

# Electrochemical behavior and differential pulse voltammetric detection of thiobencarb on 2-(4-((4-ethoxyphenyl)diazenyl)phenylamino)ethanol-modified carbon paste electrode

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**Abstract** Cyclic voltammetry, chronoamperometry, and rotating disk electrode voltammetry were used to investigate the electrochemical behavior of thiobencarb (TB) at carbon paste electrode modified with an azo dye, 2-(4-((4-ethoxyphenyl)diazenyl)phenylamino)ethanol (EDPE), EDPE/modified carbon paste electrode (MCPE). The modified electrode showed high electrocatalytic activity toward thiobencarb. The current was enhanced significantly relative to the situation prevailing when a bare glassy carbon electrode was used. The kinetics parameters of this process were calculated, the apparent electron transfer rate constant  $k_s$  and  $\alpha$  (charge transfer coefficient between electrode and EDPE) were  $14.6 \text{ s}^{-1}$  and 0.48, respectively. The experimental parameters were optimized, and the mechanism of the catalytic process was discussed. The best defined cathodic peak was obtained with 0.1 M acetate buffer (pH 3.0). The response of the sensor was very quick, and response time was approximately 5 s. The differential pulse voltammetry response of the MCPE was linear against the concentration of TB in the range of 0.96 to  $106 \mu\text{g L}^{-1}$ . The limit of detection was found to be  $0.025 \mu\text{g L}^{-1}$ . The precision was examined by carrying out eight replicate measurements at a concentration of  $25 \mu\text{g L}^{-1}$  TB; the relative standard deviation was 2.9%.

**Keywords** Thiobencarb · EDPE · Electrocatalytic activity · Modified electrode · Voltammetric measurements

## List of symbols

$k_s$	Apparent electron transfer rate constant ( $\text{s}^{-1}$ )
$v$	Scan rates ( $\text{mV s}^{-1}$ )
$D$	Diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$C^*$	Bulk concentration ( $\text{mol cm}^{-3}$ )
$A$	Electrode area ( $\text{cm}^2$ )
$K$	Catalytic rate constant ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$\Gamma$	Surface coverage ( $\text{mol cm}^{-2}$ )
$\nu$	Kinematics viscosity ( $\text{cm}^2 \text{s}^{-1}$ )
$\omega$	Rotation speed ( $\text{rad s}^{-1}$ )
$E_{pc}$	Reduction peak potential (V)
$E_{pa}$	Oxidation peak potential (V)
$\Delta E_p$	Peak-to-peak separation potential (V)
$E^{\circ'}$	Formal potential (V)
$b$	Tafel slope (V)
$F$	Faraday constant ( $\text{C mol}^{-1}$ )
$I_{pc}$	Reduction peak current ( $\mu\text{A}$ )
$I_{pa}$	Oxidation peak current ( $\mu\text{A}$ )
$\alpha$	Charge transfer coefficient
$n$	Electron transfer number

## Introduction

The broad use of pesticides contributes to both significant improvement in cultivation yields and farm efficiency. On the other hand, pesticide contamination of fresh water, which has emerged as an important environmental problem in the last few decades, is causing concern with respect to the long-term and low dose effects of pesticides on public health as well as non-target species. Pesticide contamination of surface runoff from agricultural use has been well documented in relation to fields cultivated with corn, soybeans, cotton, and grass [1,2].

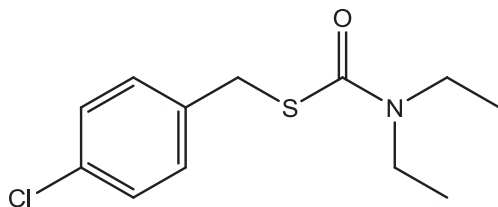
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Contamination of water by pesticides is mainly due to runoff, usually within a few weeks after application. Its fate depends on volatilization, hydrolysis, and photolysis processes [3].

Thiobencarb (TB; *S*-4-chlorobenzyl *N,N*-diethylthiocarbamate; Scheme 1) is a carbamate herbicide that has been commonly used in rice fields worldwide to control annual grasses, such as barnyard grass (*Echinochloa* sp.) and certain broadleaf weeds [4]. TB is a highly effective, nonpersistent, systemic pre-emergence herbicide. Some researchers described that TB inhibits protein synthesis, which in turn can exert many secondary effects on growth. Wide variations in sensitivity to TB have been presented in Chlorophyta and Cyanophyta, with inhibitory concentrations ranging from about 0.01–4 mg L<sup>-1</sup> [4,5]. The environmental fate of TB has been previously investigated, and several degradation products from animals, plants, and micro-organisms, along with those from abiotic processes, in rice fields have been identified [6,7].

Several methods have been reported for the determination of TB using a variety of techniques, including gas chromatography [8], high-performance liquid chromatography [9], and combination of these methods such as LC-MS [10] and GC-MS ion monitoring [11]. Although, the chromatographic techniques with mass spectrometry, spectrophotometry or photoconductivity detection provide a low level of detection (ng/L and µg/g) for TB, samples must be extensively processed (extraction and clean-up) before the analysis. On the other hand, most of these methods are time consuming and require extensive manual handling of toxic samples with various solvents. To the best of our knowledge, until now there is only one report on electrochemical detection of thiobencarb in synthetic samples [12].

