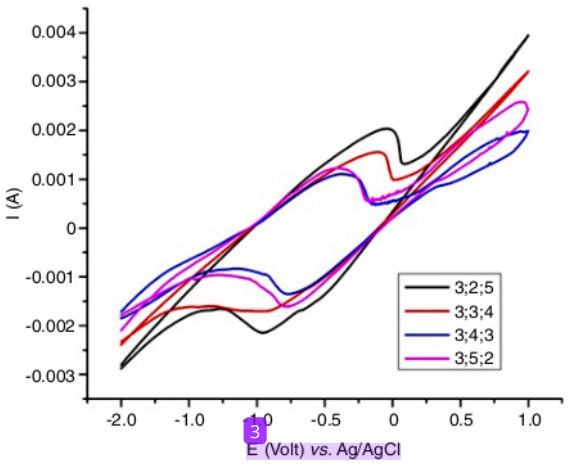

Fig. 1. Voltammogram variations in the composition of the working electrodes of graphene oxide-nano zeolite composites

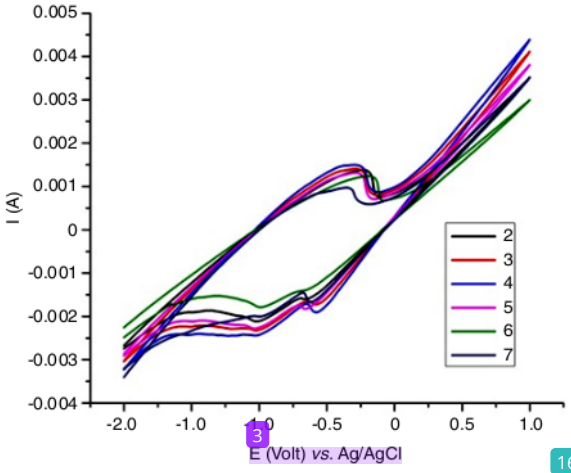

Fig. 2. Cyclic voltammogram at graphene oxide-nanozeolite composite in 0.1 M citric buffer solution (pH = 4.0) at a different pHs containing 50 ppm of aspirin and 5000 ppm potassium chloride. In all the cases, the scane rate is 100 mV s^{-1}

Optimum deposition time: To determine the time duration required for the sample to be applied on the electrode, the cyclic voltammetric analysis were carried out in the range of -2 V to 1 V with a variation of the optimum deposition time of 5 s at a scan rate of 100, 200, 300, 400 and 500 mV/s. Voltamogram variation deposition time of graphene oxide-nanozeolite composite working electrodes is shown in Fig. 3. A decrease in the value of I_{pc} is observed at the longer deposition time. This is due to the presence of aspirin that has accumulated and bound to zeolites on the surface of electrode. The longer the deposition time, more accumulation and binding of aspirin. The optimum measurement of deposition time is 5 s because it produces the highest reduction peak.

Optimum scan rate: From Fig. 4, a decrease in the value of I_{pc} is observed at the higher the scan rate. However at scan rate of 100 mV/s, a high oxidation with the highest reduction

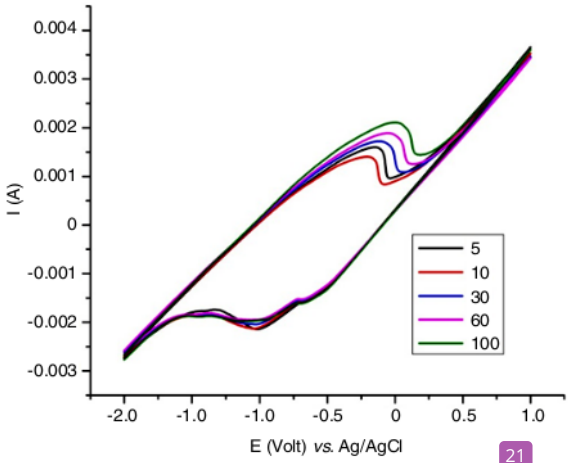

Fig. 3. Voltamogram of aspirin 50 ppm in pH 4 buffer citrate at scan rate of 100 mV s^{-1} with various deposition time

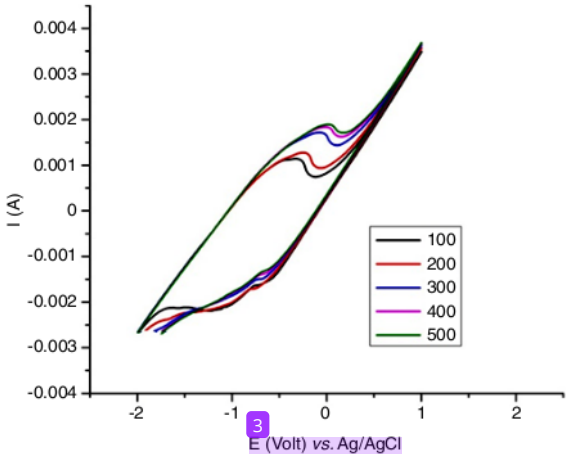

Fig. 4. Voltamogram of aspirin 50 ppm in pH 4 buffer citrate at deposition time 5 s with various scan rate

peak is observed. Moreover, at the same scan rate of 100 mV/s, there is a high increment in oxidation peak (I_{pa}) compared to other distance ranges, thus the scan rate of 100 mV/s is considered as optimized value.

Electrocatalytic oxidation of aspirin: The graphene oxide-nanozeolite composite electrode is capable to oxidize the aspirin to gentisic acid and reducing the gentisic acid to aspirin characterized by a peak at the anode and cathode. The oxidation reaction of aspirin is shown at Fig. 5.

