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Full Paper

A Sensitive Biosensor for Acrylamide Detection based on Polyaniline and Au Nanoparticles using FFT Admittance Voltammetry

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Abstract- A new electrochemical detection system was developed based on combination of a biosensor and Fast Fourier transform Admittance Voltammetry (FFTAV), which used for the sensitive detection of acrylamide. By effective self-assembling process, the biosensor was prepared of thiol functionalized single-stranded DNA (ssDNA) on gold nanoparticles, which deposited on a gold electrode decorated with polyaniline. The acrylamide has the ability to form a single complex with ssDNAs, which was linked on the biosensor surface, and changed the admittance of the electrode. Therefore, the concentration of acrylamide was detected directly by the change of admittance of the electrode. The biosensor was characterized by Scanning electron microscope-based (SEM), electrochemical impedance spectroscopy copy (EIS) and cyclic voltammetry. Under optimal conditions, the linear dynamic range of the acrylamide was 5.0×10^{-10} M to 2.0×10^{-7} M (r^2 = 0.988) limits of detection of 5.0×10^{-11} M. The data showed that the electrochemical biosensor could detect acrylamide rapidly and accurately. Moreover, the proposed method demonstrated acceptable sensitivity and long-term stability.

Keywords- Acrylamide, Electrochemical biosensor, Gold electrode modification, Fast Fourier transform Admittance Voltammetry

1. INTRODUCTION

Acrylamide is often applied in papermaking production, wastewater treatment, and tertiary oil recovery [1,2]. It can be detected in high levels even in small pro-portion of high-starch foods. Since, Acrylamide has the potential to cause strong neurotoxicity and genotoxicity in humans [3], thus its determination in quantitative scales has become an important concern. Among reported methods for acrylamide determination, gas chromatography (GC)1–mass spectrometry (MS) [4], gas chromatography nitrogen phosphorus detector (GC-NPD) [5], high-performance liquid chromatography (HPLC)–MS [6,7], and liquid chromatography (LC) [8,9], chromatography couple with mass spectrometry [10] and capillary electrophoresis [11,12] can be named.

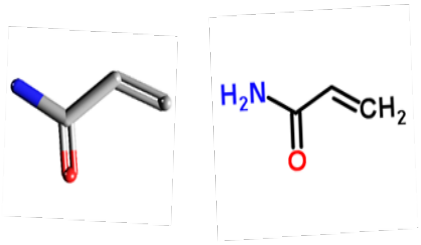

Fig. 1. Chemical structure of acrylamide

As most analytical techniques confront drawbacks such as high cost of instruments and test and complex sample pretreatment steps, there is great demand for the development of simple, efficient, inexpensive and reliable protocols for rapid and precise acrylamide determination [1,13,14]. In this point of view, the electrochemical biosensors have found specific place for detection of biomolecules like acrylamide as they are able to offer advantages including simplicity, rapidity, and high sensitivity [15-18]. Moreover, in case of using Fast Fourier Transform (FFT) in combination with the electrochemical techniques such as admittance voltammetry, voltammetric signal and background signal would be separated in frequency domain therefore; higher sensitivity in analytes determination in complex matrixes can be prepared [19-35].

In the biosensor design, it is desired to improve DNA hybridization efficiency; hence the Au nanoparticles (NPs) are used in order to modify the electrode surface [36-38]. In addition, Au NPs have noteworthy biocompatibility and the curvature of the nanoparticles can provide a larger surface area. In order to enhance the biosensor conductivity, various nanomaterials have been employed such as conducting polymers, metal nanoparticles, carbon nano-tubes and graphene [39-42]. Moreover, Au nanoparticles play an important role in the electrode transduction enhancement of the affinity reaction as well as in the efficiency of DNA immobilization on Polyaniline (PANI) forms a stable nanocomposite. PANI as conductive electrode materials has increased widely in the field of biosensor, due to strong adherence to electrode surface, with homogeneity, unique redox properties. Also, it can be simply prepared

from aqueous and organic solvents by either chemical or electrochemical oxidative polymerization PANI possesses a large specific surface area and unique property to accelerate electron transfer especially when it combined with Au NPs [43-45]. Such nanocomposite provides a suitable electrostatic interaction between the negatively charged DNA and the positively charged surface which is suitable for DNA immobilization.

