Research Article

CHEMISTRY

Cyanine-based dyes: highly sensitive sensors for the detection of the hypochlorite levels in drinking water based on fluorometry

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KEY WORDS	ABSTRACT
Fluorometric method, hypochlorite ion sensor, tap water, cyanine sensor, Limit of detection (LOD), Limit of quantification (LOQ).	Drinking water is frequently disinfected with chlorine, and it is necessary to quantify any remaining chlorine in the form of the hypochlorite ion (ClO⁻). Many sensors are in use now, including colorimetric, fluorometric, and electrochemical ones, but detection limitations and simplicity of application continue to be a problem. This study discusses the findings of two novel ClO⁻ sensors based on solvent-free microwave synthesis. The two sensors display rapid fluorescence response for ClO⁻ with excellent selectivity over other analyte species as well as a low detection limit. According to fluorometric performance, the sensors have low detection limits of 1.71 nM and 2.46 nM for sensors I and II, respectively, and they can detect ClO⁻ unaffected by other dangerous water pollutants. For the detection of ClO⁻ in real water samples, the approach produced good recovery results, ranging from 98 to 102.1%. These sensors offer a straightforward and useful approach for tracking ClO⁻ levels in the water, as well as a low-cost and highly sensitive detection method. The sensing mechanism is explained in terms of the radical cations that are produced when the cyanine sensors I and II are exposed to ClO⁻.

Introduction

Hypochlorite ion (ClO$^-$) is widely used as a bleaching agent and disinfectant at concentrations ranging from 10^{-5} to 10^{-2} mol/L (**Huo *et al*., 2012; Li *et al*., 2019; Zhang *et al*., 2022**). However, concentrated hypochlorite solutions represent a risk to both human and animal health (**Zhang, 2010; Zhang *et al*., 2022**). On the other hand, it is one of the biologically significant reactive oxygen species (ROS) and is essential for the immune system (**Gomes *et al*., 2005; Khatib *et al*., 2007; Jia and Ma 2011**). Life depends on endogenous ClO$^-$, which also possesses potent antimicrobial effects. But excessive hypochlorite production can cause diseases and tissue damage, including hepaticischemia-reperfusion injury (**Hasegawa *et al*., 2005**), atherosclerosis (**Daugherty *et al*., 1994**), lung injury (**Hammerschmidt *et al*., 2002**), rheumatoid (**Wu and Pizzo 2001, Koide *et al*., 2011**), cardiovascular disorders (**Hazen 2004**), neuronal degeneration (**Yap *et al*., 2007**), arthritis (**Steinbeck *et al*., 2007**), and cancer (**Podrez *et al*., 2000; Pattison and Davies 2006**). To detect hypochlorite (ClO$^-$), sensitive and focused probes are needed. Additionally, its detection in biological and environmental samples,

such as tap water and natural water, may be relevant to the biochemical study.

The analytical techniques used to identify chlorine species in water systems include spectrophotometry (**Mesquita and Rangel 2005; Mesquita *et al*., 2007**), chemiluminescence (**Tang *et al*., 2014; Hallaj *et al*., 2015**), liquid chromatography (**Abdighahroudi *et al*., 2020**), amperometric titration (**Salazar *et al*., 2016**), potentiometry (**Saboe *et al*., 2021**), fluorescence (**Lu *et al*., 2016; Nguyen *et al*., 2018; He *et al*., 2021**), and colorimetric techniques (**Lou *et al*., 2011; Xiong *et al*., 2017; Li *et al*., 2021**). The most efficient near-infrared fluorophores are cyanine dyes, which have longer emission and absorption wavelengths, greater absorption coefficients, higher fluorescence quantum yields, good biocompatibility, and lower cytotoxicity (**Kar *et al*., 2017; Yin *et al*., 2019; Isaad and El Achari 2022**).

In this study, we have synthesized new type of cyanine dye, derivatives I and II, using a microwave-assisted, solvent-free method and investigated as fluorometric sensors for hypochlorite (HOCl/OCl$^-$), in the presence of phosphate-buffered saline (PBS). The developed sensors were used to determine the concentration of

hypochlorite in real samples with high sensitivity, selectivity, and lower detection limits compared to other methods (**Bu *et al.*, 2022**).

