



Novel Potentiometric Sensors Based on Carbon and TiO₂ Nanotubes/ β -cyclodextrin for Meclofenoxate Hydrochloride Micro Determination in Spiked Surface Water and Urine Samples



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THE great expansion of portable analytical devices can be attributed to the development of highly efficient and stable chemical sensors. The first target of the study aims to the construction and sense of carbon paste sensors based on CNTs and TiO₂ nanotubes for meclofenoxate HCl micro determination. The role affecting the behaviour of lipophilic anionic additive as well as plasticizer is discussed carefully. The constructed sensors showed Nernstian slope 57.3 ± 0.55 and 58.3 ± 0.1 mV decade⁻¹ and detection limits 7.6×10^{-7} and 6.5×10^{-7} mol L⁻¹ and quantification limits 2.5×10^{-6} and 2.1×10^{-6} mol L⁻¹ for CNTs-CPE and TiO₂-CPE, respectively. The surface morphology of the investigated sensors was studied. The selectivity behaviour of the sensors was investigated using Bakker protocol and tested in presence of the biologically important inorganic cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺). The proposed potentiometric sensors were successfully performed for drug determination in pharmaceutical products, spiked surface water and human urine samples with good recovery data (99.5, 99.8 %) for CNTs-CPE and TiO₂-CPE, respectively.

Keywords: Potentiometric carbon paste sensors, Meclofenoxate HCl, β - cyclodextrin ionophore, Carbon and TiO₂ nanotubes.

Introduction

Meclofenoxate (MFX) (Fig. 1) is an ester of p-chlorophenoxyacetic acid and dimethylaminoethanol. MFX is a potent nootropic agent [1, 2] that acts as an antioxidant, stimulates glucose uptake, oxygen consumption and increase energy metabolism in the brain. Recently, it is used as a dietary supplement and drug in the treatment of symptoms of senile dementia and Alzheimer's disease [3]. Various methods have been used for MFX determination including HPLC [4,5], proton magnetic resonance spectroscopy [6],

cyclic voltammetry [7] and scattering method coupled with flow injection technique [8]. It is obvious that these methods are highly sensitive; however, these techniques are highly expensive due to involving several manipulation steps before reaching the final result of analysis, long analysis time as well as complex instrument setup. Consequently, the above mentioned techniques are unsuitable for routine analysis. Our goal aimed to develop a simple, selective, inexpensive diagnostic tool for the vital drug determination. An analysis using potentiometric sensors with

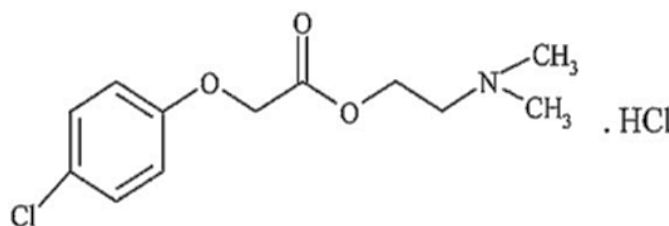


Fig. 1. Structural formula of meclofenoxate HCl.

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ion-selective electrodes (ISEs) is considered a beautiful alternative technique due to its rapid response, simple operation, time saving, accurate, low cost, fast and sensitive technique [9-13]. Recently, potentiometric sensors have attracted many researchers in Analytical Chemistry for the above mentioned properties.

The use of carbon paste potentiometric sensors enables the determination of trace ion species in industry [14,15]. Potentiometric method employing carbon paste sensors (CPSs) have attracted attention mainly due to their advantages over membrane sensors such as chemical inertness, robustness, renewability, stable response, low Ohmic resistance, no need for internal solution and suitability for a variety of sensing and detection applications [16]. Moreover, these sensors are environmentally friendly sensors. In their case, problems with passivation are simply eliminated by a simple and quick renewal of their surface [17]. Oligosaccharide involving (β -CD), as an example, consisting of seven glucose units and form a lipophilic inner cavity and hydrophilic outer surface, it is used in the pharmaceuticals, and other applications [18, 19]. In aqueous solutions, it is able to interact with a variety of guest molecules such as drugs, forming inclusion complexes[20]. Consequently, β -CD acts as a sensing material in fabrication of potentiometric sensors for pharmaceutical drug determination. Owing to their truncate cone structure, they have unique physical and chemical properties, as shown in the literature [21-23].

Recently, powerful advantages of nanomaterials including extraordinary electrical, chemical, mechanical and structural properties [24] lead them highly attractive for specific applications such as potentiometric sensor fabrication [25]. CNTs promote the performance characteristics of chemically modified sensors. Perfect physico chemical properties of CNTs such as ultra-light weight, high mechanical strength, high electrical and thermal conductivity, metallic or semi-metallic behaviour, high surface area, modifiable side wall and high reactivity make the hydrophobicity of the ISE membranes good [26-28].