In the present paper, a new ultrasensitive biosensor for determination of acrylamide is introduced based on new platform of immobilization of DNA on a modified Au electrode with a PANI-chitosan and Au NPs composite film. To increase the sensitivity of the developed biosensor, the a special square wave (SW) electrochemical method called FFT admittance voltammetry (FFTAV) [21,46-48] was used, and electrode response was obtained by calculating difference admittance of the electrode, before and after introduction to the analyte. The morphological and electrochemical characterization of electrode surface was studied by Scanning electron microscope-based (SEM) and electrochemical impedance spectroscopy copy (EIS). For determination of acrylamide, the admittance of the biosensor was calculated during the potential ramp, and the response was in form of differential admittance, which used for optimization of the parameters.

2. EXPERIMENTAL METHODS

2.1. Reagents

Acrylamide (purity≥99%), $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$, $HAuCl_4$, KCl, dimethylformamide (DMF), aniline, acetic acid, NaH_2PO_4, Na_2HPO_4, phosphoric acid and NaOH were purchased from Sigma, Double distilled water was used throughout the experiments, and the prepared solutions were kept at 4 °C before use. Chitosan solution (1%, wt%) was prepared by ultrasonically dissolving chitosan powder in 1% acetic acid. ssDNAs (5′-SH-$(CH_2)_6$-GGG GGT TTT TTT TTT-3′) was purchased from CINAGEN (Co. IRAN) and purified by HPLC. The $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture containing 0.1 M KCl was used as a redox probe in the electrochemical measurements.

2.2. Instrumentation

For FFTAV measurements a homemade potentiostat was used, which was connected to a PC equipped by an analog to digital data acquisition board (PCL-818H, Advantech Co.). During the data acquisition, the memory requirements of the computer were controlled by an electrochemical software, which was developed in our lab. The electrochemical cell included a three-electrode system consists of an Ag/AgCl reference electrode, a platinum wire as the auxiliary electrode and the working electrode. A special potential waveform was designed for FFTAV measurements (see Fig. 2A). The electrochemical program was employed to control

and. generate a potential waveform and acquire admittance readings, processed and plotted the data.

2.3. Fabrication of the biosensor

At first, polyaniline (PANI) solution was synthesized sonochemically, In brief; 1.6 mL of purified aniline was dissolved with maintaining vigorous stirring in 50 mL of HCl 1.0 M, at the same time, 40 mL of 0.4 M ammonium peroxydisulfate solution was quickly poured into the solution.

