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ORIGINAL ARTICLE / ÖZGÜN MAKALE

FABRICATION OF ELECTROCHEMICAL NANOSENSOR BASED ON CuO AND GRAPHITE POWDER AND ITS APPLICATION FOR TRACE ANALYSIS OF OP (ORGANOPHOSPHORUS) PESTICIDES IN REAL SAMPLES

CuO VE GRAFİT TOZUNA DAYALI ELEKTROKİMYASAL NANOSENSÖR İMALATI VE GERÇEK NUMUNELERDE OP (ORGANOFOSFOR) PESTİSİTLERİNİN ESER MADDE ANALİZİ İÇİN UYGULAMASI

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ABSTRACT

Objective: *Uncomplicated, low-cost, highly discerning, and sensitive electrochemically active nanosensors have been synthesized using copper salt as a precursor, surfactants, and structural directing agents. These synthesized CuO Nanoparticles (NPs) were electroactive and EC treatments were also performed by modifying these NPs with graphite powder (CPE) to enhance the electrocatalytic activity, sensitivity.*

Material and Method: *The characterization of these fabricated nanosensors was done by cyclic voltammetry (CV), differential pulse voltammetry (DPV), field emission scanning electron microscopy (FESEM), powder X-ray diffraction (PXRD), transmission electron microscopy (TEM).*

Result and Discussion: *The EC behavior of Organophosphorus (OP) pesticides in the real samples was examined by these fabricated sensors. Parameters such as pH of solution scan rate of the experiment, accumulation time, and potential difference have been optimized in the experiment for trace determination of OP pesticides.*

Keywords: *Carbon paste electrode, cyclic voltametry, electrochemical sensing, nanosensor, organophosphorus pesticides*

ÖZ

Amaç: *Karmaşık olmayan, düşükmaliyetli, son derece seçici ve hassas elektrokimyasal olarak aktif nanosensörler,bir öncü olarak bakır tuzu, yüzey aktif maddeler ve yapısal yönlendirme ajanları kullanılarak sentezlenmiştir. Sentezlenen bu CuO Nanopartiküller (NP'ler) elektroaktiftir ve elektro katalitik aktiviteyi ve hassasiyeti artırmak için grafit tozu (CPE) ile modifiye edilerek EC işlemleri de gerçekleştirilmiştir.*

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Gereç ve Yöntem: *Bu fabrikasyon nano sensörlerin karakterizasyonu, dönüşümlü voltametri (CV), diferansiyel puls voltametri (DPV), alan emisyonu taramalı elektron mikroskobu (FESEM), toz X-ışınıkırınımı (PXRD) ve transmisyon elektron mikroskobu (TEM) ile yapılmıştır.*

Sonuç ve Tartışma: *Organofosforlu (OP) pestisitlerin gerçek numunelerdeki EC davranışı bu fabrikasyon sensörlerle incelenmiştir. OP pestisitlerinin eser madde tespiti için çözelti tarama hızının pH'ı, birikme süresi ve potansiyel fark gibi parametreler optimize edilmiştir.*

Anahtar Kelimeler: *Karbon pasta elektrot, dönüşümlü voltametri, elektrokimyasal algılama, nanosensör, organofosfor pestisitler*

INTRODUCTION

Electrochemical sensing technique is an interesting tool for the analysis of original biological samples. These Electrochemical techniques have a wild range of applications such as high sensitivity and low detection limits with rapid and concurrent analysis of many samples. All these experiments required very cheap instrumentations [1-4]. Metal-based NPs can effectively increase the sensitivity and selectivity. Metal-based NPs have unique physical and electro catalytic properties such as surface-to-volume ratio is high, they are chemically stable and their electrical conductivity is also quite good, all these qualities have made these metal- based NPs a perfect candidate for sensing applications as well as for developing the Electrochemical studies for sensing purpose [5-9].

This is the reason that we have preferred electrochemical techniques for sensing purposes. In other processes, there is the use of a large number of organic solvents, time-consuming procedures, complicated procedures, and the use of expensive instrumentation [10,11].

