

# Multiwalled carbon nanotube modified electrodes for the adsorptive stripping voltammetric determination and quantification of curcumin in turmeric

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## Abstract

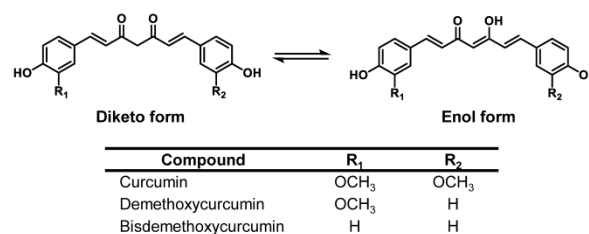
A sensitive electrochemical method for the determination and quantification of curcumin using adsorptive stripping voltammetry (AdsSV) at a multiwalled carbon nanotube modified basal plane pyrolytic graphite electrode (MWCNT-BPPG electrode) is presented exploiting the high surface area of the latter. Next the voltammetric behaviour of curcumin on the modified electrode is examined and AdsSV shown to be a sensitive method for quantifying curcumin. The adsorption of curcumin on the electrode surface is evidenced to follow a Langmuir adsorption isotherm. Linear calibration for curcumin in the range of 2 – 100  $\mu\text{M}$  was obtained with a detection limit of 0.45  $\mu\text{M}$  and a limit of quantification of 1.49  $\mu\text{M}$ . For application to real samples of turmeric, a one-step sample preparation in ethanol has developed providing a simple and rapid extraction procedure. The MWCNT-BPPG electrode with AdsSV allowed the determination of curcumin equivalent in turmeric powder sample with recoveries in the range of 92-108%. This facile and fast method will be useful for monitoring the quality of curcumin containing in commercial turmeric products.

**Keywords:** Curcumin, Adsorptive stripping voltammetry, Quality control of turmeric products

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## 1. Introduction

The yellow-orange pigments extracted from rhizome of turmeric (*Curcuma longa* L.) consist of three curcuminoids: curcumin, demethoxycurcumin, and bisdemethoxycurcumin in an approximate ratio 2:1:1 [1]. Among these curcumin is the main ingredient and is by far the most investigated curcuminoid due to a wide range of biological and pharmacological properties including anti-oxidant, anti-inflammatory, anti-mutagenic, and anti-cancer behaviour [2]. Curcumin is reported to be a significantly more effective antioxidant than demethoxycurcumin and bisdemethoxycurcumin [3]. Specifically, the chemical structure of curcumin comprises of two units of 2-methoxyphenol connected by an  $\alpha,\beta$ -unsaturated diketone moiety which exhibits keto-enol tautomerism as depicted in Fig. 1. The tautomer percentages are dependent on various parameters including solvent and temperature [4]. The enol form is more energetically stable in the solid phase and in ethanolic solution [5].



**Fig. 1** Chemical structure of curcuminoids

Curcumin has a low solubility in aqueous solution and is highly unstable under basic conditions resulting from fast hydrolytic degradation to feruloylmethane and ferulic acid for example after only 5 minutes incubation in pH 8.5 phosphate buffer [6].

The curcumin content of turmeric was found to vary depending on growing conditions, harvesting process, and extracting method [7]. The percentage of curcumin content in commercially available turmeric products is reported to be between 0.5% and 5.7% [8]. The content

of curcumin is one of the primary factors in the quality control of commercial turmeric products [7a]. Moreover, owing to the very high cost of pure turmeric, turmeric powder can be, and often is, adulterated with different chemical compounds in order to mimic the appearance of curcumin. The major compounds which have been adulterated in turmeric spices are lead chromate as well as the dye metanil yellow [7b, 9]. In October 2013, the US Food and Drug Administration (FDA) released a recall report of turmeric powder imported from one brand in Bangladesh. This recall was reportedly linked to contaminated turmeric powder with high lead levels that could cause very significant health problems to consumers. Moreover, children in a rural area in Bangladesh have been identified as having high blood lead concentrations. This lead exposure may originate from contaminated turmeric [10].