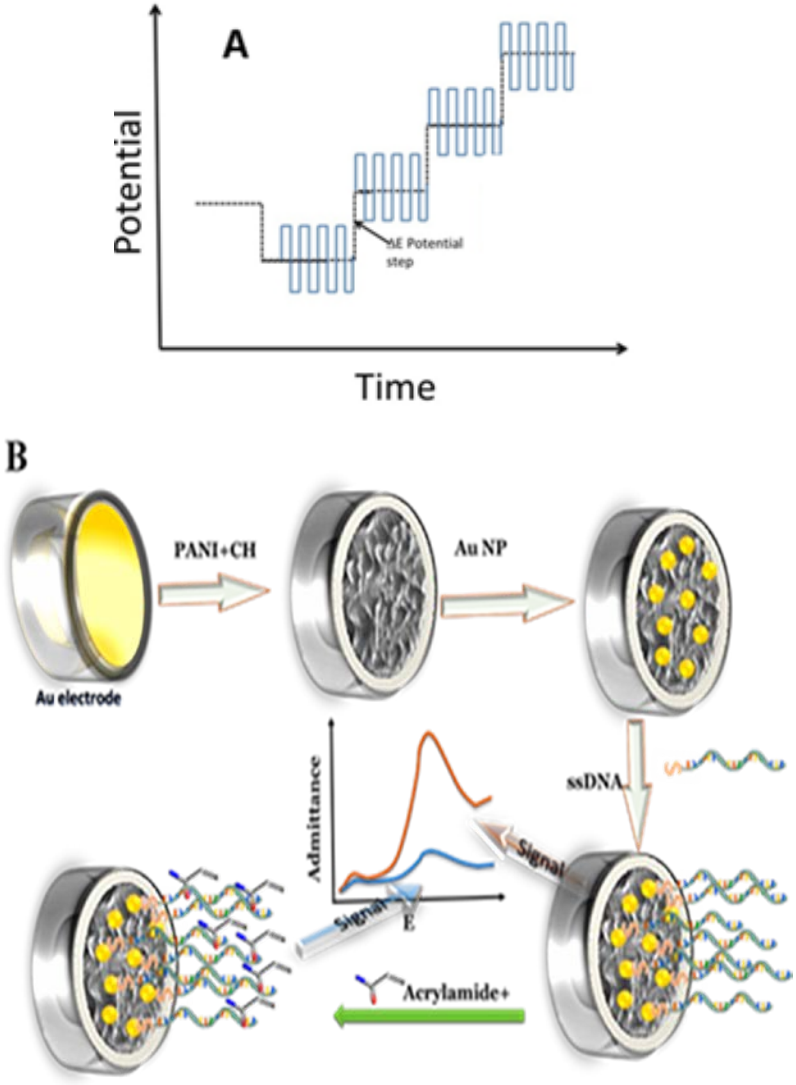

Fig. 2. Schematic presentation of A) the applied potential waveform for FFTAV measurement; B) biosensor fabrication

It was mixing in ultrasonic bath in 4º C until a green salt obtained. After washing the salt with distilled water and HCl, it was converted to a colorless form, which was dried in vacuum oven at 60º C.

A gold electrode (3 mm in diameter) was polished with 0.3 µm and 0.05 µm alumina powder, followed will ultrasonically cleaning in 100 mM NaOH solution. To obtain PANI-CHI/Au, 15 µl of the PANI suspension (0.08 g/L) dispersed in DMF, was mixed with chitosan solution (v/v50:1) and sonicated for 1 h. Then, 10 µl of above solution was deposited on the Au electrode and dried by an IR lamp. For electrodepositing, the coated electrode was immersed into a $HAuCl_4$ (3.0 mM) solution containing 100 mM KNO_3 for 100-500 s at −200 mV. After that, the surface of the Au NPs/PANI-CHI/Au electrode was carefully washed with distilled water and dried at room temperature. Then, 20 µl of 6 µM ssDNA solution was dropped on the modified electrode surface and kept for 3 h at 4 °C. To remove the non-specifically adsorbed ssDNA, the ssDNA-Au NPs/PANI-CHI/Au electrode was rinsed with a solution containing 500 mM PBS, 0.1% sodium dodecyl sulfate. Fig. 2B represents the biosensor fabrication steps.

2.4. Real Sample preparation

For preparation acrylamide dissolved in water, the solid-phase microextraction (SPME) was used. SPME fiber purchased from Supelco (Co.). The fiber was conditioned according to the manufacturer's recommended procedures before usage. For real sample analysis, an Iranian popular potato was the fried, and then it was blended and homogenized. Then10 g of the sample mixed with 100 mL of water for 30 min by supersonic nebulizer (Branson 5210, USA), then was centrifuged at 5000 rpm for 20 min. In the next step, 2 mL aliquot of the supernatant was diluted to 15 mL with water and then mixed with 20 mL PBS solution (at pH 7.5). Finally, the fiber was directly immersed in the mixed solution to extract acrylamide dissolved in water.

3. RESULTS AND DISCUSSION

3.1. Surface characterization of fabricated biosensor

In order to characterize the modified surface of the biosensor, the surface morphologies of PANI-CHI/Au and Au NPs/PANI-CHI/Au was examined by SEM method. Fig. 2 (inset) shows the SEM image of composited film PANI-CHI/Au. The results of the inset SEM analysis of the structure of the synthesized materials indicated, that the PANI layer is a homogeneously distributed is in compacted form. Furthermore, clearly illustrates the PANI on the Au electrode film forms highly entangled network structure. Fig. 2 indicates distribution of Au particles on the surface of the film, where the deposited Au NPs were

mostly in spherical forms. However, the amount of the deposited NPs on the surface of the substrate depends on the deposition time is used the electrochemical processes.