Materials and methods
Materials

The analytical grade chemicals and solvents used in this study were all obtained from Sigma-Aldrich and used without further purification. Aqueous solutions were made using distilled water. The solvent-free, microwave-assisted synthesis of the cyanine dye derivatives (sensor I and II) has been reported in the literature (**Alganzory *et al.*, 2017**). All additional supplies used in this work were of the analytical grade.

Instruments

The fluorescence spectra were measured using JASCO FP-8200 Spectrofluorometer. AD1000 bench pH - meter was used to determine the pH.

Reagent and solutions

Calcium hypochlorite (Ca(OCl)$_2$), ethanol, t-butanol, hydrogen peroxide (H$_2$O$_2$), sodium hydroxide (NaOH), starch, and hydrochloric acid (HCl). Metal salts are BaCl$_2$, CoCl$_2$.6H$_2$O, FeCl$_3$.9H$_2$O, CuCl$_2$.2H$_2$O, NiCl$_2$.6H$_2$O, CdCl$_2$, NH$_4$F, NaCl, ZnCl$_2$, KCl, Pb(NO$_3$)$_2$, CaCl$_2$, KH$_2$PO$_4$, and Na$_2$HPO$_4$. As well as potassium or sodium salts of CO$_3$$^{2-}$, NO$_3$$^-$, NO$_2$$^-$, Cl$^-$, F$^-$, H$_2PO_4$$^-$, SO$_4$$^{2-}$, S$_2O_3$$^{2-}$, I$^-$and ACO$^-$

were purchased from Merck-Aldrich Chemicals.

Procedures
Preparation of cyanine dye sensor (I, II)

According to the literature, substituted cyanine dyes were produced utilizing a microwave-assisted, solvent-free synthesis (**Alganzory *et al.*, 2017**). For sensor I, in the presence of few drops of trimethylamine, 3-Ethyl- 2-methylsulfanyl-benzothiazol-3-ium tetra fluoroborate (2 mmol) and 1-(-4-iodobutyl)-4-methylquinolin-1-ium iodide (2 mmol) were mixed and then this mixture was subjected to microwave irradiation with power 280 W for 6 min. Orange precipitate was changed into yellowish orange precipitate (87%) after cooling and washing with diethyl ether. For sensor II, in dimethylformamide (DMF) and few drops of triethylamine, the mixture from1-(3-Iodopropyl)-4-[(3-methyl-3H-benzothiazol-2-ylidene)methyl]quinolinium iodide (1 mmol) which prepared as literature (**Alganzory *et al.*, 2014**) and 4-(dimethyl amino)pyridin-1-ium (1 mmol) were dissolved . Upon stirring, the mixture was subjected to microwave irradiation (100 W) for 90 min. The reddish orange precipitate was isolated and washed with methylene chloride (CH$_2$Cl$_2$).The precipitate obtain was re-crystalized to give (85%) and dried at 60ºC.

General fluorescence spectra measurements

In order to detect ClO^-, the stock solution of both sensors in ethanol was diluted to the necessary concentration. Deionized water and calcium hypochlorite were used to prepare the ClO^- stock solution. Iodometry was used to confirm the calcium hypochlorite concentration before use. Phosphate-buffered saline was used to change the pH of the mixture from 2 to 12. Fluorescence spectra were collected in phosphate buffer solutions. To evaluate selectivity for ClO^-, stock solutions of sensors I and II (0.1 mM) in ethanol and metal ions ClO^-, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Ca^{2+}, K^+, Ba^{2+}, Cd^{2+}, Co^{2+}, NH_4^+, Na^+, NO_3^-, CO_3^{2-}, Cl^-, CH_3COO^-, H_2PO^{4-}, F^-, NO_2^-, $S_2O_3^{2-}$, SO_4^{2-} (1 mM) were made using deionized water.