Owing to threat of lead poisoning as well as other illnesses potentially caused by adulterated spices, food safety issues related to the possibility of contaminated turmeric powder are of concern to human health. Product quality assurance is essential including the quantification of curcumin content in commercially available turmeric products, since when the quantified amount of curcumin from the products is extremely low, we can infer that this product might be adulterated. A variety of techniques for the qualitative and quantitative analysis of curcumin has been proposed. Spectrometric methods have been employed for determination of curcumin content due to the high optical absorptivity of the compound at visible wavelengths [11]. Another analytical method used is high-performance liquid chromatography coupled with various types of detector [12]. However, these methods require the use of relatively expensive instruments, complicated sample preparation steps, and well-trained personnel. Analysis via an electrochemistry based technique is potentially advantageous over the above mentioned techniques due to its simplicity, speed, sensitivity, cost effectiveness as well as possibly allowing testing outside of the laboratory. Curcumin offers an electrochemical response due to the 2-methoxyphenol moieties in the molecule. The 2-methoxyphenol moieties can be oxidised to a quinone-like structure, then this benzoquinone subsequently exhibits the reversible redox behaviour typical of quinones [13]. There are several reports of curcumin detection using electrochemistry. A bare glassy carbon electrode with cyclic voltammetry was employed by Ziyatdinova *et al.* [14] and a carbon paste electrode (CPE) and hanging mercury drop electrode (HDME) in combination with differential pulse voltammetry (DPV) were used for the detection of curcumin [15]. In these methods, they reported a low sensitivity and the electrochemical oxidation/reduction

mechanism of curcumin at the electrode was not clarified. Another more sensitive electrochemical detection for the determination of curcumin was made by Daneshgar *et al.* [16]. They employed a carbon nanotube or dysprosium nanowire modified carbon paste electrode in combination with fast Fourier transform square wave voltammetry (FFTSWV) but again the electrode reaction mechanism was not reported. In contrast to previous reports employing electrochemical techniques; the present work exhibits advantages in terms of the usage of simple cyclic voltammetry as well as a simple electrode modification procedure. Specifically, adsorptive stripping voltammetry is chosen to be the electrochemical tool for determination and quantification of curcumin. The sensitivity of signal obtained from the AdsSV reflects the surface area of the electrode, hence multiwalled carbon nanotubes are a highly useful material for modifying the electrode surface owing to their extremely high surface area properties [17].

We report an electrochemical method for curcumin detection using a multiwalled carbon nanotube modified electrode with a one-step sample preparation. The electrochemical behaviour of curcumin at the carbon nanotube modified electrode is investigated. The applicability of the developed method for detection and quantification of curcumin equivalent in a real sample of turmeric is demonstrated.

## 2. Experimental

### 2.1 Chemicals and apparatus

All chemicals were purchased at their highest available purity and were used without further purification. All solutions were prepared using deionised water at a resistivity not less than 18.2 MΩ cm at 25°C (Millipore, MA, USA). Curcumin was purchased from Sigma-Aldrich (St. Louis, MO, USA). The bamboo-like multiwalled carbon nanotubes (30±10 nm in diameter and 5-20 μm in length) were purchased from Nanolab (Brighton, MA, USA). The Britton-Robinson buffer solution was made using acetic acid (BDH), phosphoric acid and boric acid (Aldrich). Tesco Ground Turmeric was purchased from a Tesco supermarket (Oxford, UK).

All voltammetric measurements were performed using an Autolab computer-controlled potentiostat PGSTAT 101 (Metrohm-Autolab, Netherlands). The basal plane pyrolytic graphite (BPPG, Le Carbone Ltd., Sussex, UK) electrode was prepared by securing the material inside an insulating PTFE housing with a stainless steel core for an electrical connection. A three-electrode configuration was

used including a modified BPPG electrode (the preparation of the modified electrode is discussed below) as a working electrode, a platinum mesh 99.99% (Goodfellow, UK) as a counter electrode, and a saturated calomel electrode, SCE, as the reference electrode (SCE +0.244 V vs SHE, BASi Inc., Japan). All experiments were carried out in a Faraday cage held at a temperature of  $25 \pm 0.2^\circ\text{C}$ .