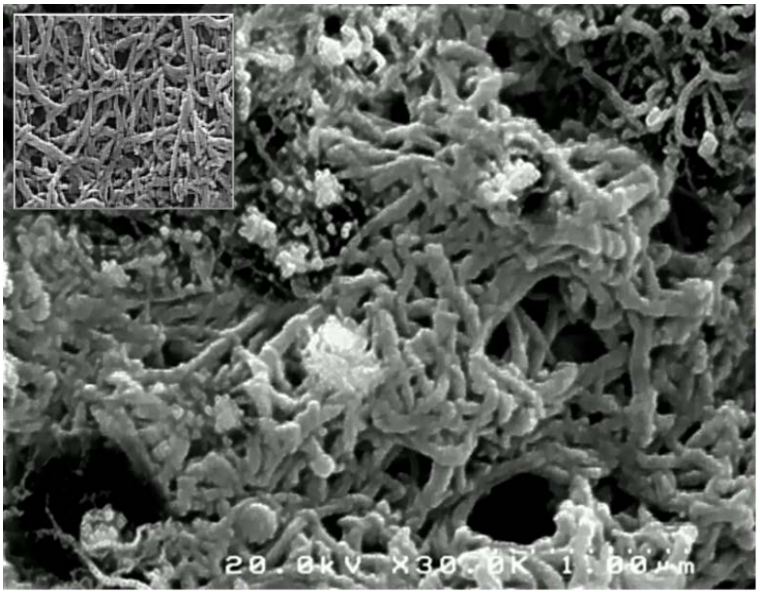

Fig. 3. SEM image of Au NPs/PANI/Au, the inset (PANI-CHI/Au)

3.2. Electrochemical characterization of the biosensor

It is well known that cyclic voltammetry (CV) can provide useful information on the barrier changes of the electrode surface during the fabrication process. Therefore, in order to study electrochemical behavior changes during fabrication steps, cyclic voltammograms of bare Au, PANI-CHI/Au, Au NPs/PANI-CHI/Au, (d) ssDNA/Au NPs/PANI-CHI/Au, electrodes in $[Fe\ (CN)_6]^{3-/4-}$ couple 3 mM, 100 mM PBS solution (pH 7.5). Fig.4A displayed the cyclic voltammograms of differently modified electrodes.

As expected the current responses of PANI-CHI/Au decreased compared with the bare Au electrode, and then the current at Au NPs/PANI/Au increased noticeably due to existence of a large surface area and excellent electrical conductivity of Au NPs. Also, it is possible that observing higher faradic current is indication of the synergistic effect for combination of Au NPs and PANI on enhancing the electroactivity.

After immobilization of ssDNA on Au NPs/PANI-CHI/Au, the peak current decreased significantly. This mainly could be ascribed to the decreased the effective surface area and the existence of the electrostatic repulsion between the negatively charged DNA and $[Fe(CN)_6]^{3-/4}$ ions, which prevent of reaching the ions to the surface. Also, modification with ssDNA causes an increase in the anodic peak and cathodic peak potential difference. All, these indicates successfulness of ssDNA attachment on the surface of modified Au electrode.

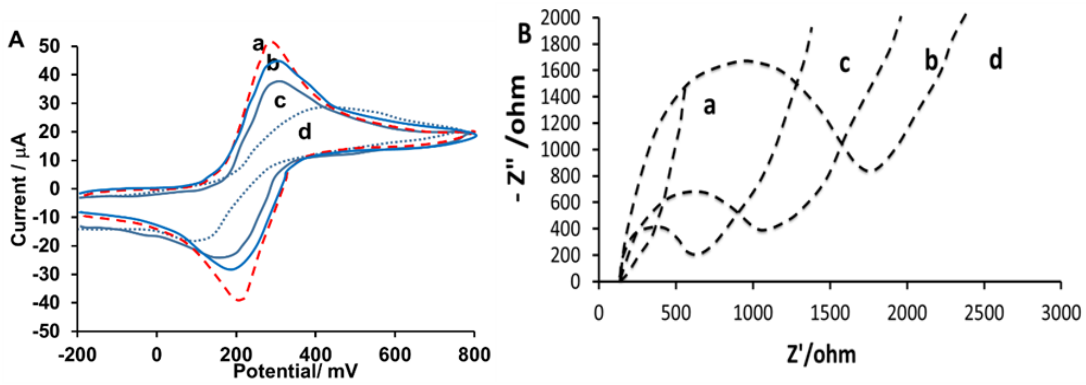

Fig. 4. A) Cyclic voltammograms of (a) bare Au, (b) PANI-CHI/Au, (c) /Au NPs/PANI-CHI/Au, (d) ssDNA/Au NPs/PANI-CHI/Au, electrodes in PBS solution, pH 7.5, Scan rate 50 mV/s^{-1}; B) EIS plots of (a) bare Au, (b) PANI-CHI/Au, (c) Au NPs/PANI-CHI/Au, (d) ssDNA/Au NPs/PANI-CHI/Au, electrodes in 100 mM PBS solution, pH 7.5, $[Fe(CN)_6]^{3-/4-}$ 3mM, Frequency range 0.1 Hz to 1 MHz, DC potential of 200 mV and AC amplitude of 10 mV.