Similarly, TiO_2 nanotubes have unique technological applications attributed to their excellent physicochemical properties such as environmentally friendly, distinguished chemical and photochemical stability, large surface area, good biocompatible, high mechanical strength

and fast electron-transfer ability[29, 30].

Due to the above mentioned properties, we decided to use carbon and TiO_2 nanotubes, in our current research aiming to improve the detection limit and stability of the investigated sensors. The study is based on fabrication of two novel sensors, the first sensor including β -CD as ionophore incorporating CNTs where as the second sensor including the same ionophore incorporated with TiO_2 nanotubes. The constructed sensors were used successfully for drug determination in pharmaceutical compounds, surface water and urine samples.

Experimental

Reagents and materials

All chemicals were of analytical grade. Bidistilled water was used throughout all experiments. Pure grade meclofenoxate hydrochloride and the pharmaceutical preparation Lucidril® were provided by Mina Pharm, Egypt. Dioctyl adipate (DOA) and sodium tetraphenylborate (NaTPB) were obtained from Fluka (U.S.A.). Dibutyl phthalate (DBP), dioctyl phthalate (DOP), acetophenone (AP) and dimethyl phthalate (DMP) were purchased from Merck (Germany). β -cyclodextrin (β -CD), dibenzo-18-crown-6 and 18-crown-6 were purchased from Euromedex (France). The metal salts were provided by BDH as nitrates or chlorides. Spectroscopic graphite powder (1-2 mm, Sigma Aldrich) was applied as sensors materials.

Apparatus

Potentiometric and pH-measurements were performed using 702 SM Titrimo (Met Rohm, Switzerland). A mLw W20 circulator thermostat used to control the temperature of the investigated samples. Scanning Electron Microscope (SEM) images were taken by (Gemini, Zeiss-Ultra 55) field emission high resolution scanning electron microscope). HRTEM image was taken by JEOL-JEM 2100 with an acceleration voltage of 200 KV used for characterization of sensors morphology.

CNTs synthesis using Co-Fe layered double hydroxide (LDH) as a catalyst

Co-Fe LDH catalyst (0.5 g) packed in a cylindrical alumina cell to perform the catalytic reaction in a continuous-flow fixed bed. An inert nitrogen gas with a flow rate 70 ml/min used to preheat the catalyst to 500 °C for 10 min and acetylene gas passed over the catalyst bed with a rate of 10 ml/min for 30 min. The maximum carbon yield % is produced at 500 °C

decomposition temperature as discussed recently by Abdel Moaty et al. [31]. Then, the product on the alumina cell was cooled to room temperature.

Synthesis of TiO₂ nanotubes

Preparation of anatase-phase TiO₂NTs was performed using 5.0 g TiO₂ powder dispersed in 150 mL of 10 mol L⁻¹ NaOH and stirred for 15 min and the solution was heated at 150°C in a Teflon-lined stainless steel autoclave for 6 days. White precipitate (Na₂Ti₃O₇) was obtained and washed with dilute HCl for neutralization the excess base and replace sodium ions forming H₂Ti₃O₇ nanosheets through ion-exchange process. Finally, TiO₂ nanotubes were obtained by dehydration process at 500 °C. The products were detected by X-ray diffraction and the sample morphologies were studied using TEM as reported by Mohassab et al. [32].

Sensors construction

The investigated sensors were fabricated as mentioned previously [33]. The performance characteristics of the two sensors were examined by adding variable percentages of β-CD ionophore and NaTPB lipophilic anionic additive, CNTs nanotubes in the first sensor and TiO₂ nanotubes in the second sensor. The sensors were preconditioned before use by soaking in a 1.0×10⁻³ mol L⁻¹ meclofenoxate hydrochloride solution for 1 h. The calibration curves were plotted by recording sensor potentials versus the negative logarithm of meclofenoxate concentration (1.0×10⁻⁹- 1.0×10⁻² mol L⁻¹).

Potentiometric determination of MFX

The potentiometric titration of different volumes (3–9 mL) of 1.0×10⁻² mol L⁻¹ drug solution were transferred to a 50 mL beaker and titrated with NaTPB. Small increments of 1 × 10⁻² mol L⁻¹ of MFX solution were added to 50 mL aliquot samples of various concentrations from pure drug or pharmaceutical formulation applying the standard addition method [34].

MFX Determination in spiked surface water and urine samples

Different amounts of MFX and 5 mL urine of healthy person or surface water samples from River Nile, Beni-Suef City, Egypt were transferred to 50-mL measuring flask and completed to the mark by bidistilled water. The contents of the measuring flask were transferred to a 100 mL beaker, and subjected to standard addition method.