Real water samples application

Without any prior treatment, tap water samples were collected from a variety of locations, including the Kafr El Zayat and Tanta water stations in the Gharbia Governorate, as well as distilled water and PepsiCo's Aquafina drinking water. Following exposure to hypochlorite, the investigated cyanine dye's fluorescence spectra were evaluated.
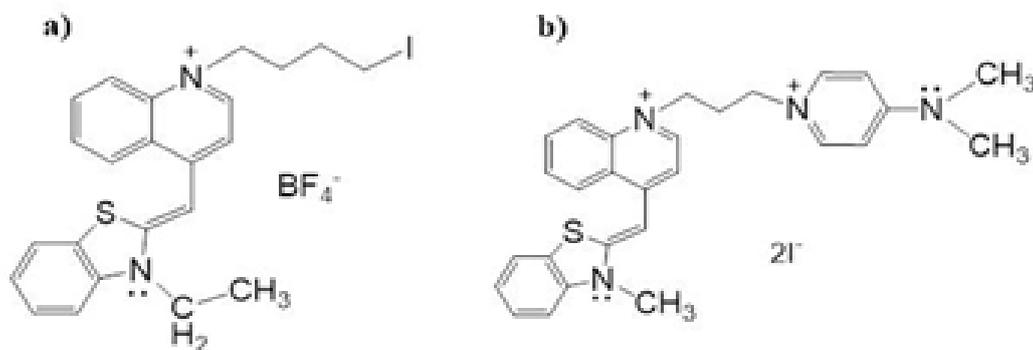
Scheme (1): Chemical structures of the synthesized cyanine sensors I (**a**) and II (**b**).

Results and discussions

Determination of the Effect of Hypochlorite on the Emission Properties of the investigated sensors

The excitation of sensor I (5μM) at λ_{Ex} 480 nm results in emission with a maximum at λ_{Em} 532nm as shown in Fig. (1a), the addition of hypochlorite into spectrofluorimetric. It has been assumed that the oxidation of sensor I by ClO^- species is the main reason for the fluorescence drop. On the other hand, this allows the assumption that the interaction of ClO^- with sensor I may lead to the formation of another product, which is structurally ethanolic phosphate buffer (10mM, pH= 9) of sensor I result in the linear decay of the fluorescence emission, and the reaction is easily monitored by different from the sensor I, and these structural differences may be responsible for the fluorescence drop observed. A linear relationship of fluorescence intensity versus $HOCl/OCl^-$ concentrations was obtained in Fig. (1c). The limit of detection (LOD) for $HOCl/OCl^-$ was estimated to be 1.71 nM based on the 3 σ/k method and the limit of quantification (LOQ) is 5.72 nM, using 10σ/K method for sensor I (**Choi et al., 2017**).

Fig. (1b) illustrates the fluorescence intensity of sensor II (5μM) towards $HOCl/OCl^-$ in EtOH (PBS 10 mM, pH= 7.2) when stimulated at 480nm. As $HOCl/OCl^-$ levels rise, the fluorescence intensiy at 537 nm gradually increased as a result of oxidation. Fluorescence intensity and $HOCl/OCl^-$ concentration were found to be linearly related (Fig. 1d). The detection limit (LOD) for $HOCl/OCl^-$ was calculated to be 2.46 nM and the quantification limit (LOQ) was calculated to be 8.21 nM.

Selectivity over other anions and metal ions

The cyanine derivatives sensor (I, II) showed high selectivity for ClO^- over other analytes, such as Zn^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, K^+, Fe^{3+}, Pb^{2+}, NH_4^+, Cu^{2+}, Na^+, Cl^-, F^-, NO_3^-, NO_2^-, CH_3COO^-, SO_4^{2-}, $H_2PO_4^-$, t-butanol and H_2O_2. As shown in Fig. (2), the fluorescence spectra of both sensors significantly changed with the addition of ClO^-. In contrast, the changes in the alternative analytes were minimal, indicating that cyanine sensors had good selectivity towards ClO^- under the same test conditions. The detection efficiency of the present sensors was compared with previously reported probes used for the detection of $HOCl/OCl^-$ as in Table (1). The detection limit is lower than the permissive level (4ppm) in drinking water set by WHO (**Reddy, 2023**),