For verification of electrode construction, EIS can give further information on the impedance changes during each step of the producer. Fig. 4B, curves *a* to *d* display the EIS for the electrode fabrication steps. Curve a displays the Nyquist diagram of the bare Au electrode, which is almost straight line that points to existence of diffusion controlled electrochemical process at the electrode surface. In, the EIS graph (Nyquist diagram, Fig. 4 B), the semicircle diameter represents the electron-transfer resistance, R_{ct}, for the electron transfer kinetics of $[Fe(CN)_6]^{3-/4-}$ at the biosensor interface. Therefore, for this electrode EIS measurement was measured in frequency range from 0.1 Hz to 1 MHz, with a DC potential of 200 mV and AC amplitude of 10 mV, in 100 mM PBS solution, pH 7.5, and 3mM $[Fe(CN)_6]^{3-/4-}$.

In case of PANI-CHI/Au electrode(curve b), the value of R_{ct} (1120 ohm) significantly is higher than the bear electrode, which may due to the high blocking effect of the formed polymer layer on diffusion of $[Fe(CN)_6]^{3-/4-}$ ions. However, in case of curve c, adding Au NPs to the electrode surface (to form Au NPs/PANI-CH/Au), causes a drop in the value of R_{ct} (670 ohm). As mentioned in the CV experiment, this could be due to improvement of the electron transfer kinetic of $Fe(CN)_6^{3-/4-}$ was by the deposited Au NPs. As shown in curve d, in case of ssDNA/Au NPs/PANI-CHI/Au electrode showed higher R_{ct} value increases to 1890 ohm, which confirms the electrode surface is blocked by ssDNA.

3.3. Analytical measurement

Fig 5A shows that the impedance of the electrode increases with concentration of the analyte from 50 to 500 nM. This could be due to a strong bonding interaction between

acrylamide and guanine base in ssDNA, which could reduce the electrochemical activity of the guanine [49]. This response change reveals that guanine can be used for monitoring the acrylamide concentration. However, the experimental data shows that the impedimetric method is not sensitive enough for trace analysis.

From analytical sensitivity point of view, in the FFTAV method the data currents are sampled eight times across the entire SW period. Where, it can be the most advantageous in FFTAV to collect more current samples in the forward and reverse pulses in order to use current averaging to increase the signal to noise (S/N). Furthermore, application of a multiple SW pulses (16) in each potential step of ramp was used for enhancing the S/N ratio. The averaged currents were used to calculate the admittance of the electrode with high precision, which is very suitable and sensitive for analytical measurement of acrylamide.

As shown in Fig 5B, the biosensor in the solution buffer, exhibited FFTA peak admittance around 720 mV, in 100 M KCl, 100 M PBS pH 7.5 solution, with SW amplitude of 25 mV in amplitude at the frequency 500 Hz, due to redox processes of the guanine bases. The admittance peak was used here as the probe for determination of acrylamide in solution. However, after increasing concentration of acrylamide from 0 to 50 nM a decline electrode response take places, which due to reduction of in electroactivity of the ssDNA (similar to changes in the biosensor impedance).

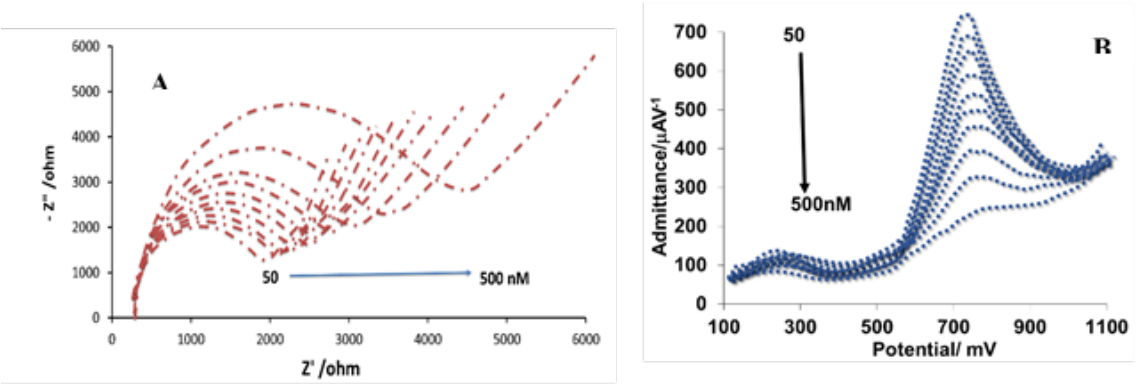

Fig. 5. EIS at ssDNA/AuNPs/PANI-CHI/Au before and after incubation with different acrylamide (50–500 nM) in 100 M KCl, 100 mM PBS pH 7.5 solution, applying a sinusoidal AC waveform of 10 mV in amplitude at the frequency range 1–1000 Hz. Experimental admittance of the solution under same condition at SW frequency 500 Hz and amplitude 25 mV