Organophosphorus pesticides have been utilized for pre-reap treatment in an assortment of harvests. This pesticide undergoes degradation to generate metabolites and these metabolites are poisonous and somewhat water dissolvable. These metabolites pollute water resources as well as soil. As far as the environmental and biological systems are concerned these pesticides must be monitored. As these OP have hazardous effect on health. Materials with dimensions less than 100nm are commonly known as nanomaterials. They have a high surface area, comparatively high reactivity, and very unique mechanical and optical properties. Due to these properties, they are used in different fields such as electronics, medicine, energy device, and sensor, etc. [15].

Some of the research articles show the use of nanomaterial as a biosensor for the assessment of total antioxidant capacity in organic product juices. Biosensors show the increased performance compared to the bare electrode, as nanomaterials have a high surface area and good electrochemical properties [16].

There exists a huge demand for new technology which can improve the quality and safety of food products, Fatima Mustafa et al. described the use of nanosized particles in the food industry with sensing technologies [17].

Reports shows that AgNPs, TiO2 NPs, and nano-encapsulates are the major nano-based material which have been used in the food industry they are mainly used as food additives and food contact materials. In a recent report, it is shown that nanoparticle-based sensors can be used for the detection of pesticides and other adulteration in food [18].

Recent research work also concludes that the Nanomaterial-based sensors showed higher sensitivity and a trustworthy technology for the detection of pesticides in fresh water in the future [19].

Garcia, et al. (2018) reviewed applications for the use of nanomaterial as a sensing element inside the packaging. They reviewed metal oxides such as TiO2, ZnO, aluminum oxide, silicon dioxide/silica and conclude that a small amount of these materials migrate from the packaging [20].

Different techniques such as liquid and gas chromatography [21, 22], spectroscopy [23], and electrochemistry [24] have been used for forensic investigations. In this field, nanomaterial-based biosensors have become very famous because of their special properties [25].

MATERIAL AND METHOD

Preparation of stock solution of 1μmol L^{-1} OP pesticide was done in ethanol, Graphite powder, $CuNO_3$, KCl, buffer solution, and surfactants. All the solutions were prepared in DI water.

The Organophosphosphorus pesticide was used without further purification. The stock solution of OP was prepared in pure ethanol. The concentration of OP was 1μmol L^{-1}, after the preparation of the solution, and it was kept in the dark at low temperature.

The composition of buffer solution: -20 mmol phosphate buffer was prepared with the help of K_2HPO_4 and its conjugate base $KHPO_4$. Both salts were dissolved in DI water.

Apparatus

Metrohm Autolab B.V. PGSTAT128N computer controlled with software NOVA version 1.11.2, with Conventional 3 electrode system, for this experiment Carbon paste electrode was used as a working electrode, Ag/AgCl (3 M KCl) used as a reference electrode and platinum wire as counter electrode. NOVA NANOSEM 450 FESEM equipped with EDX for SEM ananlysis.

Synthesis of CuO nanoparticle

CuO was prepared by using different structural agents. 1.0 g of copper salt was dissolved in 5 ml of DI water, to this 1.00 g of Tween was added followed by the addition of 2.00 g of dextran (Mw = 2×10^6 M) at room temperature. The resultant gel was heated for 30 minutes at 80°C on a magnetic stirrer to form a light blue color gel, this gel was aged for 3 to 4 days and then calcined at 600°C for 2 hours.

Another CuO was prepared by using different structural agents. The second CuO was prepared by dissolving 1.0 g Cu $(NO_3)_2.3H_20$ in 1.0 ml of ultrapure water and 1.0 g of SDS in 10 ml of ultrapure

water followed by the addition of 2.0 g CMC in 3.0 ml of ultrapure water at 25 °C, and followed by the above procedure.