Chemically modified electrodes (CMEs) have continued to be of widespread use during the two past decades and a relatively large amount of electrochemical researches have been devoted to the development and applications of different types of CMEs [13–19]. The chemical modification of electrodes using electron transfer mediators is an interesting field in analytical chemistry. One of the most important effects of any mediator is a reduction of the overpotential required for electrochemical reaction and enhancement of the sensitivity and selectivity of the method [20]. Carbon paste electrodes (CPEs), due to the ease of



**Scheme 1** Molecular structure of thiobencarb

their construction, renewability and compatibility with various types of modifiers, have been widely used as a suitable matrix for preparation of modified electrodes. Further, they show rather low background current compared with solid graphite or noble metal electrodes [21].

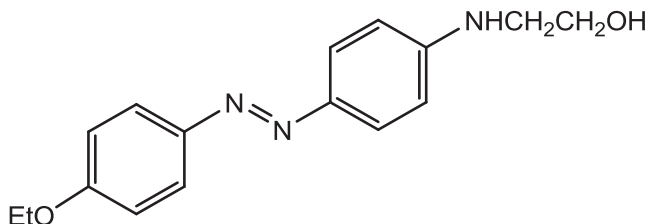
To date, various materials have been used to make modified electrodes. Among the various mediators used for electrode modification, azo dyes attracted the attention of electrochemists as excellent electron transfer mediators [22]. It is well known that azo compounds are the most widely used class of industrial synthesized organic dyes due to their versatile application in various fields, such as dyeing textile fiber, biological–pharmacological activities, and advanced application in organic synthesis [23]. Moreover, the using and application of azo dyes in electronic industries has been a subject of renewed interest in recent years. Especially, linear azo benzene dyes containing hydroxyl group are an important group of organic dyes with advanced application in high technology areas such as laser, liquid crystalline displays, electro-optical devices, and preparation of thin films [24].

In the present work, a new azo dye, 2-(4-((4-ethoxyphenyl)diazenyl)phenylamino)ethanol (EDPE), was used as a modifier and electron mediator in electrochemical reduction of TB using a modified carbon paste electrode. The electrochemical properties, stability and electrocatalytic activity of the modified electrode toward the reduction of TB was studied using various electrochemical procedures. The molecular structure of the azo dye is given in Scheme 2. The modified electrode was applied as a very sensitive sensor with an acceptable reproducibility and accuracy in the detection of micromolar amounts of TB in various water samples.

## Experimental

### Chemicals and reagents

All reagents and solvents were of the highest purity available from Merck and were used without further purification. All the solutions were prepared using double-distilled water with a specific conductivity of <1.5 µS cm<sup>-1</sup> and pH 6.8. High



**Scheme 2** Molecular structure of 2-(4-((4-ethoxyphenyl)diazenyl)phenylamino) ethanol

viscosity paraffin (density=0.88 kg dm<sup>-3</sup>), purchased from Fluka, was used as the pasting liquid for the carbon paste electrode. The graphite powder (particle diameter=10 μm), obtained from Merck, was used as the working electrode substrate. The thiobencarb (98.9% purity) was obtained from Riedel de Haen. EDPE has been synthesized based on 2-anilinoethanol with aryldiazonium salt in our department [25]. Acetate buffer solution (0.1 M, pH 3.0) was prepared by mixing 98.2 mL of 0.1 M acetic acid and 1.8 mL of 0.1 M sodium acetate. Before use, flasks and containers were soaked in 6 M HNO<sub>3</sub> for at least 24 h, then rinsed with doubly distilled water. Stock solutions of TB in a concentration range of 0.01 to 110 μg L<sup>-1</sup> were freshly prepared as required at the desired pH and purged with pure nitrogen gas (99.999%) for 10 min before the voltammetric measurements. All solutions were kept at the most 1 day to the next in the dark at 4 °C.

### Apparatus

All electrochemical experiments, including cyclic voltammetry (CV), chronoamperometry, rotating disk electrode (RDE) voltammetry, and differential pulse voltammetry (DPV) were carried out using an Autolab potentiostat PGSTAT 30 (Eco Chemie BV, Utrecht, the Netherlands) driven by the General Purpose Electrochemical Systems data processing software (software version 4.9). All electrochemical studies were performed at 25±1 °C. A conventional three-electrode cell was employed incorporating a working modified carbon paste electrode (with or without EDPE), a saturated Ag/AgCl reference electrode, and a platinum wire counter electrode. A rotating electrode system, from Autolab Company was employed. Differential pulse voltammetric experiments were performed using the pulse amplitude of 0.05 V, pulse duration time of 0.04 s, step time of 1–0.4 s, and a scan rate of 100 mV s<sup>-1</sup> over the applied potential range of 0.5 to -0.1 V versus Ag/AgCl. Chronoamperometric responses were recorded by setting potential at 0.05 V versus Ag/AgCl for 10 s.

### Preparation of modified carbon paste electrodes

The unmodified carbon paste electrode was prepared by mixing 0.75 g graphite powder with 0.25 g paraffin and thorough hand mixing in a mortar and pestle (~75:25%, w/w). One portion of the composite mixture was packed into the end of a Teflon tube (ca. 2.5 mm i.d.). Electrical contact was made by forcing a glassy carbon electrode down the Teflon tube and into the back of the paste. The modified electrode (EDPE/modified carbon paste electrodes (MCPE)) was prepared by mixing the unmodified paste with azo dye, EDPE (5%, w/w) and then mechanically homogenized.