The multiwalled carbon nanotube modified electrode was prepared by drop casting a suspension of MWCNT in acetone onto the electrode surface. The MWCNTs were first suspended in acetone ( $1 \text{ mg mL}^{-1}$ ) through sonication for 10 minutes. A  $20 \mu\text{L}$  aliquot of the casting suspension was dropped onto the BPPG electrode and the acetone allowed to evaporate [18]. The surface of the modified BPPG electrode was renewed between each scan. To expose a fresh surface prior to further modification with the MWCNT, the BPPG electrode surface was renewed by polishing the surface of electrode on the sand paper P2500 and P4000 grade respectively. Subsequently, the electrode was repeatedly pressed on cellotape, and then subsequently rinsed with acetone.

## 2.2 Sample preparation

For real sample analysis, curcumin was extracted from turmeric powder prior to analysis using electrochemical detection. An aliquot of 10 mg of turmeric powder was weighed and placed into a 50 mL volumetric flask. Ethanol (unless otherwise stated) was used to make up the volume of 50 mL. The flask was shaken to mix the sample with the solvent, placed in an ultrasonic bath and sonicated for 10 minutes. The solution was then used for electrochemical analysis without further filtration or dilution. For the optimisation of the extraction solvent, another set of samples were prepared following the procedure above but using acetonitrile in place of the ethanol. To optimise the sonication time, the sample was prepared in ethanol as described above. The flask was sonicated in the ultrasonic bath for different times between 0-20 minutes.

## 2.3 Analytical procedures

A curcumin stock standard solution of 1.00 mM was prepared before diluting to concentration of 2.0, 5.0, 10.0, 25.0, 50.0, 75.0, and 100.0  $\mu\text{M}$  as standard working solutions. To prevent any possible decomposition of curcumin, all of the solution containers were wrapped with aluminium foil over the time range of experiment and kept in the dark. Note that curcumin has a low

solubility in aqueous systems therefore ethanolic solutions were used [4].

For the voltammetric characterisation experiments using a modified BPPG electrode, the electrode was immersed in a 50  $\mu\text{M}$  curcumin standard solution prepared in ethanol. Adsorption accumulation was then performed under open circuit condition, with the electrode placed in a well-stirred curcumin solution for 1 minute before being gently rinsed with deionised water and transferred to the blank solution of 0.05 M Britton-Robinson buffer pH 1.8 for voltammetric analysis at a scan rate of  $100 \text{ mV s}^{-1}$ .

The effect of accumulation time was studied experimentally. The MWCNT-BPPG electrode was left in a well-stirred 50  $\mu\text{M}$  curcumin solution again under open circuit conditions for different accumulation times in the range of 0-15 minutes. The electrode was then moved to 0.05 M Britton-Robinson buffer pH 1.8. Cyclic voltammetric scans were recorded at a scan rate of  $100 \text{ mV s}^{-1}$ . For the study of the adsorption behaviour of curcumin on the electrode surface, a series of curcumin concentrations in the range of 0-1000  $\mu\text{M}$  were used. The electrode was placed in the ethanolic solution containing the desired curcumin concentration for 15 minutes to generate the equilibrated surface coverage. A similar procedure was used in order to record the cyclic voltammetric scans.

For the analysis of the real sample, the extracts from turmeric sample (see above) were used without dilution. The MWCNT-BPPG electrode was then immersed in the real sample matrix and allowed to accumulate at open circuit potential with stirring for 1 minute prior to commencing voltammetric analysis.

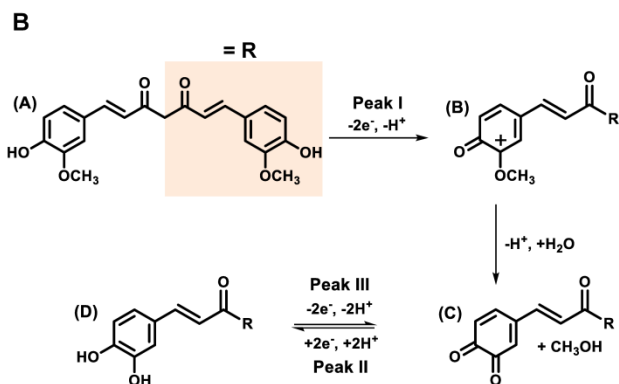
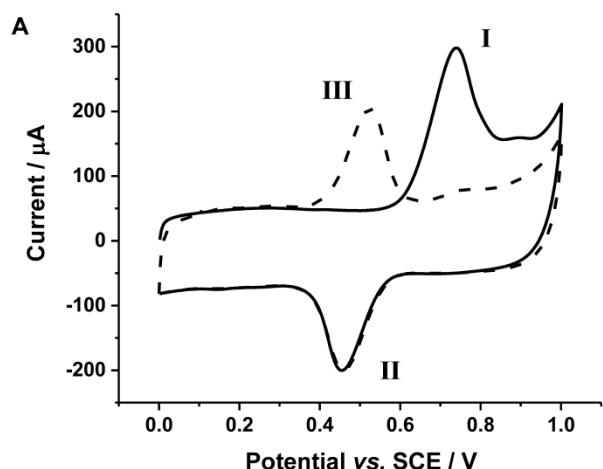
## 3. Results and discussion