Electrode sensitivity: The sensitivity of graphene oxide-nano zeolite composite working electrode with a composition of 3:2:5 in the analysis of aspirin is also investigated by keeping other conditions optimized. From Fig. 6, it can be observed that an increase in the cathodic current peak (I_{pc}) is directly proportional to an increase in the concentration of solution, thus a linearity curve can be made between the I_{pc} values against the concentration as shown in Fig. 7.

From the linearity curve in Fig. 7, regression cofficient value of $R^2 = 0.99633$ is obtained.

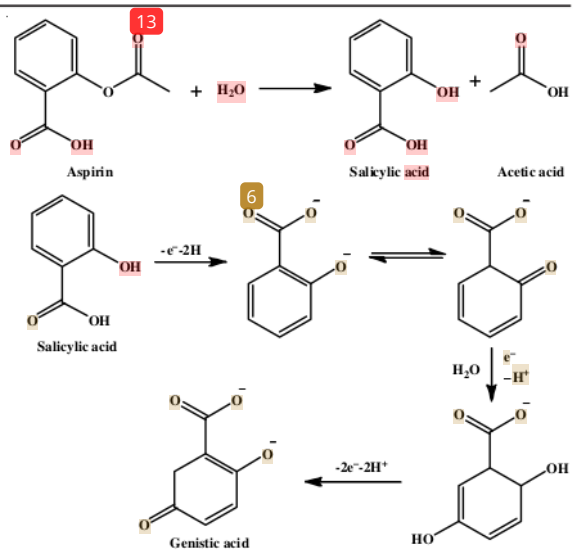

Fig. 5. Oxidation of aspirin on the surface of graphene oxide-nanozeolite composite

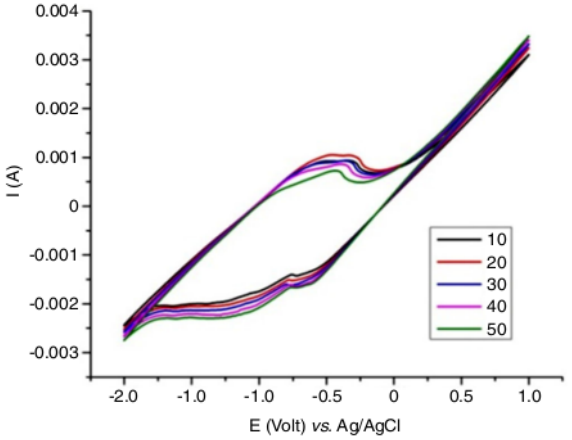

Fig. 6. Voltamogram of aspirin with a concentration 10-50 ppm in citrate buffer solution pH 4 with a 5 s deposition time and 100 mV/s scan rate

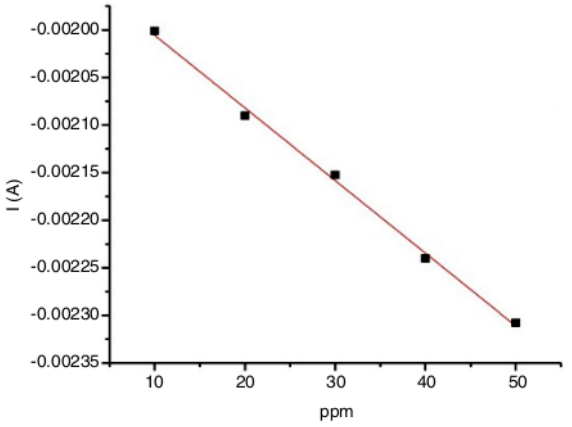

Fig. 7. Linearity curve between concentration (ppm) *vs.* current peak cathodic

$$y = -7.63297 \times 10^{-6}x - 0.00193 \quad (1)$$

Limit of detection: Based on eqn. 1, the prepared electrode sensitivity can be determined through percent data recovery and detection limits by considering the I_{pc} value of the standard 10.20,30,40, and 50 ppm. Percent recovery is calculated by using eqn. 2.

$$\text{Recovery (\%)} = \frac{\text{Concentration obtained}}{\text{Real concentration}} \times 100 \quad (2)$$

The average percentage of recovery data in the study was 99.612, while the detection limit for aspirin was 0.0611 ppm (0.002 mM or 0.200 µM). These results indicated that the sensitivity of graphene oxide-nanozeolite composite working electrode in the composition 3:2:5 is excellent.

Determination of aspirin in industrial samples: The feasibility of the prepared graphene oxide nanozeolite composite working electrode having composition of 3:2:5 is investigated for real samples. Determination of aspirin is done by taking 10 mL of aspirin sample solution (0.01 ppm), 10 mL of 5000 ppm KCl solution and 5 mL of optimum pH citrate buffer solution (pH 4). Cyclic voltammetric analyses were carried out in the range of potential difference of -2 V to with with an optimum deposition time of 5 s and an optimum scan rate of 100 mV/s. The obtained voltammograms were compared with the results of HPLC analysis to validate the performance of graphene oxide-nano zeolite composite working electrode. The results in Table-1 clearly shows that using proposed electrode in the cyclic voltametric analysis is equally good as HPLC analysis for determining the aspirin sample in industrial products.

TABLE-1
ASPIRIN IN PHARMACEUTICAL SAMPLES

Sample	Detection in electrode	Detection in HPLC
1	34,60	33,57
2	37,22	35,43
3	32,89	31,76

Conclusion

In this work, a graphene oxide-nanozeolite composite was prepared and used composite shows good linear relationship with aspirin concentrations in the range from 10 to 50 ppm and the detection limits was 0.0611 ppm. Moreover, electrode graphene oxide-nanozeolite exhibited good stability and high reproducibility in cyclic voltammetry determination. The utility of the proposed sensor was evaluated by sensing in aspirin pharmaceutical samples with good recovery results.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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