Further decline can be seen in higher concentration of acrylamide (from 50 to 500 nM in). The difference of peak intensities

$$\Delta A = A_{analyte} - A_{DNA}, \quad (1)$$

where A_{DNA} and $A_{analyte}$ are the admittance of the biosensor in absence and presence of acrylamide in solution, respectively. The experimental data indicates that employing FFT admittance voltammetric measurement, ΔA is more sensitivity than the impedimetric measurements (ΔZ). In fact, the experimental data specified that the by using value of ΔA trace level of the analyte can be measured, where under such condition any signal cannot be realized in the impedimetric measurement.

To obtain the best performance of the analytical measurement, it is needed to investigate the dependence of the ΔA on the experimental condition. The most important parameter here is pH and the parameters of the applied SW waveform (frequency and pulse amplitude.

3.4. Optimization of the parameters

In FFTAV technique the admittance voltammetric response of the biosensor depends on the applied conditions of excitation waveform, where the square wave frequency and amplitude on the analyte response. In order to optimize the biosensor response to acrylamide the SW parameters, frequency, SW amplitude in FFTAV technique were studied and amplitude 5 to 50 mV. Fig. 6 illustrates the results the calculated acrylamide signal (ΔA) with the change in value of SW frequency and amplitude for solution of 1.0×10^{-7} M of acrylamide in in 100 mM KCl, 100 mM PBS pH 7.5. As shown in the graph, the highest analytical signal was obtained for the amplitude value of 25 mV. Also, in case of changing the SW frequency in the range of 100–800 Hz ginned, the best analytical signal was obtained at 300 Hz.

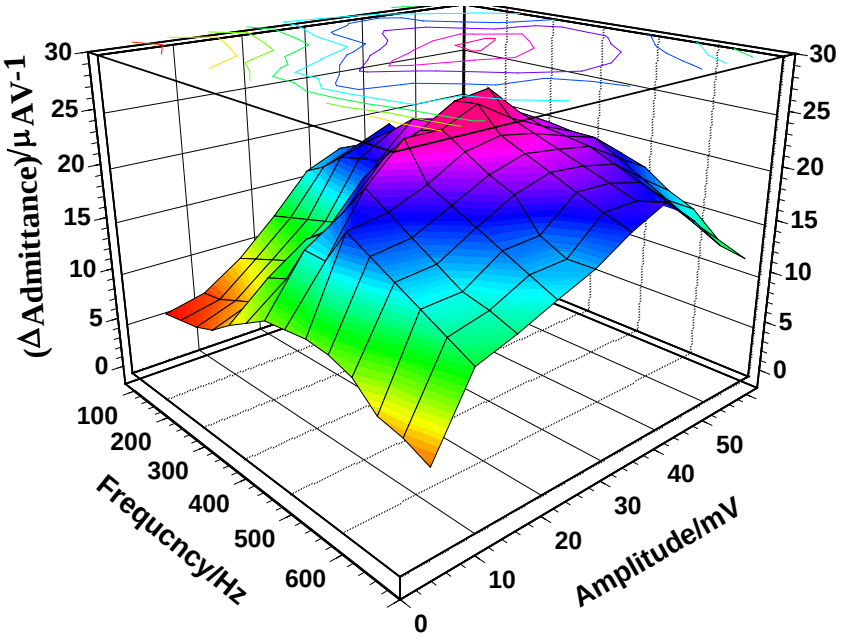

Fig. 6. The effect of frequency and amplitude on the response of the ssDNA/AuNPs/PANI-CHI/Au in 1.0×10^{-7} M acrylamide in 100 M KCl, 100 mM PBS pH 7.5 solution

Such results point out that the value of the analyte signal strongly depends on the applied SW condition in FFTA voltammetric measurements. In fact, the enhancement of the signal with the frequency (up to 300 Hz) may due to the enlargement speed of the potential excitation, (similar to the amplification of the current in cyclic voltammetric measurement with potential scan rate). However, for both parameters, after that value the signal decline, which may mainly due to kinetic limitation in the rate electrode processes of the guanine in DNA. Another possible factors may has contribution in the analytical measurement here is dependency of the background noise and peak shape of admittance voltammogram on the factors in the SW parameters. Therefore, it is expected that the value of the biosensor admittance is limited at high values of the square wave amplitudes. Consequently, these values were selected for the determination of the acrylamide in the subsequent experiments.