In the following section, first, the electrochemical behaviour of curcumin adsorbed on a MWCNT-BPPG electrode is explored. The voltammetric characterisation is investigated in Section 3.1.1. In Section 3.1.2, the effect of accumulation time is studied and the adsorption of curcumin on the electrode surface is evidenced. Second, the analytical performance of the modified electrode towards curcumin detection is studied (Section 3.2), followed by the optimisation of real sample extraction procedure where the type of solvent and the time of sonication are optimised (Section 3.3). Finally (Section 3.4), the use of the developed electrochemical detection methodology is used to quantify the curcumin equivalent in real samples of turmeric.

### 3.1 Electrochemical behaviour of curcumin on MWCNT-BPPG electrodes

#### 3.1.1 Voltammetric characterisation

In order to characterise the cyclic voltammetric profiles of adsorbed curcumin, a 50  $\mu\text{M}$  curcumin in ethanolic solution was employed and analyte adsorbed onto the MWCNT-BPPG electrode for 1 minute under open circuit conditions. In order to record the voltammetric signal, the electrode was subsequently transferred to a 0.05 M Britton-Robinson buffer of pH 1.8. The cyclic voltammetry was scanned between +0.0 V and +1.0 V at 100  $\text{mV s}^{-1}$ . As shown in Fig. 2A, on the first forward scanning (solid line), a well-defined oxidative peak was



**Fig. 2** (A) The overlaid voltammetric responses of the 1<sup>st</sup> scan (solid line) and 2<sup>nd</sup> scan (dashed line) of curcumin adsorbed (open-circuit accumulation for 1 minute) on a MWCNT-BPPG electrode in 0.05 M Britton-Robinson buffer pH 1.8 at a scan rate of 100  $\text{mV s}^{-1}$ . (B) The proposed mechanism for the electrochemical oxidation/reduction of curcumin.

observed at +0.74 V labelled as peak I and then the reductive peak (labelled as peak II) was measured at +0.45 V on the backward scanning. Upon repeated cycling of forward scan (dash line), the oxidative peak I was no longer observable and was replaced by the oxidative peak III at +0.52 V. The reductive peak II at +0.45 V remained the same as seen on the first scan. A likely mechanism for the electrochemical reaction of curcumin is shown in Fig. 2B. This is proposed on the basis of the literature in report of related molecules, especially capsaicin which ascribes the oxidative peak on the first scan to being the two-electron, two-proton oxidation and the subsequent hydrolysis of the 2-methoxyphenol unit to form an ortho-benzoquinone unit (compound C Fig. 2B) [19]. Upon reversing the scan, the ortho-benzoquinone moiety is reduced, leading to the formation of an ortho-hydroquinone (compound D Fig. 2B). Then for subsequent scanning the observed voltammetric responses correspond with the reversible redox behaviour of the ortho-hydroquinone/ortho-benzoquinone couple. As shown in the proposed mechanism, the electrochemical mechanism of curcumin undergoes two electrons per one unit of 2-methoxyphenol. Therefore, the overall contribution of both parts of curcumin is a net four electron transfer. Under the investigated conditions, demethoxycurcumin can undergo a two electron oxidation process due to the single unit of 2-methoxyphenol contained in molecule while bisdemethoxycurcumin is not oxidised under our conditions.

#### 3.1.2 Effect of accumulation time

In order to optimise the accumulation time of curcumin adsorbed onto electrode surface under an open circuit conditions, the dependence of the adsorptive peak area of curcumin in 50  $\mu\text{M}$  was investigated as a function of the accumulation time. The modified BPPG electrode was immersed into the standard curcumin solution for various accumulation times from 0 to 15 minutes and then transferred to record the voltammetric responses in 0.05 M Britton-Robinson buffer, as above.

