



Simultaneous voltammetric determination of captan, carbosulfan, 2,3,7,8-tetrachlorodibenzodioxin and pentachlorophenol in groundwater by ceria nanospheres decorated platinum electrode and chemometrics



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ABSTRACT

In this work, a linear sweep voltammetry method has been proposed for the estimation of captan, carbosulfan, 2,3,7,8-tetrachlorodibenzodioxin and pentachlorophenol using ceria nanospheres modified platinum electrode. The reduction peaks of captan and carbosulfan observed in the linear sweep voltammograms overlapped strongly and it was difficult to estimate captan and carbosulfan individually from their mixtures. Gaussian curve fitting algorithm was used to facilitate the resolution of complex linear sweep voltammograms. Quantitative analysis for each of the pesticides in a mixture was studied with the help of linear regression analysis. The analytical performance of the calibrated models was investigated with the aid of relative prediction error (RPE), root mean square error for cross validation (RMSECV) and recovery. The proposed calibrated models were then applied for the estimation of the four pesticides in several ground water samples, where the RPE, recovery and RMSECV of the spiked samples were within the acceptable limit.

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1. Introduction

Pesticides are commonly used in agriculture because of their ability to control agricultural pests [1]. However, extensive use of pesticides in agriculture results in increase in the concentration of pesticide residues in soil. An increase in the accumulation of pesticide residues poses significant risks to environment and human health [2–4]. The harmful effects of pesticide residues in human health include nerve damage, liver diseases, blurred vision, asthma, headaches, abdominal pain, vomiting and depression [2–4].

In agricultural production, India holds the second position in the world. India is also one of the world's five largest producers of rice, apple and guar gum. In India, captan, carbosulfan, 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and pentachlorophenol (PCP)

are the most widely used pesticides in apple, guar gum and rice for pest management [5–12]. These pesticides reach soil and contaminate groundwater, which enter into food chain and affects the function of central nervous system in humans and livestock [5–12]. High levels of captan, carbosulfan, TCDD and PCP can affect the germinal centers in the spleen, immune and lymphocyte response, plasma cells in popliteal lymphoid nodes, bone marrow cells and granulocyte-macrophage progenitor cells immune system, fertility, nervous system and thyroid hormone [13,14]. These pesticides also have the ability to inhibit the active sites of acetylcholinesterase (AChE) [15]. Recently, Nesakumar et al., [15] reported that the inhibition of AChE enzyme by captan, carbosulfan, TCDD and PCP were 100, 47.7, 72.7 and 68.1% respectively. In addition, Nesakumar et al., [15] developed a mathematical model based on AChE enzyme inhibition for the simultaneous determination of captan, carbosulfan, TCDD and PCP in groundwater by ceria nanospheres decorated platinum electrode. Since AChE inhibition based pesticide sensors are not specific in nature [16], nanomaterial with high catalytic activity and selectivity is preferred. Hence it is the need of the hour to develop a highly selective and sensitive sensor for the simultaneous detection of captan,

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carbosulfan, TCDD and PCP in groundwater to improve water safety and to protect the ecosystem.

High performance liquid chromatography, gas chromatography, spectrophotometry, mass spectrometry, UV–visible spectroscopy, total internal reflection ellipsometry, electrochemiluminescence technique, surface enhanced raman spectroscopy and fluorescence resonance energy transfer technique were the well-established detection methods used for the detection of captan, carbosulfan, TCDD and PCP [5–12]. Even though these analytical methods are highly sensitive and selective, they are time consuming, cost-intensive and require well trained technicians to run the analysis [5–12]. Enzyme inhibition based electrochemical biosensors for the detection of pesticides have attracted researchers owing to their simplicity, rapidity and reduced sample preparations [13,14]. However, enzyme inhibition based electrochemical biosensors are dependent on too many control parameters to exactly quantify the pesticide residues in contaminated groundwater. In order to overcome the disadvantages of enzyme inhibition based electrochemical biosensor, considerable attention has been given on the fabrication of non-enzymatic electrodes [17,18]. Metal oxide nanomaterials have attracted increasing attention in the fabrication of enzyme inhibition based electrochemical biosensor because of their large specific surface area. In particular, Ceria (CeO_2) nanoparticles have drawn the interest of researchers because of their high electrical conductivity, surface to volume ratio, biocompatibility and catalytic ability [19,20]. Recently, Nesakumar et al. [19] reported the fabrication of CeO_2 film on glassy carbon electrode for the detection of lactate in blood serum in which CeO_2 nanoparticles converted lactate into pyruvate in the absence of lactate dehydrogenase enzyme. Owing to the superior catalytic ability, CeO_2 nanoparticles were preferred in this work.

In this work, a linear sweep voltammetric method for the simultaneous determination of quaternary mixtures of captan, carbosulfan, TCDD and PCP has been developed. In addition, Gaussian algorithm and linear regression methods were used to develop calibration models for the prediction of the four pesticides. To exemplify the practicability of the proposed method, it was applied for the prediction of the four pesticide residues in groundwater samples.