Fabrication of carbon paste unmodified and modified electrodes

Working electrode Carbon paste electrode was prepared by mixing graphite powder and paraffin oil in 7:3.ie paste had the composition of graphite powder and paraffin oil 70% and 30% respectively. Homogenization was also done by mortar and pestle for 20 min. The resultant paste was allowed to rest for 2-3 days for homogenization of paraffin oil and graphite powder. This paste is packed in the tip of a plastic syringe in which copper wires are connected for providing conducting medium. The surface of these CPE was smoothed with white paper with light pressure as the surface of the CPE become shiny the smoothing process of the surface was stopped. This prepared working electrode is known as bare CPE. The modification of these bare CPE was done with synthesized NPs, for this graphite powder, NPs and paraffin oil were mixed in 7:2:1 respectively. Firstly NPs and Graphite powder were mixed thoroughly for 10 min after that paraffin oil was added. The resulting paste was also packed in the tip of the syringe and followed the same process for the smoothening of the surface of the electrode.

Real sample preparation

Water sample

Tap water was used as a real water sample. This sample of water was filtered with Whatman filter paper to avoid PMs (particulate matters). The pH of the sample was adjusted by buffer solution the resulting sample solution has pH 7. This sample solution was kept at a low temperature.

Food sample

The tomatoes were gathered from the nearby market. Tomato Samples were chopped down into little pieces, precisely gauged, and afterward exposed to homogenization. 25 gm of sample mixed with 50ml of methanol and 0.2 gm of NaOH, in a beaker than this extract was centrifuged and then evaporated to dryness, pH was adjusted to 7 [12].

General analytical procedure

For Electrochemical measurements, 0.02 M phosphate buffer (pH 7.0), supporting electrolyte (KCl), 0.02 M CTAB, and sample (OP) were taken in a clean beaker. While stirring the solution the cyclic voltammograms were recorded. The range of cyclic voltammograms was −1.00 to −1.4 V for the cathodic and anodic scans. Other voltammetric parameters were optimized as follows: modulation time 1ms, step potential −10 mV, and scan rate was $0.05Vs^{-1}$ to $0.1Vs^{-1}$.

RESULT AND DISCUSSION

Characterization of CuO NPs

The characterization of synthesized NPs was done by FESEM-EDX, X-ray diffraction, and TEM analysis. These analyses exhibited the morphological behavior of CuO NPs as shown in Figure 1-4. X-ray diffraction analysis shows clear information about the crystallinity and phase purity of CuO NPs. These studies of XRD were shows in our work [26].