The results are shown in Fig. 3A. The voltammetric peak area of the curcumin oxidation signal increases significantly on extending the accumulation time from 0 to 4 minutes, consistent with increased curcumin adsorption on the surface of electrode. At longer times beyond 4 minutes, the peak area enhances less rapidly and reaches a maximum plateau after *ca.* 8 minutes, indicating that the adsorbed curcumin on the electrode surface reaches saturation. To obtain the highest sensitivity, 8 minutes accumulation therefore reports an optimal time. However, to facilitate a rapid analytical

procedure, unless otherwise stated one minute accumulation was employed for all subsequent experiments as a compromise between high sensitivity and short analysis time.

Having explored the adsorption kinetics of curcumin onto the electrode surface, the stripping signal of curcumin was investigated as a function of the analyte concentration. Varying curcumin concentrations in the range of 0-1000  $\mu\text{M}$  were used. The modified electrode was immersed in the curcumin solution for 15 minutes to allow curcumin to adsorb onto the electrode surface and to fully equilibrate. Subsequently, the electrode was placed in 0.05 M Britton-Robinson buffer to perform the voltammetric analysis.

The results of this experiment are depicted in Fig. 3B. The obtained charge transfer enhances with increasing curcumin concentration reaching a plateau at *ca.* 1000  $\mu\text{M}$  curcumin. The experimental data was analysed using the Langmuir adsorption isotherm model. The general equation of the Langmuir isotherm is represented by the following equation [20]:

$$\theta = \frac{K[C]}{1 + K[C]} \quad (1)$$

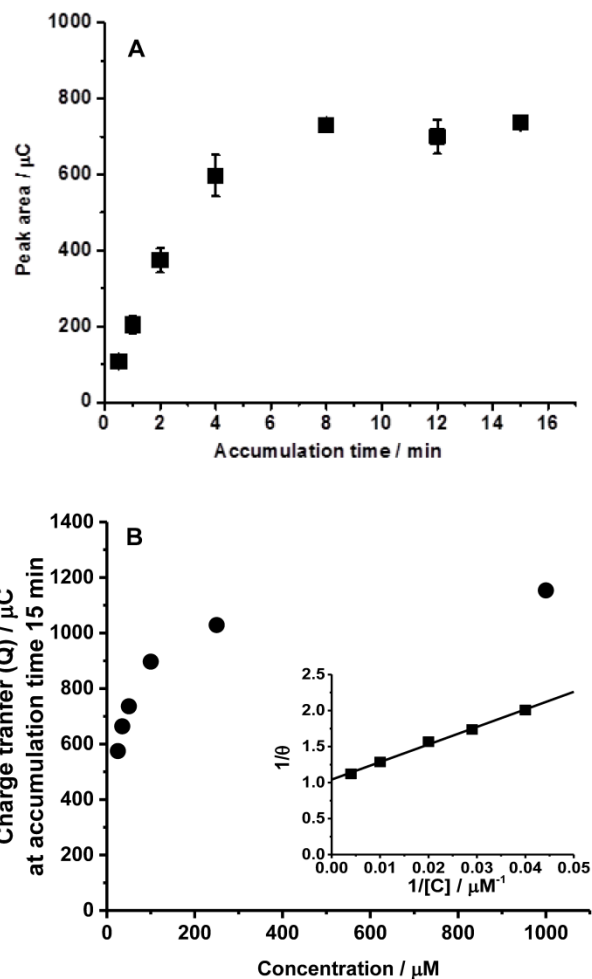
where  $\theta$  is the fractional coverage,  $K$  is the adsorption equilibrium constant, and  $[C]$  is the curcumin concentration.

The Langmuir isotherm, Eq. (1), can be rearranged to obtain the following expression:

$$\frac{1}{\theta} = \frac{1}{K[C]} + 1 \quad (2)$$

$\theta$  is the fractional coverage which can be calculated from the ratio  $\frac{Q}{Q_{\text{max}}}$  where  $Q$  is the voltammetrically measured charge transferred during the oxidation of the surface adsorbed curcumin at the concentration studied and  $Q_{\text{max}}$  is maximum charge transfer at saturated surface with curcumin. For this experiment, the voltammetrically charge transferred during the oxidation of curcumin adsorbed at concentration of 1000  $\mu\text{M}$  was measured to be *ca.* 1150  $\mu\text{C}$  and this is assigned to be the maximum charge transfer.