indicating sensor could be an effective tool to quantitatively detect HOCl/OCl⁻ in aqueous media.
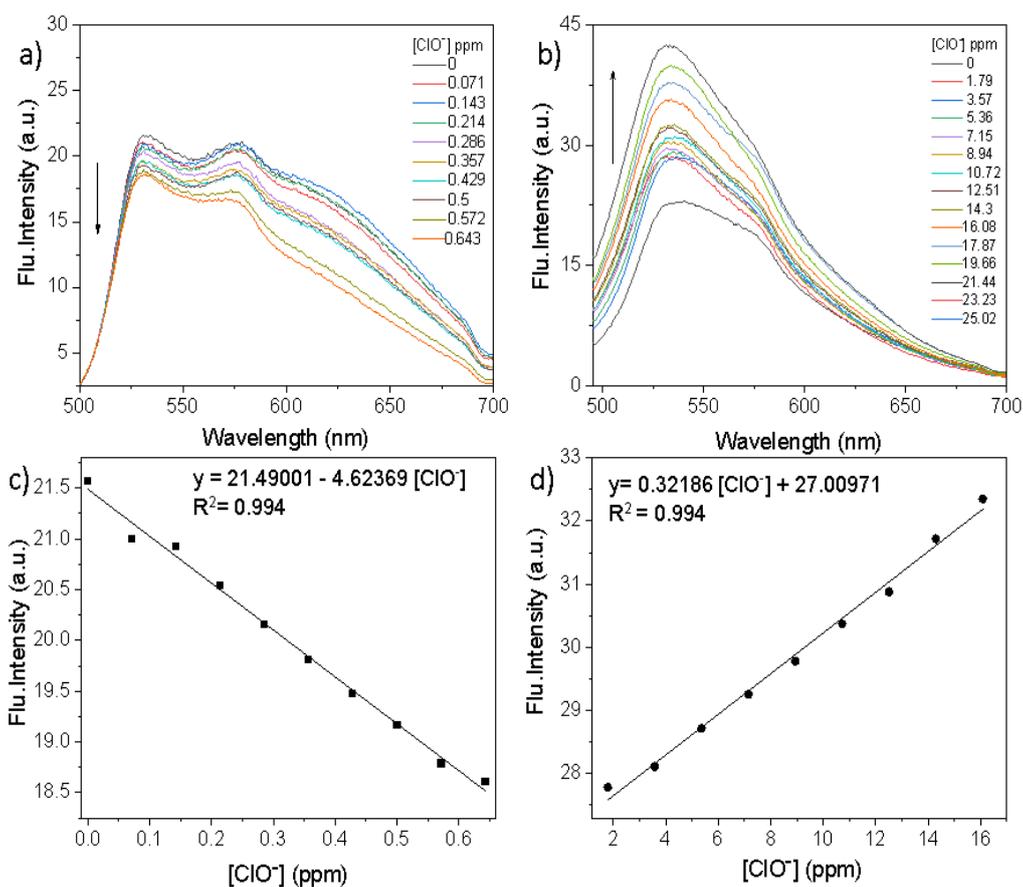
Fig. (1): Fluorescence spectra of a) sensor I (5μM) in the presence of different ClO⁻ concentrations (0- 0.64 ppm) in EtOH (PBS 10mM, pH = 9) solutions at room temperature, λ_{ex}= 480 nm, and b) sensor II (5μM) in the presence of different ClO⁻ concentrations (0- 16 ppm) in EtOH (PBS 10mM, pH = 7.2) solutions at room temperature, λ_{ex}= 480 nm. c) The linear relationship between the fluorescence of the sensor I Vs. ClO⁻ concentration, λ_{em} =532nm, and d) The linear relationship between the fluorescence of the sensor II Vs. ClO⁻ concentration, λ_{em} =537 nm.
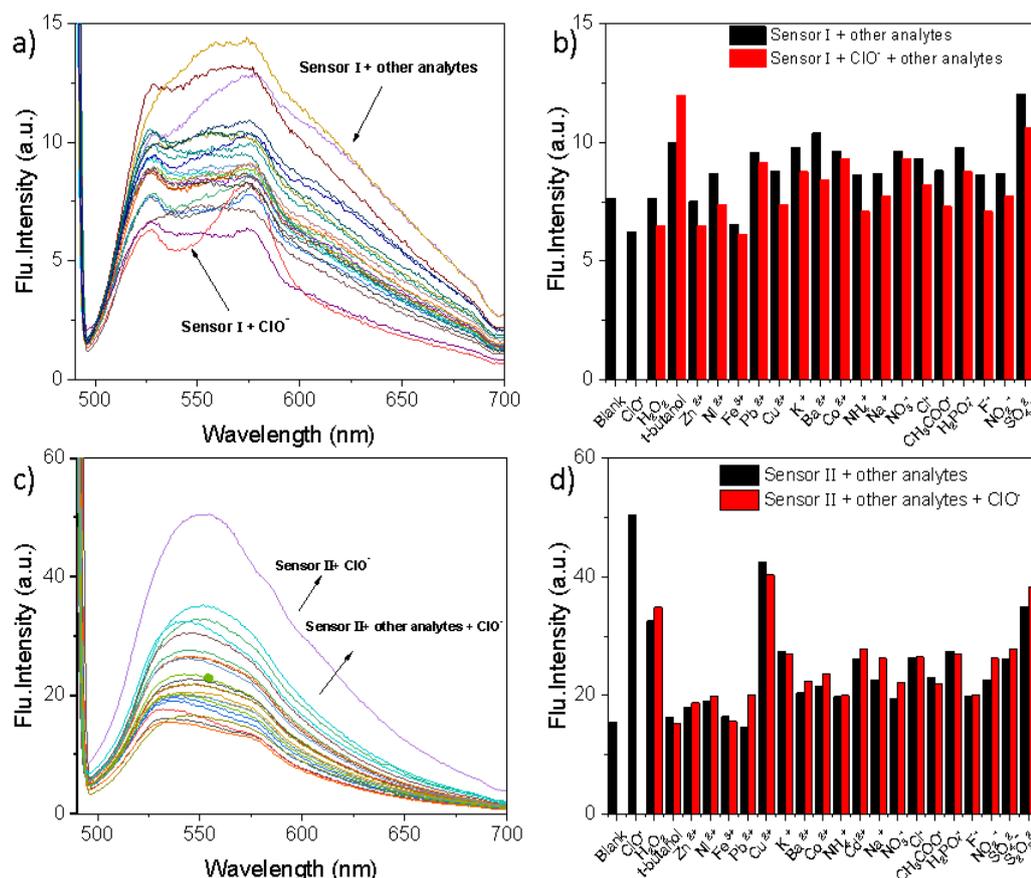
Fig. (2): **a)** The fluorescence spectra and **b)** fluorescence intensity of sensor I (5 µM) at 532 nm in the presence of various analytes (7 ppm): blank, ClO^-, H_2O_2, t-butanol, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Ca^{2+}, K^+, Ba^{2+}, Cd^{2+}, Co^{2+}, NH_4^+, Na^+, NO_3^-, CO_3^{2-}, Cl^-, CH_3COO^-, $H_2PO_4^-$, F^-, NO_2^-, $S_2O_3^{2-}$, SO_4^{2-}; **c)** The Fluorescence spectra and **d)** fluorescence intensity of sensor II, (5 µM) at 537 nm in the presence of above analytes (20 ppm) in dist.H_2O, λ_{ex} = 480 nm.