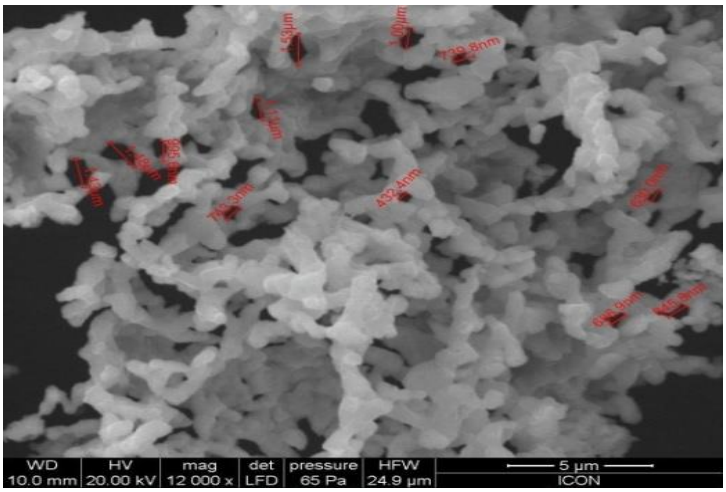

Figure 1. FESEM image of copper oxide NPs

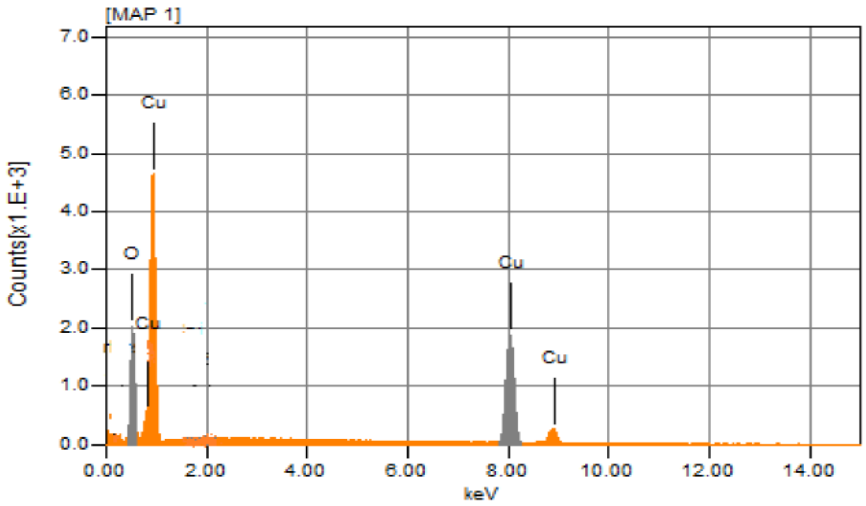

Figure 2. EDX analysis of the CuO NPs

The TEM image showed a ligament-like shape. This gives clearly close agreement with their FESEM results. The clearly shown fringes in the TEM image are the indication of the high crystalline nature of synthesized CuO NPs.

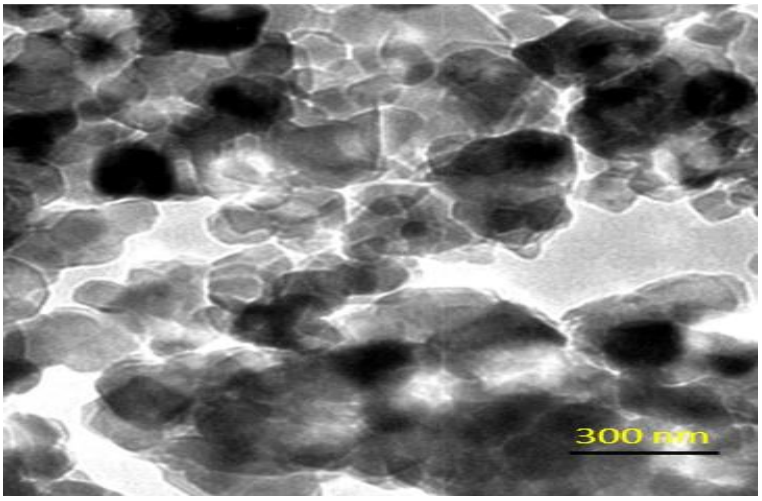

Figure 3. TEM image of porous CuO NPs

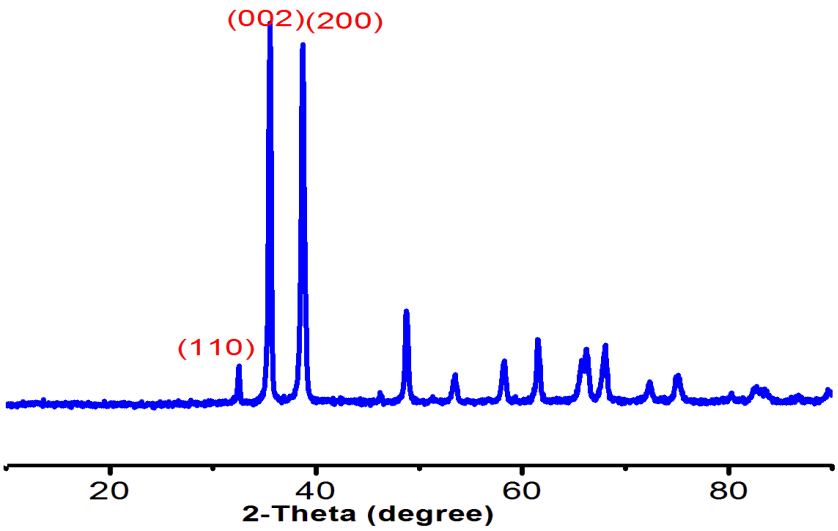

Figure 4. XRD patterns of macroporous copper-oxide (mpCuO)

EC characterization of electrode

The characterization of the surface feature of modified electrodes was done by CV.