The Langmuir isotherm predicts that a straight line should be obtained when  $\frac{1}{\theta}$  is plotted against  $\frac{1}{[C]}$  and the value of y-intercept should equal 1. As shown in Fig. 3B



**Fig. 3** A) The responses of oxidative peak I as a function of accumulation time in 50  $\mu\text{M}$  of curcumin. B) Langmuir plot showing the surface coverage against the concentration for adsorption of curcumin onto electrode surface.

inset, the Langmuir plot provided a good linearity ( $R^2 = 0.995$ ) and interception of y-axis is close to 1 (y-intercept =  $1.04 \pm 0.02$ ). This suggests that the adsorption of curcumin from ethanol on the modified BPPG electrode likely obeys the Langmuir adsorption isotherm. The value of equilibrium constant ( $K$ ) obtained from the slope of a straight line fit was  $0.041 \mu\text{M}^{-1}$ . The surface of MWCNT-BPPG electrode becomes saturated at *ca.* 1000  $\mu\text{M}$  curcumin concentration. The surface coverage of curcumin was calculated using Faraday's 1st law  $\Gamma = Q/nFA$  where the charge ( $Q$ ) was determined by integrating under the oxidative peak of 1000  $\mu\text{M}$  curcumin,  $n$  is the number of electrons ( $n=4$ ),  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ), and  $A$  is the surface area of the modified BPPG electrode (*ca.* 20  $\text{cm}^2$ , see S1 supplementary information). The surface coverage was calculated to be *ca.*  $1.5 \times 10^{-10} \text{ mol cm}^{-2}$  (or  $9.0 \times 10^{13}$

molecules  $\text{cm}^{-2}$ ) which suggests that the curcumin forms a monolayer on the surface of MWCNT-BPPG electrode [21]. Implicit in the Langmuirian nature of the adsorption is that the latter is a reversible process where the curcumin is dissolved in ethanol. In contrast when the electrode is transferred into water after adsorption in ethanol the curcumin remains irreversibly adsorbed.

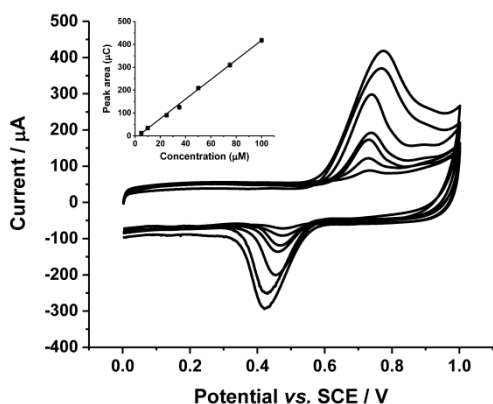
### 3.2 Analytical response of the MWCNT-BPPG electrode

Having characterised the voltammetric responses of curcumin at MWCNT-BPPG electrode, optimised the accumulation time and also investigated the adsorption of curcumin on the electrode surface, we next evaluated the applicability of the BPPG modified electrode with multiwalled carbon nanotubes for the analytical purposes of detecting the curcumin. The optimised accumulation time, 1 minute, was used to perform the adsorption of curcumin onto the electrode surface by open circuit adsorption. We first immersed the MWCNT-BPPG electrode to the solution of differing curcumin concentrations over the range of 2-100  $\mu\text{M}$  in 100% ethanol. The electrode was gently rinsed with deionised water and was placed in 0.05 M Britton-Robinson buffer pH 1.8 to perform the adsorptive stripping voltammetry. The voltammetric signal was recorded as a function of the curcumin concentrations as depicted in Fig. 4. The analytical response of MWCNT-BPPG electrode towards curcumin was determined by integrating the peak area of