Results and Discussion

Optimization of sensor composition

In fact, ionophores are considered the most important sensing component in fabricating potentiometric sensors. The target ion (MFX) has a very high affinity to form inclusion complexes with ionophore via quick exchange kinetics with sufficient stability constant. The sensing components have the sufficient solubility and high lipophilicity to prevent its leaching into the sample solutions. The sensitivity, linearity and DL values for the blank sensor lead to bad potentiometric response, as predicted. Therefore, the sensitivity of the sensor towards MFX ions was lowered. The potentiometric response is improved (slope 43.9 mV decade⁻¹), concentration range (1.0 × 10⁻⁵–1.0 × 10⁻² mol L⁻¹), DL (5.86 × 10⁻⁶ mol L⁻¹ and QL (1.9 × 10⁻⁵), when 0.7% β-CD ionophore is added to the carbon paste composition. However, further addition of the ionophore displays lowering in potentiometric response of the investigated sensor to some extent. In fact, NaTPB as a lipophilic anionic additive and guest molecules such as MFX ion, in presence of host compound (β-CD), is required to stabilize the inclusion complexes and ensure perm selectivity and electro neutrality of the carbon paste. In addition, it promotes the interfacial ion-exchange kinetics and increases the bulk conductivity by providing mobile ionic sites [35, 36]. The data showed that incorporation of 0.5% NaTPB additive in the paste enhanced the potentiometric response.

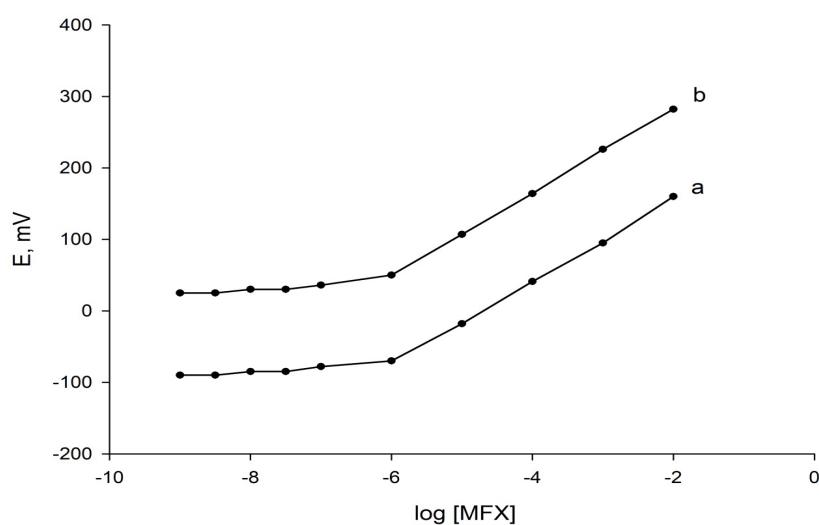
Potentiometric response of the fabricated sensor (CNTs-CPE) improved significantly by adding 7 % CNTs in the composition of the carbon paste, where the transduction of the ion to electron signal, the conductivity of the sensor as well as surface to volume ratio of the carbon paste were enhanced [37, 38]. Consequently, Nernst slope, concentration range, DL and QL values improved and reached 57.3 mV decade⁻¹, 1.0×10⁻⁶- 1.0×10⁻², 7.6 × 10⁻⁷ and 2.5×10⁻⁶ mol L⁻¹ for this sensor (Table 1, Fig.2). Excessive addition of 7 % CNTs in the composition led to lowering response of the sensor.

Finally, addition of TiO₂ nanotubes to the paste improved the potentiometric characteristics of the investigated sensor (TiO₂-CPEs), as predicted. This can be attributed to the excellent properties of these nanotubes. The data showed that 1.0 % TiO₂ nanotubes was the best percent composition. Upon increasing TiO₂ NTs more than 1.0 %, a lowering in potentiometric response was observed.

TABLE 1. Optimization and electrochemical response characteristics of the proposed MFX sensors.

	CNTs-CPE	TiO ₂ -CPE
Composition(%)	0.7% β -CD +0.5% NaTPB +7.0% CNTs +42.4% G +49.4%DBP	0.7 % β -CD + 0.5NaTPB + 1.0% TiO ₂ + 48.4% G + 49.4%DBP
Graphite/ Plasticizer ratio	0.85	0.97
Slope (mVdecade ⁻¹)	57.3	58.3
Concentration range (mol L ⁻¹)	1.0 x10 ⁻⁶ -1.0 x 10 ⁻²	1.0 x10 ⁻⁶ -1.0 x 10 ⁻²
Detection Limit (mol/L ⁻¹)	7.6 x 10 ⁻⁷	6.5 x 10 ⁻⁷
Quantification limit (mol/ L ⁻¹)	2.5x10 ⁻⁶	2.1x10 ⁻⁶
Correlation coefficient (<i>r</i> ²)	0.998	0.999
SD	0.55	0.1
RSD (%)	0.97	0.17
Response time (sec)	10	8
Thermal coefficient (V/°C)	0.0010	0.0011
pH range	2.0-7.0	2.0-7.4
Life time (day)	58	63

RSD: Relative standard deviation, SD: Standard deviation, G: Graphite.