For the calculation of surface area of CPE and NPs modified CPE Cyclic voltammograms were recorded. 1.0 $\times 10^{-3}$M $K_3Fe(CN)_6$ in.1 M KCl solution were taken and cyclic voltagrammes were recorded. For calculation of surface area of electrodes Randles-Sevick equation [2, 9] was used. The Randles-Sevick is as follows:

$I_{pa} = 0.4463(F^3/ RT)^{1/2} N^{3/2} AoDo^{1/2} C_v^{1/2}$

Where I_{pa}= anodic peak current

N= number of electrons transferred

A_0= surface area of the electrode (cm^2)

D_0 = diffusion coefficient

C= concentration of $Fe(CN)_6^{3-/4-}$ion

The surface area was calculated 0.0124, 0.154and 0.140 cm^2 for carbon paste electrode, and CuO modified electrode respectively.

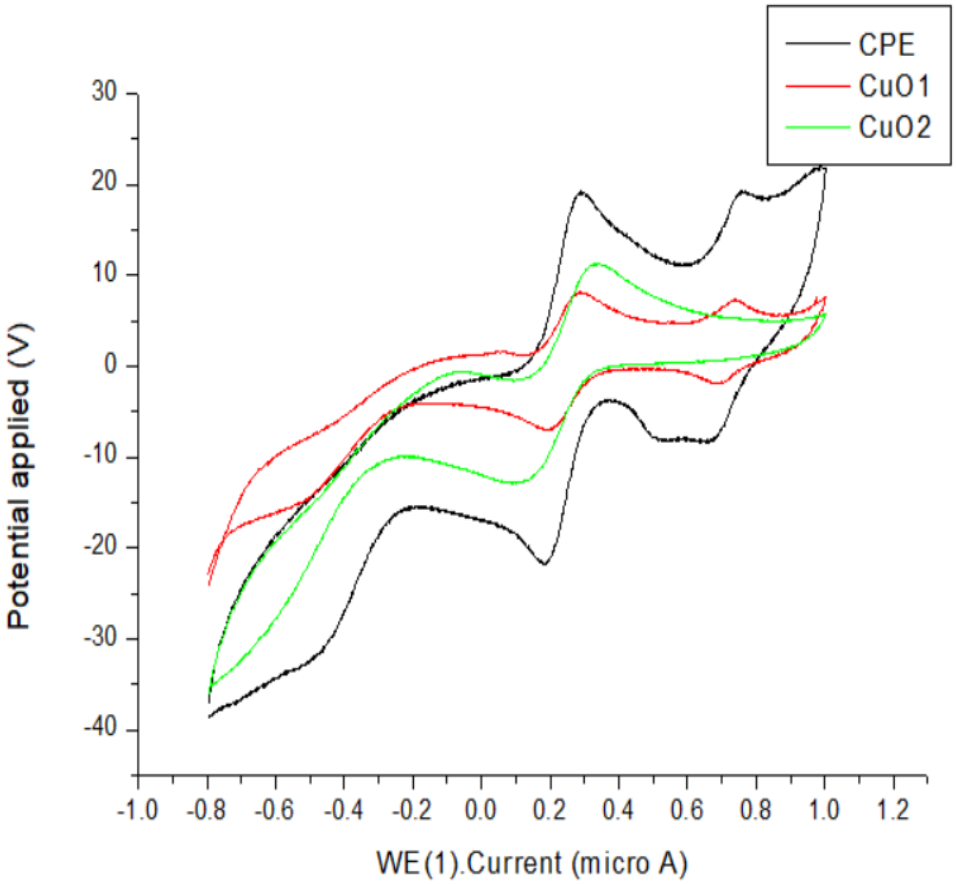

Figure 5. Cyclic voltammogram of 1.0 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M KCl at CPE and modified electrodes

Voltammetric behavior of pesticide

EC property was evaluated by Cyclic voltammetry.CV also provides information about the voltammetric behavior of OP pesticide. Cyclic voltammograms are shown below. The cyclic voltammogram exhibits a catholic peak at −825mV between the potential ranges from −1.0V to −1.4 V as shown in Figure 6.

