ELECTROCHEMICAL DETECTION OF CIPROFLOXACIN FROM WATER USING A GRAPHENE QUANTUM DOTS - CARBON NANOTUBES PASTE ELECTRODE

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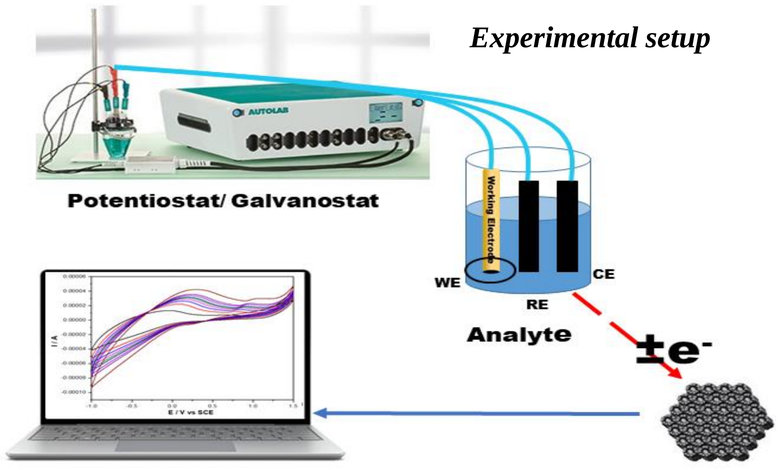
Introduction

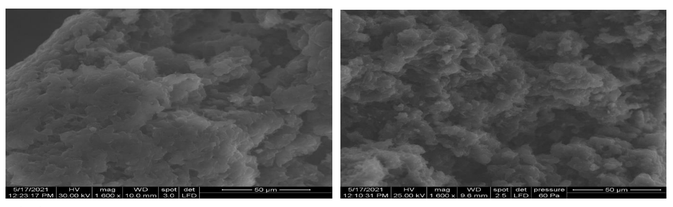
Ciprofloxacin (CFX) is one of the most potent quinolone derivatives in clinical use for the treatment of diseases in human life and livestock industry. Even if the most of the conventional methods, e.g. high performance liquid chromatography, high performance thin layer chromatography and molecular absorption spectrometry, used for CFX detection exhibit sensitivity and accuracy, they also have certain disadvantages related to time-consuming extraction procedures, complicated operations, a large number of organic solvents, high instrumentation costs and skilled personnel. Due to the advantages of easy miniaturization, high sensitivity, fast operation, reproducibility, ease of on-site determination, accuracy, relatively low cost, limit of detection at trace levels, the electrochemical detection has became an attractive alternative technique for detecting electroactive compounds in water. The composition and electrode material represent the core of the sensor performance. Carbon allotropes such as carbon nanotubes (CNT) and, more recently, graphene quantum dots (GRQD) as novel nanomaterials have received significant interest in the field of electroanalysis applications due to its attractive features, such as: high electrical conductivity, high specific surface, electrochemical mobility and environmentally friendly. In this work, GRQDs were used for improving the performance of CNT based voltammetric sensor in CFX detection from simulated water.

Materials and methods

All electrochemical studies were carried out in a three-electrode setup consisted of platinum electrode (counter electrode), saturated calomel electrode – SCE (reference electrode), unmodified paste electrode (carbon nanotubes-paraffin oil - CNT) and modified carbon paste electrode (graphene quantum dots-carbon nanotubes-paraffin oil – GRQD/CNT (carbon based working electrodes) using Autolab Pontentiostat/ Galvanostat 302. Carbon based working electrodes were obtained by simple mechanical mixing different percentages of certain amounts of GRQD, CNT and specific amount of paraffin oil to become homogeneous and to get stable composition of the paste electrode. The electrochemical technique applied for electrochemical detection of CFX was cyclic voltammetry (CV).



CARBON PASTE ELECTRODES CHARACTERIZATION



(a) (b)

Fig. 1. SEM image of the cross-section of the: a) CNT b) GRQD paste electrode surface

Table 1. Sensitivity of the electrochemical detection CFX using CV

Electrode Material/ Ratio %	E/V vs. SCE	Sensitivity/ $\mu AmgL^{-1}$
CNT:Ulei_ 1:3	-0.909	13.3
	+1.15	17.2
GRQD:CNT: PARAFFIN OIL 1:1:1.83	-*	-*
GRQD:CNT: PARAFFIN OIL 1:2:5	-*	-*
GRQD:CNT: PARAFFIN OIL 1:2.5:7.5	+0.770	**30.3**
	-0.700	**50.3**
GRQD:CNT: PARAFFIN OIL 1:5:18	-0.530	10.8
	+1.05	15.4
	+1.34	30.5
GRQD:CNT: PARAFFIN OIL 1:7.5:25	-0.803	4.02
	+1.06	7.13
	+1.42	20