### Preparation of real sample

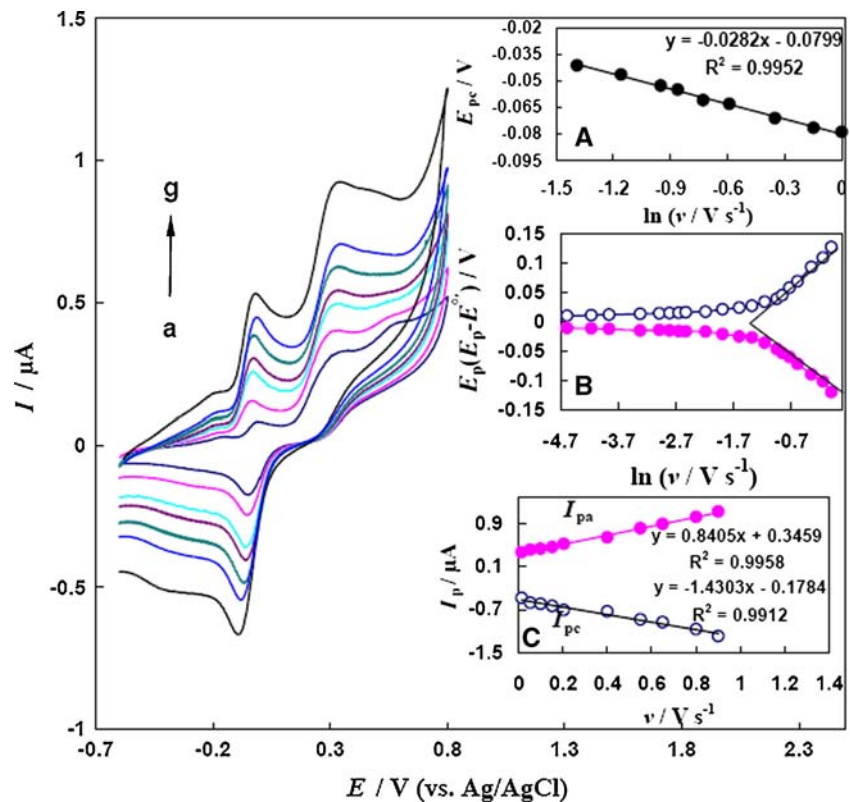
For analytical purpose, water samples collected from different regions. Standard addition method was adopted to evaluate the determination results. A validation study was carried out, according to an approved technical protocol [26]. For this purpose, water sample (10 mL) was transferred into a 50-mL tube, followed by the addition of NaCl (1 g) and acetonitrile (5 mL). After the sample tube was vigorously shaken for 1 min, the mixture was centrifuged at 2,000 rpm for 5 min. The supernatant was transferred to a flask through a layer of anhydrous sodium sulfate (2 g). The extract in the flask was concentrated to near dryness. Then the residues dissolved in diethyl ether (1 mL) for GC injection. The system was a Hewlett-Packard 6890 instrument equipped with mass selective detector model 5973 and auto sampler model 7683. The capillary column was 30 m×0.25 mm i.d., DB-5MS fused silica column filled with 5% phenyl-95% methyl silicon, and with 0.25-mm film thickness

## Results and discussion

### Electrochemical behavior of EDPE

The EDPE/MCPE prepared under optimum conditions (graphite powder/paraffin/EDPE ratio of 70/25/5%, w/w, in 0.1 M acetate buffer solution of pH 3.0) was characterized by cyclic voltammetry. The representative cyclic voltammograms obtained for the EDPE/MCPE are shown in Fig. 1 for various scan rates (10–400 mV s<sup>-1</sup>). The observation of well-defined and persistent cyclic voltammetric peaks indicating that the EDPE exhibits electrochemical responses which are characteristic of the redox species confined on the electrode. Figure 1(A) shows the magnitudes of reduction peak potential ( $E_{pc}$ ) as a function of logarithm of scan rate. For EDPE/MCPE the peak-to-peak separation potential ( $\Delta E_p = E_{pa} - E_{pc}$ ) of the cyclic voltammogram recorded at low scan rate (10 mV s<sup>-1</sup>) in the presence of acetate buffer as the supporting electrolyte is about 20 mV. In addition, the formal potential ( $E^{\circ} = (E_{pa} + E_{pc})/2$ ) is almost independent of the potential scan rate for sweep rates below 100 mV s<sup>-1</sup>, suggesting facile charge transfer kinetics over this range of scan rate. However, for scan rates above 100 mV s<sup>-1</sup>, the peak separations begin to increase, indicating the limitation arising from charge transfer kinetics (Fig. 1(B)). The plots of anodic and cathodic peak currents as a function of potential scan rate are shown in Fig. 1(C), indicating that the EDPE exhibits electrochemical responses which are characteristic of the redox species confined on the electrode surface.