**Fig. 2. Calibration curves of (a) CNTs-CPE and (b) TiO₂-CPE sensors.**

Effect of g/p ratio

In fact, sensitivity and selectivity of the sensors are highly affected by g/p ratio [39]. Different graphite/plasticizer ratios with DBP as a plasticizer and constant amount of ionophore (i.e. 0.7 %) were investigated. The paste with a (g/p) ratio of 0.85 and 0.97 gave the best sensitivity and reproducibility for CNTs-CPE and TiO₂-CPE respectively.

Effect of plasticizer

The nature of plasticizer influences the dielectric constant of the paste, the flux of ion species and the paste softness [40]. It is not surprising that many factors affect the performance of plasticizers used in the construction of CPEs such as lipophilicity, viscosity, volatility, dielectric constant, molecular weight, cost, toxicity and capacity to dissolve the substrate and

other additives present in the paste. Evaluation of the behaviour for various plasticizers having a wide range of dielectric constant (ϵ 3.1–17.4) for (DBP, DOP, DOA, AP, and DMP as synthetic plasticizers as well as Olive Oil as a natural plasticizer) was investigated. The sensor fabricated with DBP plasticizer (ϵ 6.4) showed an excellent potentiometric response compared with the sensor plasticized with AP (ϵ 17.4)[41]. The bad behaviour of AP can be attributed to the high volatility and solubility in water. It is worthy to mention that DBP improves the polarity of the carbon paste and so the charged MFX ions can be extracted from aqueous solution to the

paste easier and the potential response exhibited Nernstian behaviour.

Morphology characterization of the prepared CPEs

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate the morphological features of CNTs-CPE and TiO₂-CPE sensors. SEM image (Fig. 3a) showed paste homogeneity due to the high viscosity and conductivity of DBP plasticizer. No CNTs were observed on the surface of graphite sheets or even between the layers. This behaviour can be attributed to the

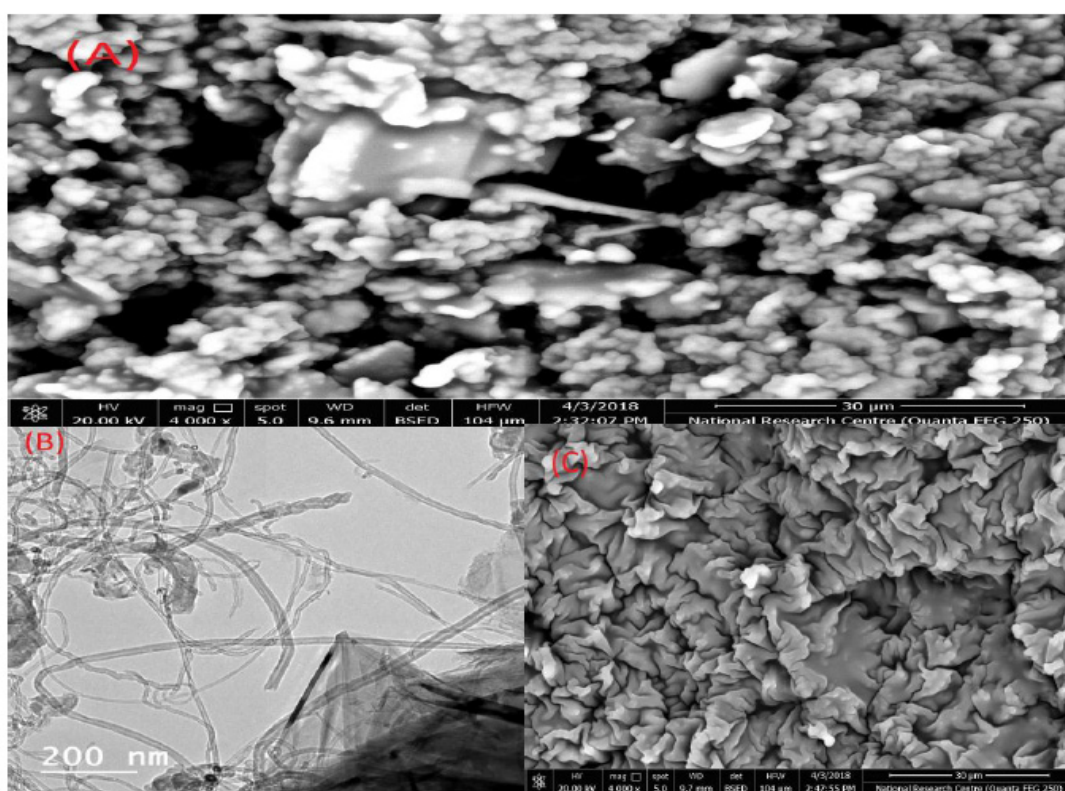


Fig. 3. SEM image of CNTs-CPE (A), TEM image of CNTs-CPE (B) and SEM image of TiO₂-CPE sensor (C).

magnification and resolution limit of the used SEM. Therefore, same paste was investigated using HRTEM (Fig.3b). It is clear that CNTs are highly distributed on the surface and between the graphite layers. SEM image for TiO₂ based sensor (Fig. 3c) showed that TiO₂ spread all over the carbon surface. Consequently, fine distribution of CNTs or TiO₂ nanotubes in the paste improves the conductivity, sensitivity and selectivity of the investigated sensors.