Table (1): Comparison of the limit of detection (LOD) for the detection of ClO^- /HClO with different analytical methods

Method	Sensing method	LOD (µM)	Linear range (µM)	Ref
DPD reagent (APHA and AWA, 2017)	Colorimetric	5.0	0.01–5	**(Moberg and Karlberg 2000)**
NH2-MIL-53(Al) MOF	Fluorometric	0.04	0.05–15	**(Lu *et al.,* 2016)**
CD-RhB/Fe3O4 @ZIF-8	Fluorometric	6.7	15–180	**(Ma *et al.,* 2018)**
Green-emitting carbon dots (G-CDs)	Colorimetric	1.82	10–150	**(Bu *et al.,* 2022)**
Microbial potentiometric sensor	potentiometric	2.7	0– 2.7	**(Saboe *et al.,* 2021)**
Commercial platinum Electrodes	Amperometry	10.0	0.1–10	**(Wilson *et al.,* 2019)**
Coumarin-salicylic hydrazide Schiff base (CMSH)	Fluorometric	0.128	0–80	**(He *et al.,* 2020)**
Cyanine sensor I	Fluorometric	1.71 nM	0– 4.5 ppm	The Current work
Cyanine sensor II	Fluorometric	2.46 nM	0–12.5 ppm	The Current work

Time-dependent response of cyanine sensors

With a time-dependent kinetic investigation, the fluorescence intensity of sensors I and II is examined toward hypochlorite. The cyanine sensors I and II in Fig. 3 (a and b) showed a gradual decrease in fluorescence intensity at 532 nm and 537 nm, respectively, reaching a plateau within 25 min and nearly remaining constant within 30 min, indicating that they were "fast response" fluorescent sensors for real-time monitoring of hypochlorite levels.