**Fig. 1** Cyclic voltammograms of an EDPE/MCPE in 0.1 M acetate buffer solution of pH 3.0 at various scan rate *a* 10, *b* 50, *c* 100, *d* 150, *e* 200, *f* 300, and *g* 400  $\text{mV s}^{-1}$  vs. Ag/AgCl. Inset A  $E_{pc}$  vs.  $\ln \nu$ , inset B  $E_p(E_p - E^\circ)$  vs.  $\ln \nu$ , and inset C  $I_p$  vs.  $\nu$



Laviron derived general expressions for the linear potential sweep voltammetric response for the case of surface-confined electroactive species with a concentration small enough [27]:

$$E_{pa} = E^\circ + A \ln(1 - \alpha/m) \quad (1)$$

$$E_{pc} = E^\circ + B \ln(\alpha/m) \quad (2)$$

For  $E_{pa} - E_{pc} = \Delta E_p > 200/n \text{ mV}$ :

$$\begin{aligned} \log k_s &= \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha \\ &\quad - \log(RT/nF\nu) - \alpha(1 \\ &\quad - \alpha)nF\Delta E_p/2.3RT \end{aligned} \quad (3)$$

Where  $A=RT/(1-\alpha)nF$ ,  $B=RT/\alpha nF$ , and  $m=(RT/F)(k_s/n\alpha)$ .

From these expressions, it is possible to determine the transfer coefficient ( $\alpha$ ) by measuring the variation of the peak potentials with scan rate ( $\nu$ ) as well as the apparent charge transfer rate constant ( $k_s$ ) for electron transfer between the electrode and the modifier. A plot of  $E_p=f(\log \nu)$  yields two straight lines with slopes equal to  $-2.3 RT/\alpha nF$  and  $2.3 RT/(1-\alpha)nF$  for the cathodic and anodic peaks, respectively. It has been found that at high scan rates (above  $300 \text{ mV s}^{-1}$ ), the values of  $E_p$  were proportional to the logarithm of scan rate as was indicated by Laviron. The plots are shown in

inset B of Fig. 1. Using such a plot and Eq. 3, the values of  $\alpha$  and  $k_s$  were 0.48 and  $14.6 \text{ s}^{-1}$ , respectively, for the EDPE/MCPE in the presence of 0.1 M acetate buffer.

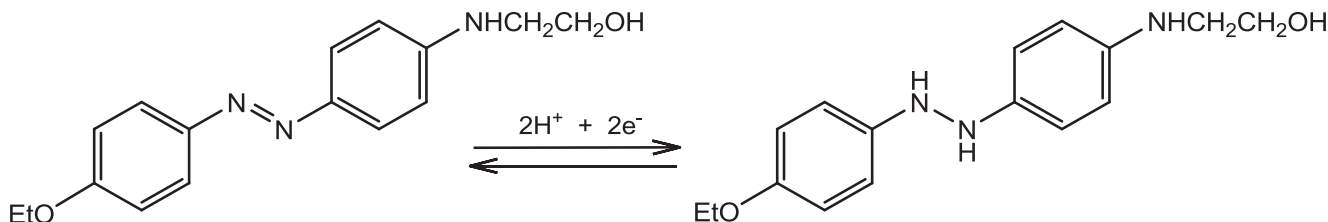
#### Effect of pH on the peak potential

The voltammetric behavior of the EDPE/MCPE was characterized at various pHs by CV. The peak potential of the azo dye shifts to negative potentials with increasing pH at all voltammetric measurements. There is a linear relationship between the cathodic peak potential and the pH value, and the linear regression equation is:

$$E_p = -58.37 \text{ pH} + 488.4 (R^2 = 0.9977) \quad (4)$$

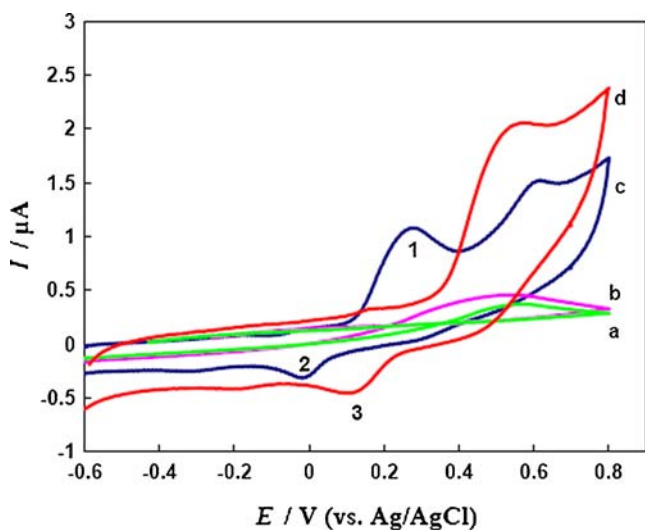
According to these results, the shift in the peak potential values of the reduction peak to negative potentials with increasing pH denotes that the electrode reaction is involving hydrogen ions [22]. The above equation showed that the slope ( $E_p/\text{pH}$ ) is 58.37 mV/pH units over a pH range from 2 to 7. This slope was close to the Nernstian value of 59.2 mV at  $25^\circ \text{C}$  for equal number of protons and electrons transfer reaction [28]. According to the equation,  $-59x/n = -58.37$ , where  $n$  is the electron transfer number and  $x$  is the number of hydrogen ion participating in the reaction, it can be concluded that the proton number involved is equal to the electron transfer number in the electrochemical reaction and

$x=n=2$  for electroreduction of the  $N=N$  double bond to the hydrazo group (HN–NH) [29]. Therefore, the redox reaction