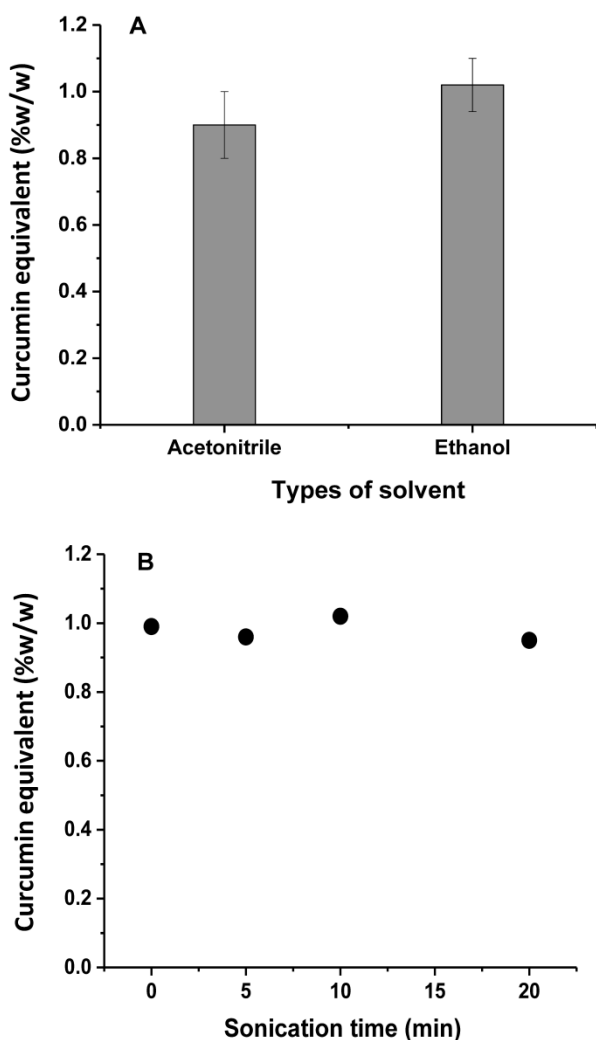
oxidative peak of the 1st scan (peak I). As shown in the inset of Fig. 4, the plot of peak area of curcumin oxidation peak versus curcumin concentrations revealed the linear response in the concentration range of 2-100  $\mu\text{M}$  with a correlation coefficient of 0.999 ( $N=7$ ). The calibration equation is  $Q/\mu\text{C} = (4.26 \pm 0.04)[\text{curcumin}](\mu\text{M}) - (8.53 \pm 2.41)$  with a limit of detection of 0.45  $\mu\text{M}$  (based on  $3\text{SD}/S$ ) and a limit of quantification of 1.49  $\mu\text{M}$  (based on  $10\text{SD}/S$ ) where SD is standard deviation and S is a sensitivity of calibration plot. A reproducibility of responses between three repeated drop-cast modifications of the BPPG electrode with MWCNT was found to be less than 7%, as measured by the variation in peak area measured of 10 and 50  $\mu\text{M}$  curcumin standard solutions.

### 3.3 Analysis of a real sample using a MWCNT-BPPG electrode

A real sample employed in this work is in the form of turmeric powder which was purchased from a local supermarket. Finding a suitable solvent for extracting or dissolving the analyte of interest from real samples is the first step in any extraction method. Organic solvents, especially ethanol, methanol, acetone and acetonitrile, have been widely used to extract compounds from botanical and herbal samples [22]. Among these solvents acetonitrile and ethanol have been commonly used in order to extract curcumin in previous reports [23]. Hence, a choice was made between these two different solvents namely acetonitrile and ethanol to select the best solvent for curcumin extraction. 10 mg of turmeric powder sample was dissolved in 50 mL of acetonitrile and ethanol separately. For each solvent, triplicate extractions were performed. After sonicating the sample mixture for 10 minutes, the extracted sample was detected directly without further filtration or dilution. The AdsSV analysis for curcumin was performed in 0.05 M Britton-Robinson buffer at pH 1.8. In this work, the efficiency of acetonitrile and ethanol on the extraction of the curcumin from turmeric powder sample was compared, where the results have been expressed as the curcumin equivalent (%w/w) of the original sample. The result are shown in Fig. 5A, it can be seen that the use of acetonitrile and ethanol resulted in  $0.90 \pm 0.10\%$  w/w and  $1.02 \pm 0.08\%$  w/w of curcumin equivalent respectively. The curcumin equivalent obtained from both solvents shown approximately similar extraction results. Although acetonitrile has been used as an extraction solvent for curcumin extraction in several previous literatures and also gave roughly the same extraction result compared to ethanol in the present study, the toxicity of acetonitrile is