2. Experimental

2.1. Materials

Cerium(III) nitratehexahydrate and sodium hydroxide were obtained from Merck India Ltd., India. Captan, carbosulfan, TCDD, PCP, zinc acetate were purchased from Sigma Aldrich, USA. Cupric acetate and nickel chloride were purchased from Thermo Fisher Scientific Pvt. Ltd., India. Cadmium acetate dehydrate was procured from Loba Chemie Pvt. Ltd., India. Pt working electrode (CHI102, 2 mm diameter), Pt wire counter electrode (CHI115, 0.5 mm diameter) and 0.4 M KCl saturated Ag/AgCl reference electrode (CHI111, 0.5 mm diameter) were procured from CH Instruments, Inc., USA. All solutions and reagents were prepared using deionized water (Millipore, USA).

2.2. Synthesis and characterization of CeO_2 nanoparticles

0.2 mM of cerium(III) nitratehexahydrate solution was added to 0.4 mM NaOH solution and the mixture was stirred for 30 min at room temperature. After 30 min stirring, the mixture was transferred into hot air oven and maintained at 353 K for 5 h. The obtained precipitate was found to be pale yellow in colour. The resulting pale yellow precipitate was washed with distilled water and dried at 323 K for 12 h in air. Finally, the powder sample

was annealed at 573 K for 2 h. Later, the surface morphology of prepared CeO_2 powder sample was examined using field emission scanning electron microscope (FE-SEM, Model JSM 6701F, JEOL, Japan).

2.3. Fabrication of Pt/ CeO_2 /Chitosan electrode

10 μL of CeO_2 nanoparticles (0.5 mg mL^{-1}) was added to 100 μL of chitosan solution (0.05 wt%) and the mixture was sonicated for half an hour. After that, 5 μL of the sonicated mixture was deposited onto the surface of Pt working electrode. Then the modified Pt working electrode (Pt/ CeO_2 /Chitosan) was allowed to dry at room temperature for 2 h. Finally, the Pt/ CeO_2 /Chitosan electrode was rinsed thoroughly with deionized water.

2.4. Electrochemical analysis

Electrochemical measurements were performed using an electrochemical workstation (CHI600C, CH Instruments, USA). The three electrode system comprised of Pt/ CeO_2 /Chitosan as working electrode, platinum wire as an auxiliary electrode and Ag/AgCl saturated with 0.4 M KCl as a reference electrode. Linear sweep voltammetry was carried out in a 20 mL electrochemical cell with 5 mL PBS solution. In the experimental procedure, mixtures of several pesticide solutions were prepared and transferred to electrochemical cell. After a static period of 5 s, linear sweep voltammetry was recorded from -0.75 to 0.80 V (vs Ag/AgCl) using Pt/ CeO_2 /Chitosan electrode at a scan rate of 0.1 V s^{-1} . All linear sweep voltammetric studies were carried out at room temperature.

2.5. Data analysis

In order to identify pesticide residues and their concentrations, Gaussian curve fitting algorithm was applied on linear sweep voltammograms measured at different concentrations of pesticides. In addition, electrochemical parameters namely full width at half maximum of cathodic peak height ($E_{p1/2}$), cathodic peak potential (E_{pc}), cathodic peak current (I_{pc}) and the amount of charge consumed (Q) for different concentration of pesticides were calculated using Gaussian function (Eq. (1)).

$$I = I_0 + \frac{Q}{E_{p1/2} \sqrt{\pi}} \exp\left(-\frac{(E_{app} - E_{pc})^2}{E_{p1/2}^2}\right) \quad (1)$$

where I_0 is the baseline offset and E_{app} is the applied potential. Linear regression models were also formulated to bring out the correlation between added pesticides and their corresponding cathodic peak current.

$$I_{pc} = m[\text{pesticide}] + c \quad (2)$$

where m and c are the slope and intercept of the calibration curves. Besides, analysis of variance (ANOVA) was carried out at 0.05 level to determine the existence of significant differences between regression coefficients. P value less than 0.05 was considered to be significant. The prediction ability of each linear regression model for the estimation of pesticides in groundwater samples was compared and validated by calculating percentage recovery (Eq. (3)), relative prediction error (RPE) (Eq. (4)) and root mean square error of cross-validation (RMSECV) (Eq. (5)).

$$\% \text{ recovery} = 100 \times \left[\frac{1}{n} \sum_{i=1}^n \frac{\text{pesticide}_{(\text{predicted})}}{\text{pesticide}_{(\text{added})}} \right] \quad (3)$$

$$\text{RPE}_s = \left[\frac{\sum_{i=1}^n (\text{Pesticide}_{(\text{predicted})} - \text{Pesticide}_{(\text{added})})^2}{\sum_{i=1}^n (\text{Pesticide}_{(\text{predicted})})^2} \right]^{0.5} \quad (4)$$

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