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Highly Selective Perchlorate Coated-Wire Electrode (CWE) based on an Electrosynthesized Dixanthylinum Dye and Its Application in Water Samples

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ABSTRACT

The fabrication, performance, and utilization of perchlorate coated-wire electrode (perchlorate-CWE) based on dixanthylinum dye concerning the response towards perchlorate ions was defined. The recommended electrode exhibits a Nernstian response for perchlorate by a wide concentrations range of 1.0×10^{-6} to 6.1×10^{-2} M, with a slope of -57.4 mV in comparison to other anions. The limit of detection is 5.0×10^{-7} M. It has a quick response time of ~4 seconds. The recommended electrode shows adequately good discriminating ability towards perchlorate ions in comparison to other anions and it is profitably applied to the direct determination of perchlorate ions in water samples.

1. Introduction

Different factors including chemical and physical nature, present challenges for the analysis and the remediation cause an upswing interest in a perchlorate ion. A perchlorate ion is considered a substitute for rising persistent inorganic contamination attributable to its distinct properties, like high water solubility, quality and, wide stability. The perchlorate and the iodide ion have a similar size; hence, can incorporate instead of it by the mammalian thyroid gland. Hence, perchlorate can influence the secretion of thyroid hormones. Additionally, other physiologic systems may be indirectly affected. The effects of this ion cause developmental abnormalities in kids and who have thyroid cancer. It poses the greatest risk to the drinking water of pregnant women, kids under 12 years, and people with dysfunctioning thyroids [1, 2].

A perchlorate ion has used in fattening cows as a growth stimulant and as a thyrostatic drug. [3]. A thyroid gland tumor was viewed in rodent animals once exposed to a high dose of perchlorate [4]. The toxicological mechanisms action of perchlorate and its effects are expressed in some reports [5-7]. One of the main origins of this environmental pollution is the production, inaccurate storage, or removal of ammonium perchlorate used as a primary component of a solid catalyst for explosive fireworks [8-11]. Perchlorate has also been found in processed food [12,13], soil [14], milk [15], fertilizers [8], plants, [16] and human urine [17]. according to the results, several institutions have been determined standard levels for perchlorate. The National Academy of Sciences (NAS's), In January 2005, a maximum permissible dose of 0.7 µg / kg / day was reported for perchlorate concentrations, associated with a drinking water level of 24.5 µg / L if drinking water was considered the sole source of perchlorate. [18]. Also in February 2005, the US Environmental Protection Agency (US EPA) set an official reference dose (RFD) of 24.5 micrograms per liter for drinking water perchlorate, which remained unchanged with the RFD recommended by NAS. [19]. Therefore, it is of great importance to determine perchlorate ions in various samples like subsurface water, propellants, explosives, and urine along with the presence of other anions. Directly or indirectly determination of perchlorate ions has been accomplished by classical and physical methods, involving Electrochemiluminescence [20],

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Capacitance Voltage [21], gravimeters [22], spectrophotometry [23], atomic absorption spectrophotometry [24], and chromatography [25]. Most of the applied methods are time-consuming and require skilled users. In addition, most of the existing anions and cations are interfering with the determination of perchlorate ions by these methods. Accordingly, it is crucial to develop approaches that directly determine perchlorate and eliminate the effect of interfering ions. Some attempts have been made to achieve an extremely selectable anion measurement.

Carrying out potentiometers measurements with an ion-selective electrode (ISE) is a very practical technique for routine monitoring. ISEs supported by potentiometric detection, as an easy method, have several benefits including speed, easy preparation and need, simple instrumentation, fast response, pollution-free, non-destructive, no color or turbidity effect, dynamic range extensive and selective enough [26,27]. Relying on the attribute of the ionophore, ISE is an analytical technique used to determine both positively and negatively charged ions. As a matter of fact, a variety of uses of ISEs for determining of purposed cations and anions are publicized [28]. These methods also become infected with various interferences.