### Cyclic voltammetric investigations

Preliminary experiments for elucidation of the catalytic activity of the EDPE/MCPE toward TB were performed using cyclic voltammetry. Cyclic voltammograms were recorded using unmodified and MCPEs in deaerated solutions. The processes associated are typically illustrated in Fig. 2 by cyclic voltammograms of  $10 \mu\text{g L}^{-1}$  TB solution at pH 3.0. These voltammograms were recorded at the surface of unmodified and MCPEs in the potential range of  $-0.6$ – $0.8$  V versus Ag/AgCl reference electrode. There was no measurable wave for the unmodified electrode in absence and  $10 \mu\text{g L}^{-1}$  of TB in the potential range studied (Fig. 2a, b). As can be seen, electroactivity toward TB on modified electrode was significant (Fig. 2c, d). This figure shows that after the addition of TB, a significant current enhancement is seen at around  $0.15$  V versus Ag/AgCl electrode (peak 3) with a simultaneous decrease in the corresponding anodic



**Fig. 2** Blank cyclic voltammograms of unmodified CPE (a) and EDPE/MCPE (c). Cyclic voltammograms of  $10 \mu\text{g L}^{-1}$  TB on unmodified CPE (b) and EDPE/MCPE (d). Supporting electrolyte:  $0.1$  M acetate buffer solution with pH 3.0; scan rate,  $50 \text{ mV s}^{-1}$

of EDPE is a two-electron and two-proton process and the electrode reaction equation is as follows.

peak. In fact, the anodic peak of EDPE (peak 1) disappeared completely. Additionally, by comparing the peaks 2 and 3, a significantly decrease in the reduction potential of EDPE can be distinguished (more than  $100$  mV). This observation is a clear evidence of electrocatalysis, attributable to the reaction of electrogenerated hydrazo compound ( $\text{H}_2\text{EDPE}$ ) with diffusing TB according to the following equation:



The cyclic voltammograms of EDPE/MCPE at various scan rate ( $10$ – $200 \text{ mV s}^{-1}$ ) in the presence of  $10 \mu\text{g L}^{-1}$  TB was studied (Fig. 3). The reduction current for TB increased linearly with the square root of scan rate (Fig. 3(A)), suggesting that the reaction is mass transfer controlled. Also, a plot of current function ( $I_p/\nu^{1/2}$ ) versus scan rate exhibits an indicative shape typical of an EC catalytic process (Fig. 3(B)).

In order to obtain the information on the rate determining step, the Tafel plot was drawn using the following equation valid for a totally irreversible diffusion-controlled process [28,30]:

$$E_p = (b/2)\log \nu + \text{constant} \quad (6)$$

On the basis of Eq. 6, the slope of  $E_p$  versus  $\log \nu$  plot is  $b/2$ , where  $b$  indicates the Tafel slope. The slope of  $E_p$  versus  $\log \nu$  plot is  $\delta E_p/\delta(\log \nu)$  was found to be  $0.097$  V in this work (Fig. 3(C)), so,  $b=2 \times 0.097=0.194$  V. The value of Tafel slope ( $b=2(0.059/\alpha n)$ ) indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient of about  $0.48$ .

### Chronoamperometry measurements

The chronoamperometry as well as the other electrochemical methods was employed for the investigation of electrode processes at chemically modified electrodes.

**Fig. 3** Cyclic voltammograms of an EDPE/MCPE in 0.1 M acetate buffer solution of pH 3.0 containing  $10 \mu\text{g L}^{-1}$  TB at various scan rate *a* 10, *b* 30, *c* 80, *d* 100, *e* 150, and *f*  $200 \text{ mV s}^{-1}$  vs. Ag/AgCl. *A*  $I_p$  vs.  $\nu^{1/2}$ ; *B*  $I_p \nu^{-1/2}$  vs.  $\nu$ ; *C*  $E_p$  vs.  $\log \nu$