Response time and Lifespan

The dynamic response time for the

investigated sensors was recorded at different MFX concentrations. The reversibility of the sensors could be evaluated using a procedure in the opposite direction. The measurements were carried out in the sequence of high-to-low (1.0×10^{-2} – 1.0×10^{-6} mol L⁻¹) concentrations as shown in Fig.4. The response time for CNTs-CPE and TiO₂-CPE sensors reached 10 s and the lifespan was 58 and 63 days, respectively. This means that the investigated sensors could be kept stable without any measurable change in potential for a long time.

Evaluation of statistical parameters

Subsequent measurements of 1.0×10^{-4} mol L^{-1} MFX solution immediately after measuring the first set of solutions at 1.0×10^{-3} mol L^{-1} MFX

were carried out to examine the repeatability of the potential reading of the sensors. The potential response for five replicate measurements of CNTs-CPE and TiO_2 -CPE sensors was evaluated

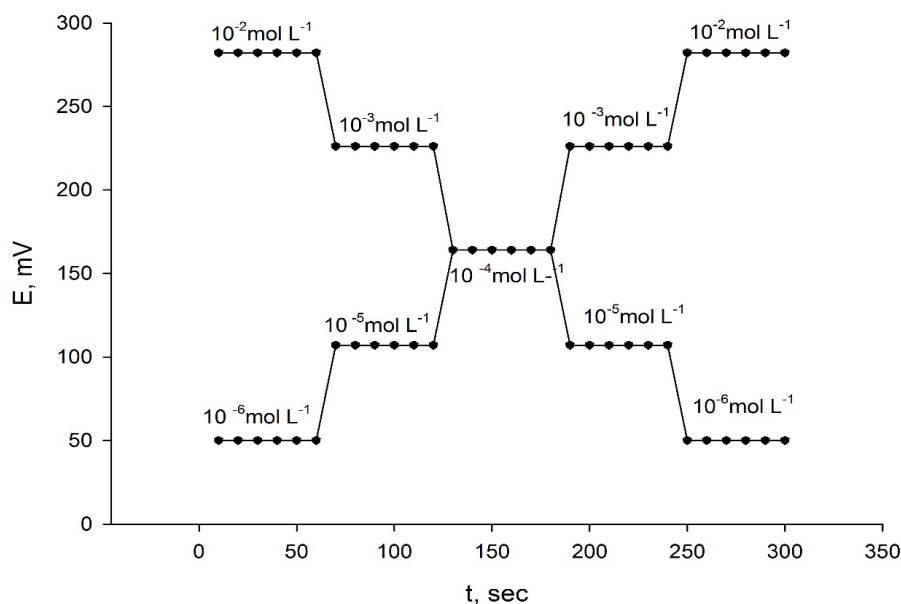


Fig. 4. Dynamic response time of TiO_2 -CPE sensors.

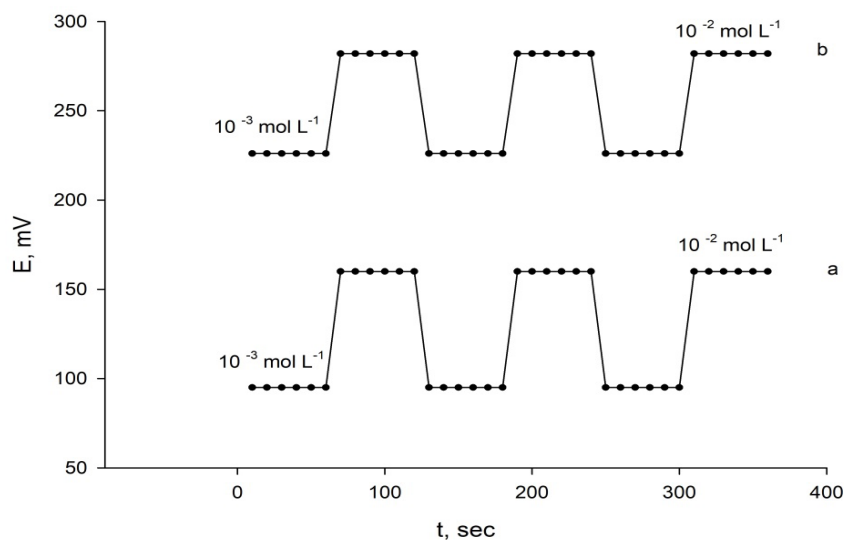


Fig. 5. The reversibility of (a) CNTs-CPE and (b) TiO_2 -CPE sensors for several low-to-high sample cycles.