As a result, it requires a sensitive, fast, simple, and selective approach to the determination of perchlorate ions. Traditional ion exchangers with ISE support always display a selective Hofmeister sequence, as follows: perchlorate< thiocyanate< iodide ≈ salicylate< nitrate< bromide< nitrite< chloride< sulfate, in which the selectivity of the membrane is limited by the free energy of hydration of the ions involved. Further studies are on electrodes that use poly (vinyl chloride) (PVC) plastic membranes that combine different complexes as carriers [29,30]. Perchlorate sensors based on CWE has developed over a period of 40 years and has a comprehensive history [31]. Various perchlorate-CWE based on ion pair complexes with perchlorate anions and organic compounds such as long chain type IV ammonium cations, organic bases, organic dyes and metal chelates have been reported [30, 32-43].

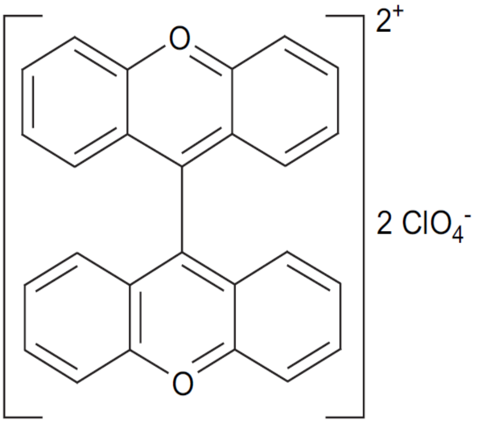
Most of the studies for perchlorate ions are involved membranes that contain an ISE. An electro-active species consists of perchlorate ions or conductive polymers or organic colors [43-46]. The concentration of Perchlorate anion is high (above 1000 mg/l) in surface and groundwater worldwide. These pollutants are usually caused by percolate salts that are present within the waterway or due to their adjacency to industrial stations and factories [47].

The aim of the present study is to develop and fabricate a perchlorate-CWE that be used for direct determination of perchlorate ions in water samples without pre-separation steps. In the present study, we characterize the manufacturing and evaluation of a plasticized PVC membrane perchlorate-CWE based on the new ionophore “dixanthylinum dye” that has been electro synthesized from the previous work [48]. Not merely the method is uncomplicated and affordable, but also the electrode has the profit of being highly selective for perchlorate ions in the existence of various anions species, such as SCN^-, NO_3^-, ClO_3^-, Cl^-, Br^-, IO_4^- and oxalate that usually cause serious disturbance in the determination of perchlorate by the ion-selective electrodes.

2. Experimental

2.1. Reagents

Low molecular weight polyvinyl chloride (PVC) powder was prepared from Aldrich as well as 2-nitrophenyl octyl ether (o-NPOE) and tetrahydrofuran (THF). Sodium or potassium salts were prepared from Merck Company with the highest purity and without any other treatment. HCl or NaOH solution was use to decrease or increase the pH of the solution, respectively. The other chemical compounds used had a degree of analytical purity. Doubly distilled deionized water was applied in the tests. A 0.1 M stock solution was prepared with appropriate amount of $NaClO_4$. The standard solutions of perchlorate prepared freshly by consecutive dilution of the suitable stock solution with doubly distilled-deionized water. The synthesis and characterization of ionophore “dixanthylinum dye” is described somewhere else [48]. The structure of the ionophore that was used for perchlorate-CWE is illustrated in Scheme 1.



Scheme 1. The structure of the dixanthylinum dye as an ionophore for the proposed perchlorate-CWE

2.2. Fabrication of perchlorate-CWE

The general instruction to make a wire coated electrode was as follows: Ionophores (dixanthylinum dye) in different amounts coupled with appropriate amounts of PVC and plasticizer (o-NPOE) to give a total mass of 100 mg were dissolved in 2 ml of dry tetrahydrofuran (THF), and the solution was stirred appropriately. The component of the mixture is shown in Table 1.

Table 1. Optimization of the membrane ingredients for perchlorate-CWE

Number	Composition (%)w/w			Slope (mV per decade)	Linear range (M)	R^2
	Plasticizer (NPOE)	PVC	Ionophore			
1	66.66	33.33	0	-12.4	$1.3\times10^{-3} – 1.2\times10^{-5}$	0.8652
2	66.00	30.50	0.5	-33.6	$7.9\times10^{-3} – 1.1\times10^{-5}$	0.9976
3	66.00	33.00	1	-57.4	$6.1\times10^{-2} – 1.6\times10^{-6}$	0.9996
4	65.33	32.66	2	-32.2	$2.4\times10^{-3} – 1.6\times10^{-5}$	0.9994
5	64.66	32.33	3	-44.2	$2.6\times10^{-3} – 1.7\times10^{-5}$	0.9992
6	61.33	30.66	8	-44.7	$2.4\times10^{-3} – 1.5\times10^{-5}$	0.9997