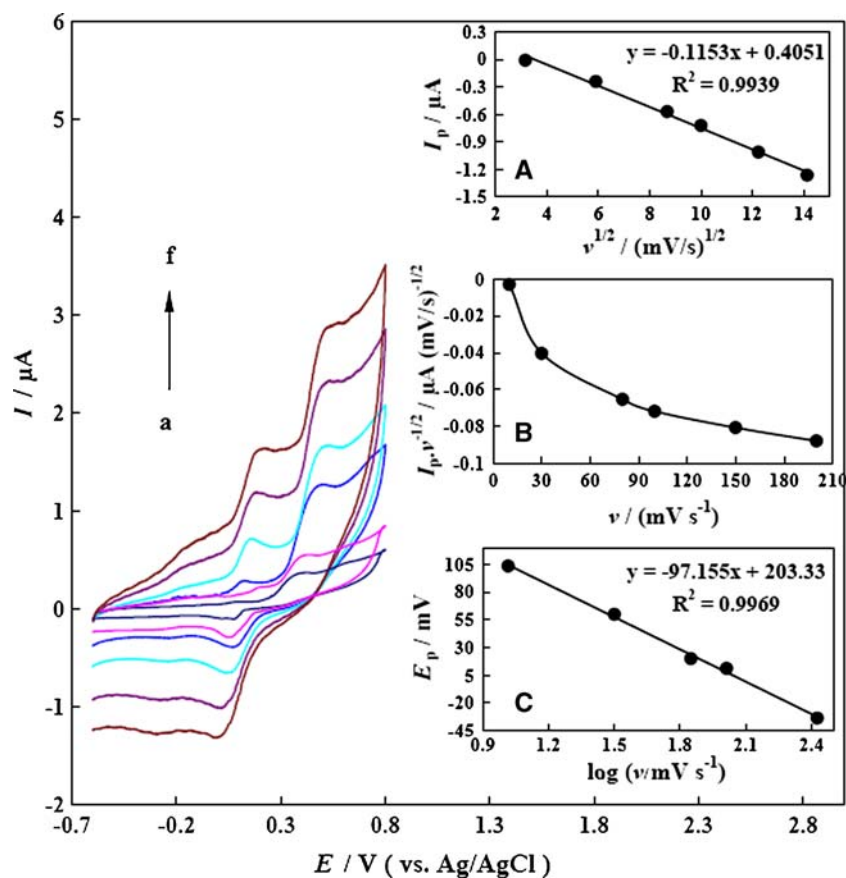


Figure 4 shows chronoamperometric measurements of TB at EDPE/MCPE. This figure represents the current–time profiles obtained by setting the working electrode potential at 0.15 V versus Ag/AgCl for different concentrations of TB. The reduction current for the electrochemical reaction (under mass transfer control) of an electroactive material with a diffusion coefficient,  $D$  is described through the Cottrell equation [28,30]:

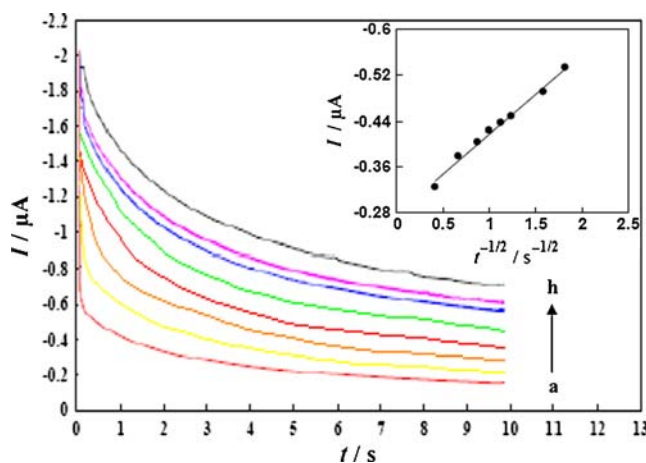
$$I = nFAD^{1/2}C^* / \pi^{1/2} t^{1/2} \quad (7)$$

Where  $D$  and  $C^*$  are the diffusion coefficient  $\text{cm}^2 \text{s}^{-1}$  and the bulk concentration  $\text{mol cm}^{-3}$ , respectively. The plot of  $I$  versus  $t^{-1/2}$  for a modified electrode in the presence of TB will be linear, and from the slope, the value of  $D$  can be obtained (Fig. 4(inset)). Diffusion coefficient of TB was found to be  $3.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

#### RDE voltammetry

There are many electrochemical techniques in which the electrode moves with respect to the solution. The advantage of these techniques is that a steady state is attained rather quickly, and measurements can be made with high

precision. The electrocatalytic activity EDPE/MCPE toward reduction TB was evaluated by RDE voltammetry technique. In the case that the reduction of TB at EDPE/MCPE is controlled solely by the mass transfer process in the solution, the relationship between the limiting current and rotating speed should obey the Levich equation [28,30].



**Fig. 4** Chronoamperometry obtained at EDPE/MCPE in presence of *a* 1, *b* 5, *c* 10, *d* 20, *e* 30, *f* 35, *g* 40, and *h*  $50 \mu\text{g L}^{-1}$  of TB and acetate buffer solution (pH 3). *Inset*, plot of  $I$  versus  $t^{-1/2}$  obtained from chronoamperogram (*a*)

$$I_L = I_{Lev} = 0.620 nFD^{2/3} \nu^{-1/6} \omega^{1/2} C^* \tag{8}$$

Where  $D$ ,  $\nu$ ,  $\omega$  and  $C^*$  are the diffusion coefficient, the kinematics viscosity, the rotation speed, and the bulk concentration of the reactant in the solution, respectively, and all other parameters have their conventional meanings. Based on Eq. 8, the plot of limiting current  $I_L$  as function of the  $\omega^{1/2}$  should be a straight line. According to the Levich plots (Fig. 5(A)), the current increases with increasing electrode rotation speed, but was found to be nonlinear, indicating kinetic limitations.