pH effect on the investigated cyanine sensors

The performance of the examined cyanine sensors was significantly influenced by the pH level. The influence on both sensors' fluorescence behavior at various PBS pH was examined to ascertain whether both sensors responded to ClO^- under physiological conditions. At 532 and 537 nm, respectively, both sensors showed noticeable changes in fluorescence performance before and after the addition of ClO^- in various PBS pH mediums. However, sensors I and II had high ClO^- sensitivity at pH = 7 (Fig. 4), indicating that the sensors could be used in physiological conditions. The aforementioned findings looked into the possibility of using both sensors under physiological circumstances. As a result, under physiological conditions, ClO^- might be detected by current sensors for practical detection applications. The results above investigated that both sensors could be used in physiological conditions. As a result, the current sensors can detect $HOCl/ClO^-$ under physiological conditions for practical detection purposes.

Concentration effect of the investigated cyanine sensors

It was investigated how cyanine concentrations affected the intensity of the fluorescence. The emission intensity increased in range (0.1-0.9μM) for sensor I, while for sensor II, the emission intensity increased in range (0.9– 9 μM). According to Fig. (5), sensors I and II fluoresced more intensely with increasing cyanine sensor concentrations at 532 nm and 537 nm, respectively. Based on fluorescence performance, 0.9μM and 9μM for sensors I and II, respectively, were the optimal concentrations that might be employed for the detection of ClO^- due to their high emission intensities. All of the results showed that ClO^- could be detected using cyanine sensors at low concentrations.
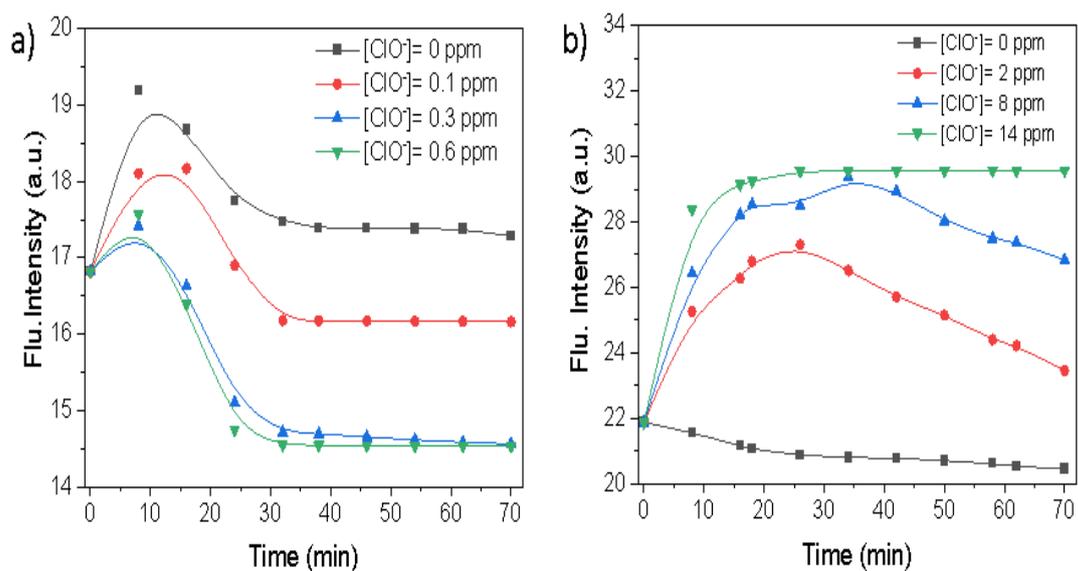
Fig. (3): Time-dependent emission intensity changes in the absence and presence of different ClO⁻ concentrations of **a)** sensor I (5 μM) EtOH (PBS 10 mM, pH = 9) at 532 nm; **b)** sensor II, (5μM) in EtOH (PBS 10 mM, pH = 7.4) at 537nm.
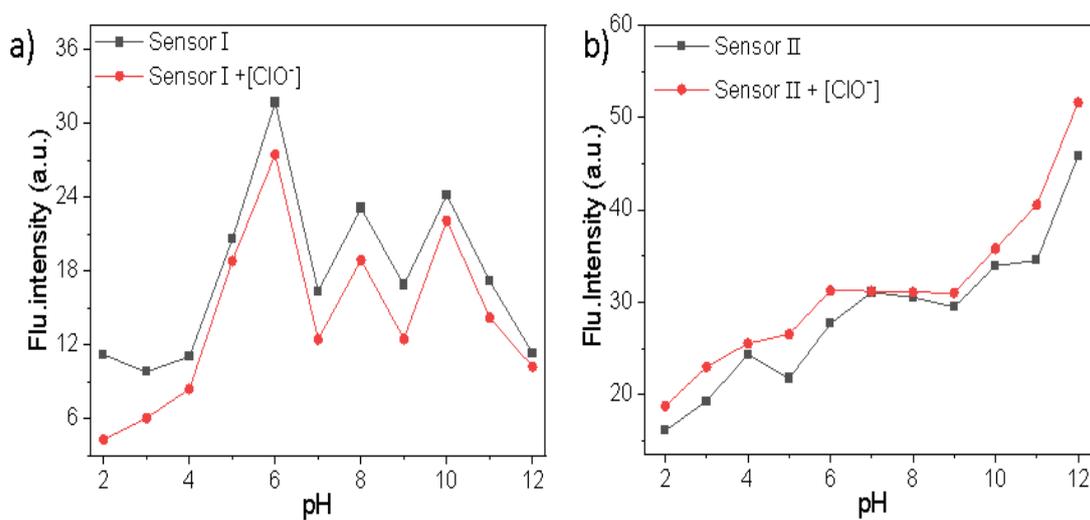
Fig. (4): pH-dependent changes of on the Fluorescence intensities of **a)** sensor I (5 μM) in the absence and presence of ClO⁻ (0.55 ppm) at 532 nm; **b)** sensor II (5μM) in the absence and presence of ClO⁻ (9 ppm) 537 nm.
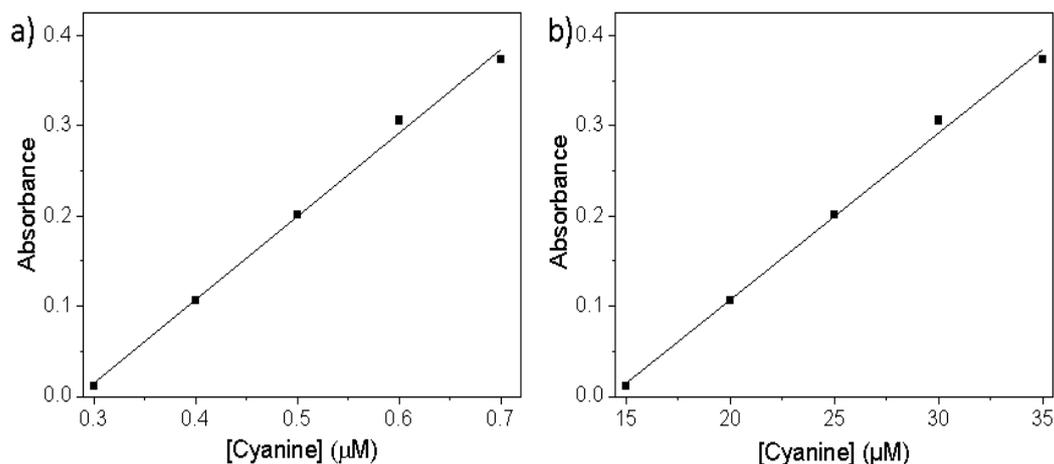
Fig. (5): Linear relationship between the fluorescence of **a)** sensor I with ClO⁻ (0.3 ppm) at 532 nm; **b)** sensor II with ClO⁻ (10 ppm) at 537 nm Vs cyanine sensor concentrations in EtOH (PBS 10 mM, pH = 7.4), λ_{ex} = 480 nm.