and the standard deviation values were 0.55 and 0.1 for the sensors, respectively. Consequently, the sensors possess excellent repeatability with no memory effect (Fig.5). The reproducibility

of five independent MFX sensors was checked in 1.0×10^{-5} mol L^{-1} MFX solution. The sensors showed high reproducibility with R.S.D less than 1.0 and 0.5% for CNTs-CPE and TiO_2 -CPE,

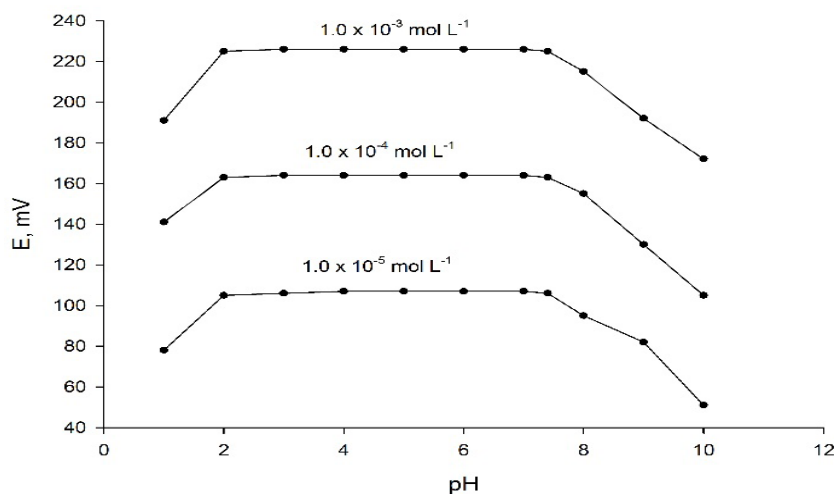


Fig. 6. Effect of pH at different MFX concentrations on the potential response of TiO₂-CPE.

respectively and application of the second sensor is highly precise compared with the first sensor.

The Effect of pH and temperature

In fact, the pH plays an important role influencing the electrochemical response of the sensors. Three different concentrations (1.0×10^{-5} , 1.0×10^{-4} , 1.0×10^{-3} mole L⁻¹) of the investigated drug ion solutions were tested. The study revealed that the pH interval (2.0-7.4) was obtained for TiO₂-CPE sensors (Fig.6).

The sensors characteristics were tested at different temperature (20-60)°C and the study

revealed that the thermal stability coefficient values were 0.0010 and 0.0011(V/°C) for sensors CNTs-CPE and TiO₂-CPE, respectively. This indicates the high thermal stability of the investigated sensors.

Selectivity

Bakker protocol, an excellent approach, is applied to investigate the selectivity behaviour of potentiometric sensors. Traditional methods of evaluation such as the separate solution and matched potential methods [42, 43] biased by the consequences of the ion-exchange processes at the membrane/solution interface as well as trans-

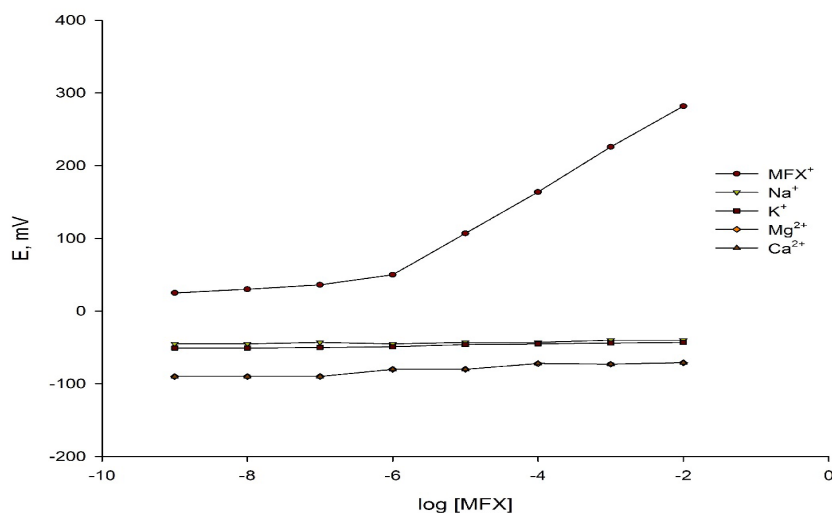


Fig. 7. Response to MFX and some interfering species using TiO₂-CPE sensor.

membrane ions fluxes. In 2002, Bakker proposed a method of measurements of the so-called unbiased selectivity, called Bakker protocol [44]. Calibration curves are performed in other biologically important inorganic cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}), finally, in solutions containing the primary ions (Fig. 7). It is evident that, no significant response of the sensors for all interfering species tested. Based on this protocol, neither the trans-membrane flux, nor the ionexchange at the membrane/solution interface distorts the sensor potential.