For irreversible reaction, relation between the limiting current and rotating speed has been given by Koutecky–Levich equation [28,30]

$$[I_L]^{-1} = [nFA C^* K \Gamma]^{-1} + [0.620 n F D^{2/3} \nu^{-1/6} \omega^{1/2} C^*]^{-1} \tag{9}$$

Where  $A$ ,  $C^*$ ,  $K$ ,  $\Gamma$ ,  $\nu$ , and  $\omega$  are the electrode area ( $\text{cm}^2$ ), substrate concentration ( $\text{mol cm}^{-3}$ ), catalytic rate constant ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ), surface coverage ( $\text{mol cm}^{-2}$ ), kinematics viscosity ( $\text{cm}^2 \text{s}^{-1}$ ), and rotation speed ( $\text{rad s}^{-1}$ ), respectively. According to Eq. 9, the plot of  $[I_L]^{-1}$  versus  $\omega^{-1/2}$  gives a straight line (Fig. 5(B)). It can be seen that the intercept of linear plots is positive, clearly indicating the kinetic limitation of the electrode process. In addition, the slopes and intercepts are inversely proportional to the bulk concentration of TB, suggesting that the current is not limited by the rate of electron transport within the electrode and it has a diffusional nature. The value of the rate constant for the catalytic reaction,  $K$ , can be obtained from the intercept of the Koutecky–Levich plot. The value of heterogeneous electron transfer rate constant for EDPE modified electrode by using intercepts of the Koutecky–

Levich was found to be  $8.2 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$  for TB in the concentration of  $10 \mu\text{g L}^{-1}$ . Diffusion coefficient of TB,  $D$ , may be obtained from the slope of Koutecky–Levich plots. The mean value of  $D$  was found to be  $4.5 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ .

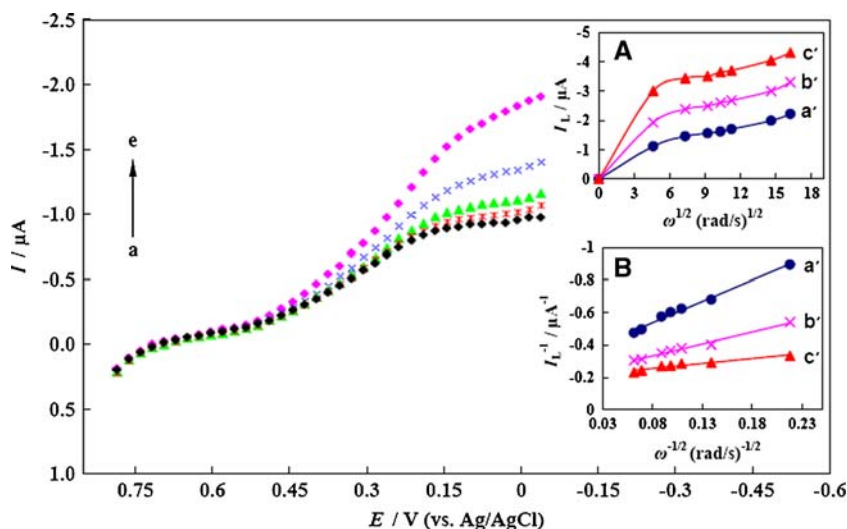
### Differential pulse voltammetry investigations

The electrocatalytic activity of the EDPE/MCPE was tested towards reduction of thiobencarb by DPV technique at different concentrations of the electroactive species in acetate buffer solution (pH 3.0). A linear relationship could be established between the mediated reduction current of TB at the carbon paste electrode using EDPE as mediator ( $I_{pc}$ ) and the concentration of TB in the range of 0.96 to  $106 \mu\text{g L}^{-1}$  (Fig. 6(inset)). The linear regression equation was  $I_{pa} (\mu\text{A}) = 0.008 C (\mu\text{g L}^{-1}) + 0.1186$ ,  $R^2 = 0.9935$ , the detection limit of TB was found to be  $0.025 \mu\text{g L}^{-1}$  ( $S/N = 3$ ). Thus the catalytic reduction of TB can readily be applied for the determination of TB.

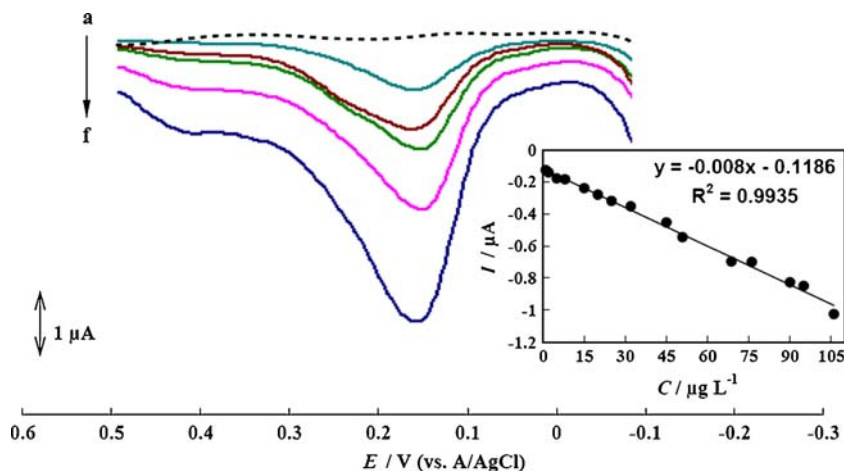
### Stability of the modified electrode

The stability of the EDPE/MCPE was investigated by keeping the electrode at room temperature when the electrode was not in use. 96.8% of the initial current response was retained after 2 weeks storage. After 1 month of testing, the peak current response decreased about 8%. Then the modified electrode was evaluated by examining the cyclic voltammetric peak currents after continuous scanning for 300 cycles, 91.5% of the initial current response was retained, indicating that EDPE/MCPE was stable in buffer solution. To investigate the precision of the determination, the same EDPE/MCPE was used for eight parallel determinations of  $25 \mu\text{g L}^{-1}$  TB and the relative standard deviation (RSD) was determined as 1.58%,