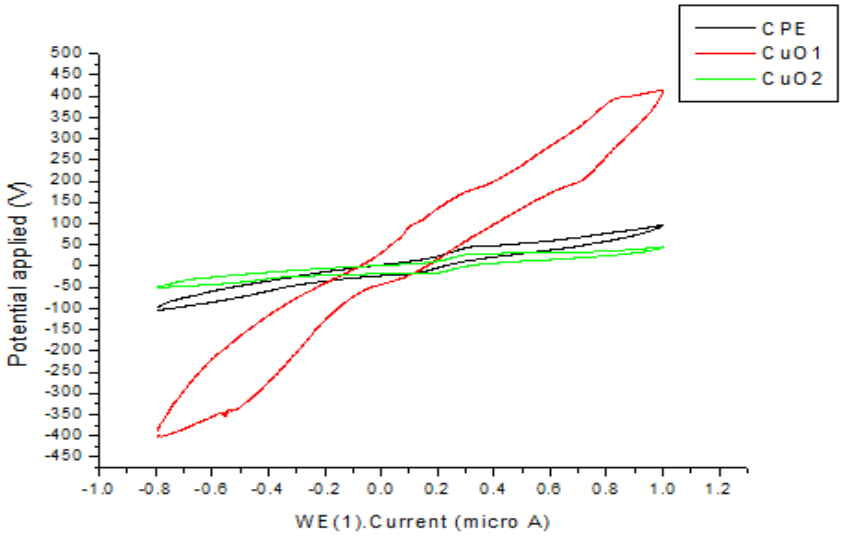

Figure 6. CV of 1.0 µM pesticide in 20mM CTAB, supporting electrolyte KCl, and 20 mM Phosphate buffer solution having pH 7.0 at all CPE and modified electrodes

EC property and the voltammetric behavior of OP pesticide were also studied with help of AdDPV. The AdDPVvoltammogram of 1.0 µM OP in 20mM CTAB and 20mM phosphate buffer shows a single well-defined peak at 0.05 V as shown in Figure7.

Effect of pH

All these studies show the effect of pH on different parameters such as peak current potential and the shape of voltammogram. So the pH of the solution is very important in the evaluation of the proton to electron ratio. Peak current is directly proportional to pH of the solution and the maximum value of peak current obtained at pH 7±0.01.

Effect of surfactant concentration

The rate of electron transfer may be changed if the electrode surfaces adsorb the surfactants. These surfactants affect the EC reactions as they can stabilize the radical and another reaction intermediate [13]. Surfactants can cause the formation of micellar aggregates these can affect the transportation of mass of sample to the electrodes [14] due to which change in peak current value and peak potential value is observed as the concentration of surfactants increases.

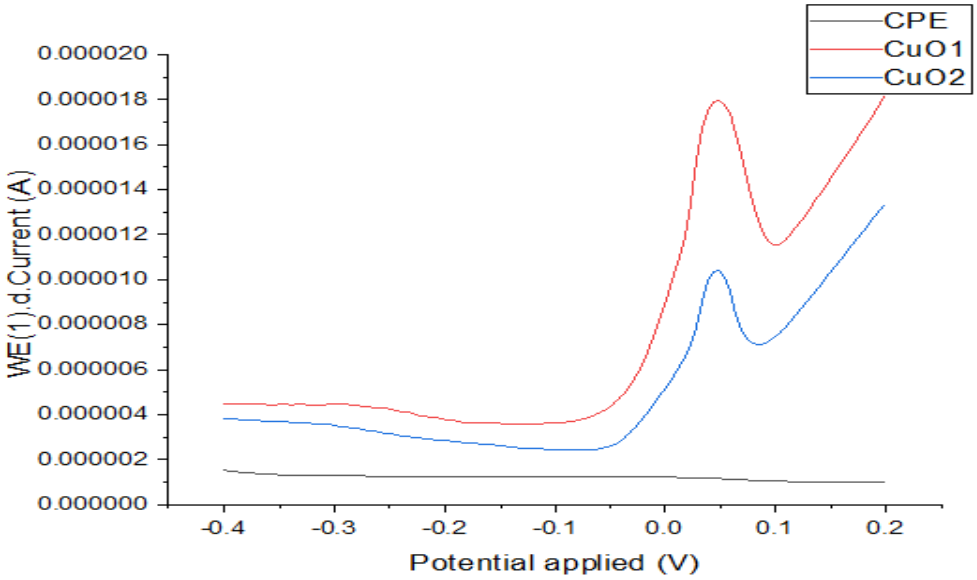

Figure 7. AdDPSvoltammogram CPE and CuO electrode without pesticide in electrolyte and phosphate buffer solution