*no signal was found

Results and Conclusions

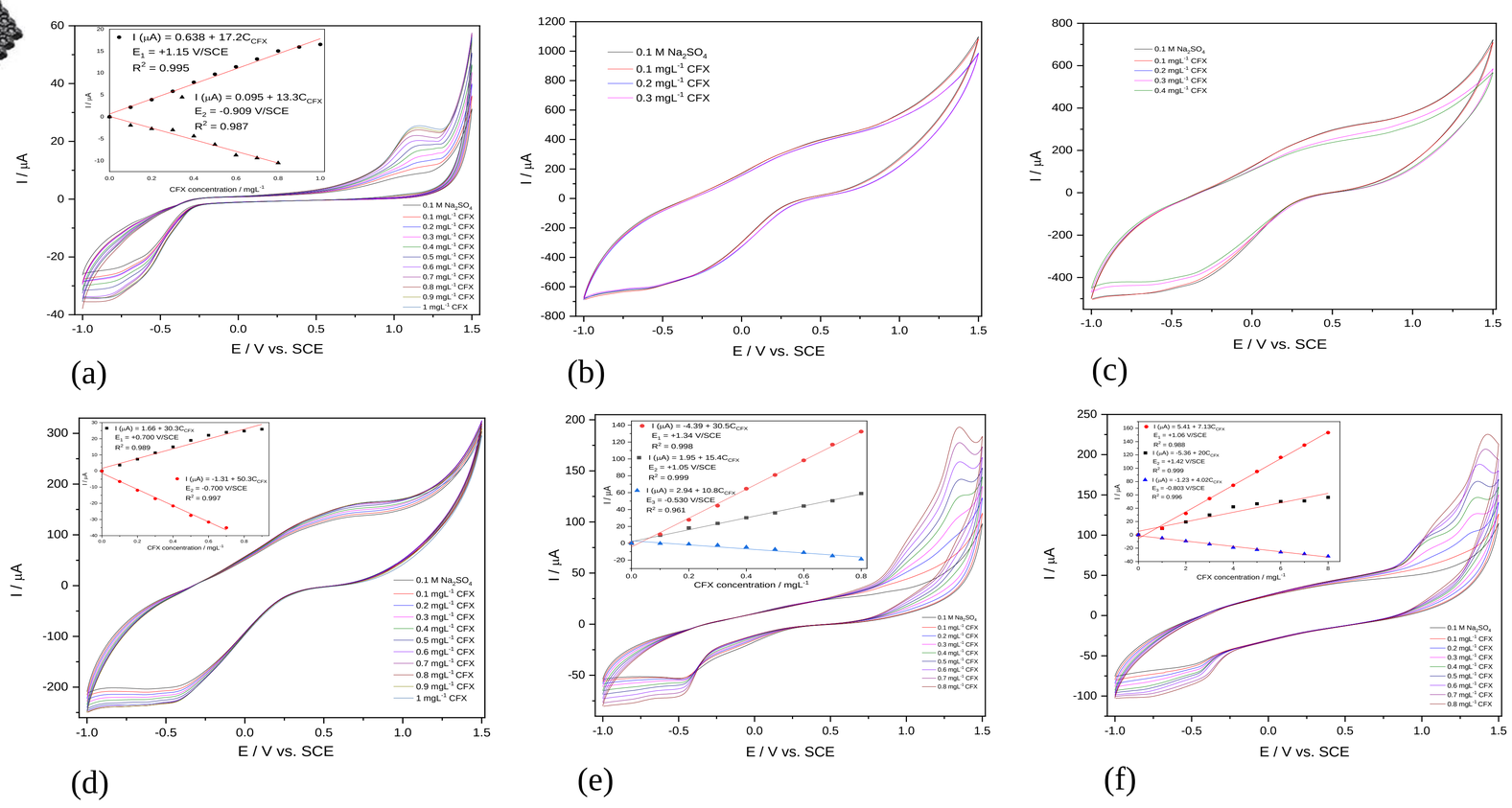


Fig. 2. Cyclic voltammograms recorded in 0.1 M Na_2SO_4 supporting electrolyte and various CFX concentrations on: CNT paste electrode (a) and GRQD-CNT paste electrode at different ratio (b) - (f); Insets: Calibration plots for CFX detection in the concentration range of 0.1-1 mgL^{-1}.

The best results related to the electrode composition were obtained for the ratio 1:2.5:7.5 of GRQD, CNT and paraffin oil. CNT exhibited lower background current own to the capacitive component and lower electrochemical conductivity that led to about three times lower sensitivity in comparison with the graphene quantum dots (Fig. 2a). The presence of GRQD enhanced the electrochemical response in CPF detection due to the good catalytic activity towards CFX oxidation and reduction (Fig. 2d), which is expressed in lower value of the detection potential. Based on the results related to the stability, selectivity, repeatability, sensitivity and reproducibility using cyclic voltammetry, it can be concluded that GRQD-CNT paste electrode should be considered for further development envisaging the real practical detection application in water quality control.

Acknowledgments

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