**Fig. 5** Typical example of rotating disk voltammograms for TB ( $10 \mu\text{g L}^{-1}$ ) reduction at EDPE/MCPE. The rotation speed is in rpm: a 200, b 500, c 800, d 2,000, and e 2,500. Potential sweep rate:  $100 \text{ mV s}^{-1}$ , supporting electrolyte: 0.1 M acetate buffer (pH 3.0). A Levich plots for catalytic reduction of TB at EDPE/MCPE with various concentrations a'  $10 \mu\text{g L}^{-1}$ , b'  $30 \mu\text{g L}^{-1}$ , and c'  $60 \mu\text{g L}^{-1}$ . B Koutecky–Levich derived from the data of (A)



**Fig. 6** Differential pulse voltammograms for reduction peak current vs. TB concentration (*a* 0.0, *b* 30 mL river water solution containing 0.1 M acetate buffer with pH 3.0, *c*  $b+3 \mu\text{g L}^{-1}$ , *d*  $b+4.5 \mu\text{g L}^{-1}$ , *e*  $b+9.8 \mu\text{g L}^{-1}$ , and *f*  $b+16.5 \mu\text{g L}^{-1}$ ). The pulse amplitude of 0.05 V; pulse duration time of 0.04 s; step time of 1–0.4 s; and a scan rate of  $100 \text{ mV s}^{-1}$  over the applied potential range of +0.5 to  $-0.1 \text{ V}$  versus Ag/AgCl). *Inset*, calibration curve



indicating the electrode showed good repeatability. Five EDPE/MCPEs were fabricated with the same procedure and applied to determination of  $25 \mu\text{g L}^{-1}$  TB with a RSD value of 2.1%, indicating the good reproducibility. The response time of the EDPE/MCPE was determined by measuring the current response under optimal conditions where the potential was kept at 0.15 V in 0.1 M acetate buffer solution with pH 3.0. It is confirmed that a well-defined response was observed after successive additions of  $5 \mu\text{g L}^{-1}$  TB. In the case of each injection, a sharp increase of the current response was observed less than 5 s.

#### Analytical application

In order to demonstrate the catalytic reduction of TB in real samples, we examined this ability in determining TB in various water samples. The determination of TB in each sample was carried out by the standard addition method for prevention of any matrix effect. Figure 6 shows related voltammograms for this purpose. As can be seen in this

figure, adding TB to the solution caused an increase in the reduction peak height (curves b–f). Thus, the peak was attributed to TB reduction. By this method TB concentration in various real samples were obtained and the results are presented in Table 1. Accuracy was examined by comparison of data obtained from this method with a recognized common method for determination of TB [26]. The results from the statistical calculation indicate good agreement between the mean values (*t* test) and precision (*F* test) for two methods (for  $p=0.95$ ).

Dynamic range, detection limit and precision in voltammetric measurements of TB in the present work is comparable and in some aspects superior to the previous report based on bare glassy carbon electrode [12]. In comparison to that, EDPE/MCPE has high-performance characteristics, ease of preparation and modification, and also simplicity of the renewability of its surface by simple polishing. Therefore, this voltammetric sensor can be used as a very highly sensitive detection device for TB in various environmental waters samples.

**Table 1** Determination of TB in various water samples by the two proposed and reference methods

Sample	TB concentration ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>		<i>t</i> test <sup>b</sup>	<i>F</i> test <sup>c</sup>
	Proposed method	Reference method		
Tap water	<DL	<DL	–	–
Spring water <sup>d</sup>	<DL	<DL	–	–
River water <sup>e</sup>	$2.73 \pm 0.24$	$2.94 \pm 0.21$	1.14	1.31
River water <sup>f</sup>	$3.42 \pm 0.33$	$3.59 \pm 0.27$	0.69	1.49

<sup>a</sup> Mean  $\pm$  standard deviation ( $n=4$ )

<sup>b</sup> Tabulated *t* value for 6 degrees of freedom at *p* value of 0.05 is 2.45

<sup>c</sup> Tabulated *F* value for 3, 3 degrees of freedom at *p* value of 0.05 is 9.28

<sup>d</sup> Obtained from Sefidab spring, Talesh, Guilan, Iran

<sup>e</sup> Obtained from Sefidrood, Talesh, Guilan, Iran

<sup>f</sup> Obtained from Karganrood, Talesh, Guilan, Iran



## Conclusions

This work demonstrates the construction of a chemically MCPE by using EDPE as modifying species. EDPE/MCPE can catalyze the reduction of TB via layer mediated charge transfer. Compared with its response at unmodified CPE, the electrochemical signal of TB was improved dramatically at the proposed electrode. Under the optimized conditions, a sensitive and selective method was established for the determination of TB. The catalytic reduction peak current showed a linear dependent on the TB concentration and a linear calibration curve was obtained in the range of 0.96 to 106  $\mu\text{g L}^{-1}$  of TB and a detection limit equal to 0.025  $\mu\text{g L}^{-1}$  was obtained. Catalytic reduction of TB can be employed as a new method for determination of TB in water samples. The EDPE/MCPE offers the advantages of easy fabrication, fast response time, high sensitivity, a low background current, and detection limit, which are suitable for routine determinations.

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