Analytical applications

The investigated sensors were successfully used for titrating of MFX against NaTPB as a titrant. MFX amounts in 50 mL solution were determined successfully in the range 2.94-14.71 mg with the recovery from 99.5 to 102 % and RSD from 0.2- 1.1 % (Table 2). Potentiometric titration and differential curves for TiO_2 -CPE are shown in Fig. 8. It is clear that MFX^+ ion can be determined accurately with the investigated sensor.

TABLE 2. Application of the proposed sensors for MFX determination in pure and pharmaceutical preparations.

Sensor type	Statistical parameter	Standard addition			Potentiometric titration		
		Taken	Recovery	RSD	Taken	Recovery	RSD
		mg	%	%	mg	%	%
CNTs-CPE	Pure solution	2.94	101.0	0.89	2.94	100.0	1.0
		8.83	100.0	0.76	8.83	101.2	0.755
		14.71	100.1	0.61	14.71	99.5	0.503
	Mean \pm SD		100.4 \pm 0.551			100.23 \pm 0.87	
	N		4				
	F- ratio		2.49 (9.28) ^a				
	t-test		0.64 (3.18) ^b				
	Lucidril®tablets 250mg/tablet	2.94	99.90	0.899	2.94	100.3	0.264
		8.83	100.5	1.007	8.83	100.2	0.208
		14.71	100.5	0.915	14.71	101.1	0.400
	Mean \pm SD		100.3 \pm 0.345			100.5 \pm 0.491	
	N		4				
	F- ratio		2.02 (9.28) ^a				
	t-test		0.49 (3.18) ^b				
TiO_2 -CPE	Pure solution	2.94	100	0.68	2.94	100.4	0.66
		8.83	100	0.20	8.83	100.2	1.058
		14.71	101	0.99	14.71	99.8	1.043
	Mean \pm SD		100.5 \pm 0.498			100.1 \pm 0.305	
	N		4				
	F- ratio		2.66 (9.28) ^a				
	t-test		0.56 (3.18) ^b				
	Lucidril®tablets 250 mg/tablet	2.94	102	0.980	2.94	101	0.990
		8.83	101.5	0.769	8.83	102	0.980
		14.71	100.3	0.701	14.71	102.5	0.845
	Mean \pm SD		101.3 \pm 0.874			101.8 \pm 0.764	
	N		4				
	F- ratio		1.3 (9.28) ^a				
	t-test		0.94 (3.18) ^b				

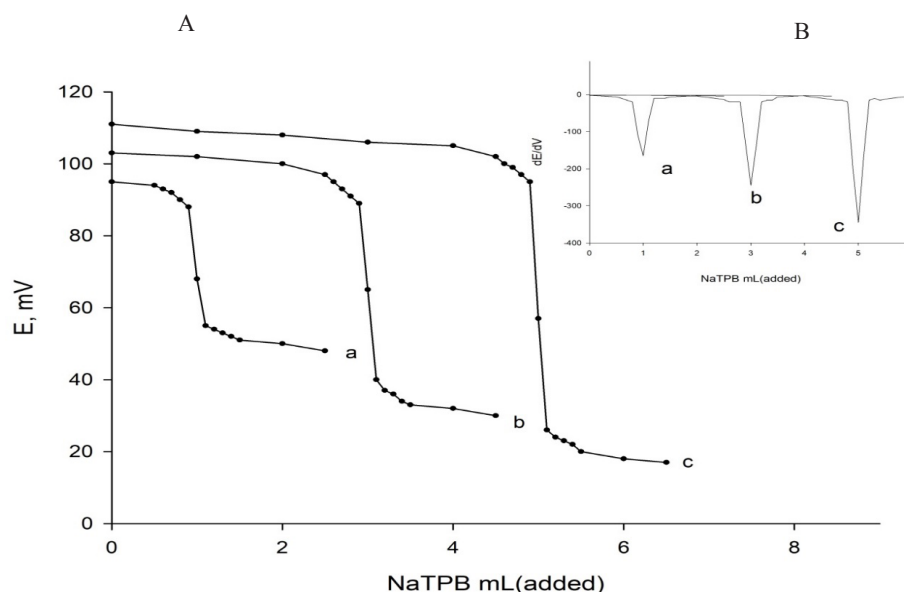


Fig. 8. (A) Potentiometric titration curves of (a) 1, (b) 3 and (c) 5 mL of 10^{-2} mol L^{-1} MFX using TiO_2 -CPE against 10^{-2} mol L^{-1} NaTPB as titrant and (B) its first order derivative.