3.5. Optimization of pH

Fig. 7 demonstrates the dependence of the biosensor response (ΔA) to the solution pH for determination of 1.0×10^{-7} M acrylamide in 100 mM KCl, 100 mM PBS pH 6 to 9. All of the FFTA voltammograms were recorded at frequency 300 Hz and amplitude 25 mV. The results showed that the analyte signal increased with pH of the PB solution up to 7.5, this is an induction of at that pH enhances the rate electron transfer at the biosensor surface. On the other hand, at pHs higher than 7.5 the magnitude value of ΔA decreased. It seems that the best signal obtained at pH 7.5, where the DNA is very electroacitve and stable. Moreover, in such pHs, the chemical nature of the DNA may lose its stability on the electrode surface or the interaction of the analyte with DNA inhibited. Therefore, pH 7.5 was selected as the optimal pH for analyte analysis in the following experiments.

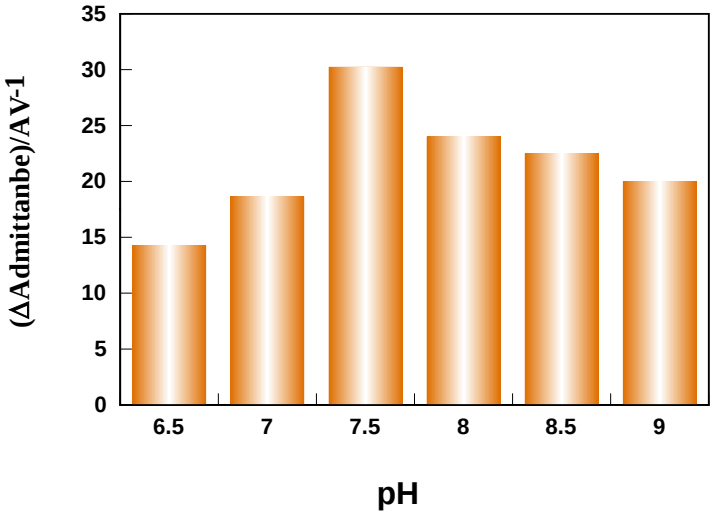

Fig. 7. The effect of pH on the response of the biosensor in solution of 1.0×10^{-7} M Acrylamide 100 mM KCl and 100 mM PBS. The SW frequency was 300 Hz at amplitude 25 mV

3.6. Calibration curve and sensor characterization

Under optimized conditions the change of ΔA with concentrations of synthetic acrylamide in solution was investigated. Fig. 8 shows the calibration curve for acrylamide solution in the range of 5.0×10^{-10}M to 8.0×10^{-7}M in 100 mM KCl, 100 mM PBs at pH 7.5. The standard deviations were estimated using for both the calibration curves and standard addition methods. For the measurements of 10 μL of the analyte standard solutions were introduced into the cell, and the FFTA voltammograms were recorded. This figure data represent the averaged signal for 5 consecutive additions of the acrylamide standard solutions. As can be seen in Fig. 8, the ΔA of acrylamide solutions increases in logarithm value with increments of the concentration of the analyte and lastly leveled off. But there is a linear relationships concentration of acrylamide over two concentration ranges, from 5.0×10^{-10} M to 2.0×10^{-7} M (the inset of Fig. 8).