**Fig. 4** Adsorptive stripping cyclic voltammetric responses (1<sup>st</sup> scans) of a MWCNT-BPPG electrode to increasing curcumin concentrations from 2 to 100  $\mu\text{M}$  in a 0.05 M Britton-Robinson buffer solution pH 1.8, after the open-circuit accumulation for 1 minute; scan rate 100  $\text{mV s}^{-1}$ . Inset: the corresponding calibration curve plot using the oxidation peak (I).



**Fig. 5** A) Effect of solvent on extraction of curcumin equivalent from turmeric powder sample and B) Effective curcumin equivalent (%w/w) in turmeric powder at different ultrasonic extractions time from 0 to 20 minutes.

a concern especially in the context of food [24]. Therefore, ethanol was chosen as the extraction solvent for the further study of real samples.

Having identified a suitable organic solvent we next explore the effect of sonication on the extraction efficiency. The turmeric powder sample was prepared using the procedure in experimental Section 2.2. We investigated the extracted efficiency at different sonication times in the range of 0-20 minute. 10 mg of the sample was weighed prior to addition of 50 mL of ethanol. The sample and solvent were mixed by shaking and then sonicated in an ultrasonic bath for the desired time period. The results are depicted in Fig. 5B and show that the curcumin equivalent from each sonication time was found to be ca. 0.95%w/w - 1.02%w/w. The results show no significant difference in the curcumin extraction

efficiency regardless of the sonication time. Accordingly sonication is seen to be pointless and we can simply prepare the sample prior to perform the electrochemical analysis in one step namely mixing the sample with ethanol and shaking rapidly giving a rapid extraction procedure suitable for routine sample analysis.

To evaluate the practicality of the developed method, we employed the method to quantify the curcumin equivalent of the turmeric powder sample sourced from a local supermarket. Measurement of the curcumin equivalent in the sample was carried out with minimal sample preparation by simply shaking the sample with ethanol for 1 minute prior to determination of curcumin content using the developed AdsSV method. From the quantification experiment, the curcumin equivalent in sample was calculated to be ca.  $0.99 \pm 0.08\%$  w/w which is consistent with the values reported in the literature using HPLC techniques where the curcumin content in various types of turmeric products is reported to lie between the range of ca. 0.5%w/w and 5.7%w/w [8]. Accuracy of the determination was evaluated from the percentage recovery of the sample [25]. Different known amounts of curcumin standard solution were added to separate samples portion before AdsSV analysis. The percentage recovery was calculated based on

$$\% \text{Recovery} = \frac{C_1 - C_2}{C_{\text{std}}} \times 100$$

where  $C_1$  is the concentration of curcumin equivalent in sample added the known amount of standard solution,  $C_2$  is the concentration of curcumin equivalent in sample, and  $C_{\text{std}}$  is the concentration of standard solution. We found that the recoveries of our method were in the range of 92–108%, indicating good accuracy for the developed method as shown in Table 1. The results indicated that the method developed for the determination of curcumin equivalent in real sample using the multiwalled carbon nanotube modified BPPG electrode was accurate and feasible.

Table1. Summary of curcumin equivalent determination in turmeric samples and recoveries

Sample	Original found in sample ( $\mu\text{M}$ )	Standard added ( $\mu\text{M}$ )	Total found ( $\mu\text{M}$ )	Recovery (%)
Extracted curcumin from turmeric powder	5.78	5	$10.29 \pm 2.1$	92
		25	$29.37 \pm 2.6$	94
		50	$60.26 \pm 2.9$	108



## 4. Conclusions

Adsorptive stripping voltammetry has been applied to detection and quantification of curcumin in turmeric samples using multiwalled carbon nanotube modified BPPG electrodes. The voltammetric characteristics were determined. The good linear calibration plot in the range 2-100  $\mu\text{M}$  ( $R^2 = 0.999$ ) was obtained. The preparation of a real sample (turmeric powder) for analysis has been simplified to a one-step procedure. This facile, easy method of detection will be likely useful for applications in the food industry.

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