TABLE 3. Application of the proposed sensors for MFX determination in human urine in human urine and piked surface.

Statistical parameter	Urine			Real water		
	Taken mg	Recovery %	RSD %	Taken mg	Recovery %	RSD %
CNTs-CPE	2.94	100.5	0.498	2.94	99.5	0.503
	8.83	101	0.857	8.83	99.8	0.379
	14.71	102	0.980	14.71	100	0.551
Mean \pm SD	101 ± 0.764			99.77 ± 0.252		
TiO_2 -CPE	2.94	100.0	1.0	2.94	100.5	0.262
	8.83	100.3	0.288	8.83	100.7	0.298
	14.71	100.4	0.320	14.71	100.4	0.152
Mean \pm SD	100 ± 0.208			100.5 ± 0.153		

MFX content in the pure solution and Lucidril® were determined by standard addition method. The result shown in Table 2 indicated that recoveries ranged from 100.5-102 % with small RSD less than 1.01 from 0.61-1.007 and 0.2-0.980 for CNTs-CPE and TiO_2 -CPE, respectively. The

sensors were also applied to the determination of MFX in surface water and urine samples as good matrices. Different amounts of MFX were spiked into surface water or urine samples and the drug contents were measured (Table 3).

TABLE 4. Comparison between the investigated and published sensors.

Sensor	LR mol L^{-1}	DL mol L^{-1}	QL mol L^{-1}	Slope mV Decade	pH range	TC V/ $^{\circ}C$	Ref
PVC membrane	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	1.0×10^{-5}	3.3×10^{-5}	54.05	4-7.5--		[45]
PVC membrane	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	8.0×10^{-6}	2.6×10^{-5}	58.80	3-5.5	0.00147	[46]
CPE	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	8.0×10^{-6}	2.6×10^{-5}	59.74	2-5.0	0.00138	[46]
CNTs-CPE	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	7.6×10^{-7}	2.5×10^{-6}	57.3	2-7.0	0.0010	[P.S]
TiO_2 -CPE	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	6.5×10^{-7}	2.1×10^{-6}	58.3	2-7.4	0.0011	[P.S]

Comparison

Potentiometric sensors based on ion-pair [45, 46] are usually blocked by limited selectivity which inherent their application in complex biological samples. Therefore, the in-situ potentiometric sensors are useful to improve the sensitivity and selectivity through the formation of inclusion complexes with the target analytes. The proposed sensor showed lower DL, 6.5×10^{-7} and QL, 2.1×10^{-6} , pH 2-7.4 and high thermal stability $0.0010 \text{ V/}^\circ\text{C}$ compared with other published sensors (Table 4).

Conclusion

The aim of this work was to construct novel, rapid, highly selective and sensitive carbon and TiO_2 nanotubes modified sensors for MFX micro detection. The unique properties of carbon and TiO_2 nanotubes in terms of large active surface area offered a remarkable enhancement in the response of MFX. The detection limit reached 7.5×10^{-7} and $6.5 \times 10^{-7} \text{ mol L}^{-1}$ for CNTs-CPE and TiO_2 -CPE sensors. The morphological behaviour of the investigated sensors was studied and discussed. The sensors possess high thermal stability with excellent recovery (99.5 %) and RSD (0.2 %), indicating the high accuracy and precision of the sensors and their applicability for routine analysis.

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تحضير وتطبيقات تحليلية لمحسسات جديدة لميكروفينوكسات هيدروكلوريد تعتمد على انابيب الكربون وثنائي اكسيد التيتانيوم النانوميتريّة والبيتا سيكلودكسترين

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الانتشار الواسع للأجهزة التحليلية المحمولة ترجع الى الكفاءة العالية والثبات الكيميائي للمحسسات الجهدية. الهدف الاساسى من هذه الدراسة هو تحضير وقياس محسسات عجيبة الكربون التي تعتمد على انابيب نانوميتريّة من الكربون وثنائي اكسيد التيتانيوم وذلك للقياس الدقيق لعقار الميكروفينوكسات هيدروكلوريد. تم دراسة تأثير المضافات الانيونية وبعض الملدنات. لوحظ أن المحسسات المحضرة تتميز بميل نيرنست ممتاز وحد كشف صغير يصل الى 7.5×10^{-7} و 6.5×10^{-7} مول/لتر وحد كمي يصل الى 2.5×10^{-6} و 2.1×10^{-6} مول/لتر وذلك للمحس الاول و الثاني علي الترتيب. تم دراسة مورفولوجيا السطح للمحسسات محل الدراسة. فحصت انتقائية المحسسات المحضرة تجاه بعض الكاتيونات الهامة بيولوجيا. تم تقدير العقار بنجاح في المنتجات الصيدلانية وعينات حقيقية من المياه والبول.