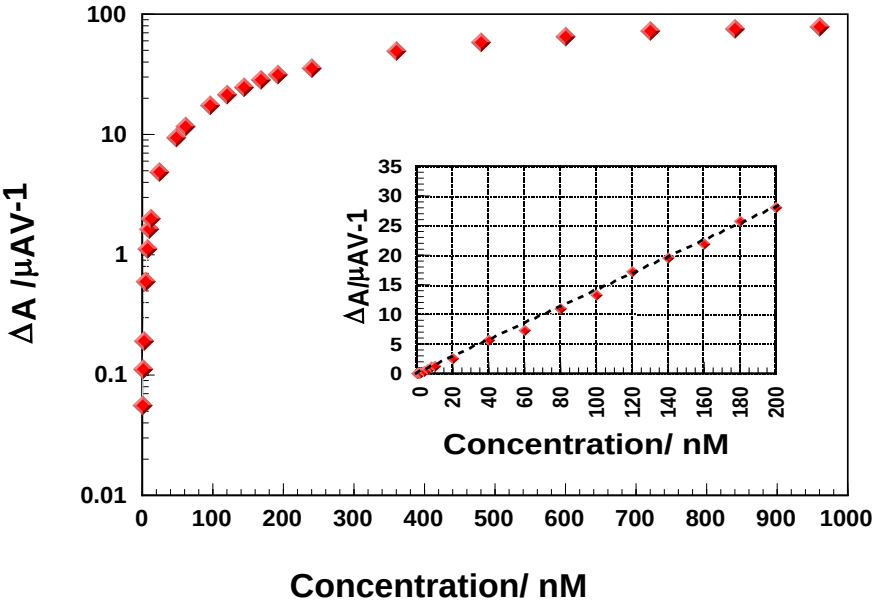

Fig. 8. The calibration curve for acrylamide standard solutions in the range of 0.01 nM to 800 nM the inset shows the linear relationship between ΔA and log(C) (nM) in the range of 0.1 nM to 200 nM, Inset voltammogram

At low concentration, the linearity observed in biosensor responses over concentration changes revealed that the biosensor could be possibly applied to the analysis of real samples for acrylamide determination. The limit of detection (LOD) of the developed method was calculated according to IUPAC recommendations;

$$LOD=3Sb/b \qquad (2)$$

Where Sb is the standard deviation (n=5) of the blanks, and b refers to the slope of the calibration graph) at a concentration level of 5.0×10^{-11} M. Therefore, according to the calculated LOD it can be concluded that the ssDNA/AuNPs/PANI-CHI/Au is highly sensitive. The results obtained by the proposed biosensor in this study were compared with those of previous works reported in the literature and are presented in Table 1. In evaluation, the performances of the fabricated biosensor is compared with some of the best previously reported.

Table 1. Comparison of the proposed biosensor with other reported methods for acrylamide determination

Electrode	**Linear range**	**LOD**	**Ref.**
Hb-DDAB carbon-paste modified electrode	1.3×10^{-11}–4.8×10^{-5} M	1.2×10^{-10} M	[50]
Hb-GNP modified ITO glass electrode	10^{-8}–10^{-5} M	4×10^{-8} M	[51]
SWCNT/Hb modified glassy carbon electrode	0.00001–1000 µM	0.001 µM	[52]
Hb/GNPs modified ITO glass electrode	0.04–10 µM	0.04 µM	[53]
DNA/GO modified glassy carbon electrode	0.05–1000 µM	0.05 µM	[54]
ssDNA/AuNPs/PANI-CHI/Au	0.01–200 nM	5×10^{-11} M	This work

In these measurement systems, the obtained recoveries for the spike samples were ranged from 99% to 101% and the contents of acrylamide found are in good agreement with that specified by the manufacturers. The results are shown in Table 2. These results indicate that the FFTSW voltammetry method has acceptable precession and accuracy for rapid and sensitive determination of acrylamide in pharmaceutical tablets.

Table 2. Determination of acrylamide in water by standard addition method (concentration in (nM))

Samples	**Detected (nM)**	**Added (nM)**	**Found (nM)**	**Recovery (%)**
1	7.0	12.0	18.2	95.7
2	7.5	20.0	27.8	101
3	6.5	40.0	46.0	99.0
4	6.8.	40.0	46.5	99.3

Also, in evaluation, the performance of the biosensor is compared with some of the best previously reported acrylamide detection techniques, which confirms that the presented biosensor for acrylamide with FFTAV exhibited excellent sensitivity and a linear range.

3.7. Stability and reproducibility of the Electrode

The stability of ssDNA/AuNPs/PANI-CHI/Au was evaluated by examining the analyte response, using FFTAV technique over a long time period. It storage stability was investigated for 60 days at room temperature when not in used. The results showed that the sensitivity reduce only 8.6±0.3% up that time, then it gradually decreases afterwards might be due to the adsorption of impurities.

4. CONCLUSION

Here, a new combined electrochemical technique was developed for the detection trace level of acrylamide in real sample (Iranian brand potato) using the FFTAV method, and ssDNA/AuNPs/PANI-CHI/Au biosensor. Under optimal conditions, the designed ssDNA/AuNPs/PANI-CHI/Au exhibited a wide linear response to acrylamide concentration, good sensitivity, repeatability and long term stability, 60 days. These would be a promising for developing new sensitive biosensor with this electrochemical method. However, more experiments will be required to study the various factors in detail so as to lessen to design a portable device for the environment applications.

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