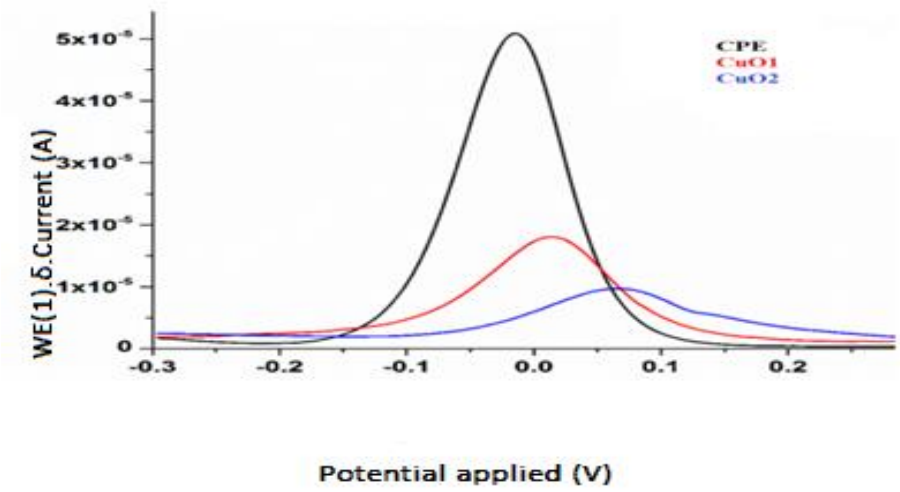

Figure 8. AdDPSvoltammogram of 1.0 µM OP in 20mM CTAB, KCl and 20mM phosphate buffer at all CPE and modified CPEs

Specificity

In order to judge the analytical application of this suggested method, it is necessary to examine the effect of the interfering ions and organic compounds for selective determination of OP on CuO Modified CPE. Generally, some organic compound exist in the environmental samples this method have no effect of such interfering organic compounds. This method can be validated by calculating the LOD

and linearity rage of OP pesticides by using peak current as a function of the concentration of the analyte at least five times under the optimized conditions [2].

Analytical application

To examine the practicability of this method and electrodes, both were used for the determination of OP pesticide in real samples. Initially, voltammetric responses were not obtained. This can be due to less concentration of pesticides or the absence of pesticides. Afterward, a very less amount of OP pesticide was added to samples. The recorded voltammogram was compared from the voltammograms which were obtained from the 1.0×10^{-6} g mL^{-1} standard stock solution of pesticides. No such difference in peak response was observed. This indicates the better sensitivity of the newly designed electrode and practicability of the suggested method for real samples. The method is quick, cost-effective, and environmentally friendly.

Herein we have reported a sensitive and selective electrochemical sensor. This has been designed by using exclusive properties of CuO NPs such as high surface area, efficient electron transfer, and electrocatalytic properties. CV results clearly show that the CuO is effective in transferring charge on the electrode surface in the applied potential range. The designed electrode applied for examining the presence of OP pesticide in surfactant media. This method reports an accurate determination of OP pesticides in real samples with a low detection limit.

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AUTHOR CONTRIBUTIONS

Conception: *R.D.*; Design: *A.C., R.D.*; Supervision: *R.D.*; Resources: *R.D.*; Materials: *A.C.*; Data collection and/or processing: *A.C.*; Analysis and/or interpretation: *R.D.*; Literature search: *A.C.*; Writing manuscript: *A.C., R.D.*; Critical review: *R.D.*; Other: -

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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