Table (2): Validation for sensors (I, II) using fluorometry

Real sample	ClO⁻ spiked (ppm)	ClO⁻ recovered (ppm)[a]	Recovery (%)	R.S.D (%) n=3
**Validation for the sensor I**			
1	0.143	0.145 ± 0.004	102.1	0.17
	0.286	0.279 ± 0.038	98	1.25
2	0.143	0.141 ± 0.045	99	2.6
	0.286	0.29 ± 0.046	101.4	1.48
3	0.143	0.142 ± 0.002	99.3	0.17
	0.286	0.287 ± 0.009	100.3	0.37
4	0.143	0.145 ± 0.033	101.4	2.87
	0.286	0.287 ± 0.009	100.3	0.405
**Validation for sensor II**			
1	6.15	6.16 ± 0.4410	100.2	0.631
	7.58	7.57 ± 0.322	100	0.403
2	6.15	6.17 ± 0.1200	100.3	0.11
	7.58	7.57 ± 0.369	100	0.31
3	6.15	6.1 ± 0.0360	99.3	0.0192
	7.58	7.7 ± 0.2650	102	0.132
4	6.15	6.11 ± 0.1830	99.3	0.091
	7.58	7.57 ± 0.1610	100	0.077

[a]Mean ± standard deviation (n = 3),

1: Tap water from Water Station Kafr El Zayat- Gharbia Governorate, Egypt;

2: Water Station Tanta- Gharbia Governorate, Egypt 3: Distilled water and 4: Aquafina drinking water- PepsiCo

Practical application of sensor in the water sample

Tap water samples were measured directly without special treatment. A certain amount of ClO⁻ was added to the ethanolic solution of both sensors and then newly collected water samples were added to this solution. After mixing evenly, the spectral properties of the solution were studied at room temperature. The recovery rate of ClO⁻ was determined by the emission for sensors (I, II) with the standard addition method. The average recovery rate of ClO⁻ in the real water samples is about 97.4~103% and excellent analytical precision (<4%) in detecting ClO⁻ spiked water samples, indicating that our sensors are effective for ClO⁻ in the real water samples as shown in Table (2).

Conclusion

This study produced novel fluorescence sensors with fluorescent responses to hypochlorite ions. The sensors demonstrated efficient detection of the hypochlorite ion in an aqueous solution, including high specificity, low LOD, and quick response times. The sensors might also be used to identify the presence of hypochlorite ions in a variety of tap water and drinking water samples.

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أصباغ السيانين: مستشعرات عالية الحساسية للكشف عن تركيزات الهيبوكلوريت في مياه الشرب بالاعتماد على القياس الفلوريسيني.

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كثيرًا ما يتم تطهير مياه الشرب بالكلور ، ومن الضروري تحديد كمية الكلور المتبقي على شكل أيون هيبوكلوريت (ClO^-) . كما يلزم أحيانا تقدير أيون الهيبوكلوريت بتركيزات عالية الانخفاض تحت الظروف الفسيولوجية.

حالياً يتم استخدام العديد من المستشعرات ، بما في ذلك المستشعرات اللونية والفلورومترية والكهروكيميائية ، لكن قيود الكشف وبساطة التطبيق لا تزال تمثل مشكلة. حيث تناقش هذه الدراسة نتائج اثنين من المستشعرات الجديده (I ، II) للهيبوكلوريت والتي تعتمد في تحضيرها على تقنية الميكروويف الخالية من المذيبات.

يعرض المستشعران (I ، II) استجابة فلوروسينيه سريعة لهيبوكلوريت مع انتقائية ممتازة مقارنة بالأنواع التحليلية الأخرى بالإضافة إلى حد اكتشاف منخفض.

اعتمادا علي القياس الفلورومتري ، تتمتع المستشعرات بحدود اكتشاف منخفضة تبلغ ١.٧١ نانومولر ، ٢.٤٦ نانومولر للمستشعرين (I، II) ، على التوالي ، ويمكنهما الكشف الانتقائى عن الهيبوكلوريت في وجود ملوثات المياه الخطرة الأخرى. وقد تم اختبار استخدام المستشعرين لاكتشاف الهيبوكلوريت في عينات المياه الحقيقية ، وكانت نتائج هذه الدراسة استرداد جيد للهيبوكلوريت ، تتراوح من ٩٨ إلى ١٠٢.١٪ لتوفر هذه المستشعرات دراسة مباشرة ومفيده لتتبع مستويات الهيبوكلوريت في الماء ، بالإضافة إلى طريقة اكتشاف ذات تكلفة منخفضة وحساسة للغاية. وقد تم تفسير آلية الأستشعار من خلال أكسدة مستشعرات السيانين (I ، II) عندما تتعرض للهيبوكلوريت.