The optimum composition was 30.0% of powdered PVC, 66.0% of a plasticizer (o-NPOE), and 1.0% of the corresponding ionophore. The sample solution is poured into a glass tube. (5 mm i.d. and 20 mm long). The mixed solvent was slowly evaporated until a thick oily composition was obtained. A platinum wire with dimensions of 150 mm in length and 0.5 mm in diameter with a spherical head with a diameter of 1 mm was washed with acetone solvent to remove organic contaminants and finally washed with distilled water. The result of immersing (10 seconds) of platinum wire in the sample mixture is the formation of an opaque membrane with a thickness of about 0.5 mm and then kept at room temperature for about 6 hours. To be conditioned, the perchlorate-CWE was immersing in perchlorate solution with a concentration of 1.0×10^{-2} M.

2.3. EMF measurement

The electromotive force (emf) values were measured on the Following cell assembly:

Pt (wire)-PVC membrane | sample solution || Ag-AgCl (double junction)

To measure the potential of the sensor made at different concentrations of perchlorate, a Corning ion analyzer of 250 pH / mV been used at room temperature. The emf measurement was performed relative a silver/silver chloride electrode with double junction and the sample solutions stirred continuously during the measurements.

Perchlorate solution in a concentration range of 1.0×10^{-2} to 1.0×10^{-7} M was traditionally used to accurately evaluate sensor performance. The potential reading of each solution was documented when it became constant, and then plotted as a logarithmic function concentration of perchlorate anion. Activities were calculated as stated in the Debye–Hückel procedure.

3. Results and Discussion

3.1. Optimization of the perchlorate-CWE ingredients

Perchlorate-CWE is ionophore-based membranes electrode that produce a potential (response) when they are immersed in a solution containing a perchlorate ion. The dixanthylinum ion as an ionophore, was employed as a sensing species. It is obvious that the selectivity and sensitivity of perchlorate-CWE are extremely related to the membrane constituent. Membrane ingredients affect the potential responses of the perchlorate-CWE. Experimental tests evidenced that the perchlorate-CWE incorporating the ionophore (dixanthylinum dye) produces constant potential responses in solutions containing perchlorate ions. Concentration ranges of 1.0×10^{-6} to 1.0×10^{-2} from different anions used to measure the potential of the sensor, which sufficiently indicates the sensor's poor response to these ions.

The impact of the membrane composition on the potential response of perchlorate-CWE based on dixanthylinum dye was investigated and the findings are summarized in Table 1.

As it is readily apparent in Table 1, the missing of the ionophore in the membrane composition results in a very poor response (no. 1), which exhibits the significant rule of the dixanthylinum dye. *o*-NPOE as a highly lipophilic plasticizer with a high dielectric constant (23.9) mainly performs as a fluidizer that permits homogeneous diffusion and dissolution mobility of the ionophore inside the perchlorate-CWE. The amount of the plasticizer must be suitably controlled aiming to minimize the electrical asymmetry of the membrane and to restrict fouling of the perchlorate-CWE. From perchlorate-CWE numbers 2–6, it was discovered that the potentiometric response of the perchlorate-CWE toward perchlorate ion related to the concentration of the ionophore incorporated within the composition of the perchlorate-CWE. The sensitivity of the perchlorate-CWE response increases along with increasing ionophore content up to a value of 1%. This is obviously due to the decreased number of active sites, at <1% dixanthylinum; further increasing the amount of ionophore approximately unchanged the perchlorate-CWE response, assumably due to possible saturation or inhomogeneity of the perchlorate-CWE. As it is shown in Table 1, the finest slope and linear dynamic range were attained, when the weight ratio of plasticizer/PVC was doubled (electrode number 3). Thus, the composition of 33% PVC, 1% ionophore and, 66% *o*-NPOE was the optimum values for the sensor design. A perchlorate solution with a concentration of 1.0×10^{-2} M was used to electrode conditioned for 1h, after that, it would produce a stable potential when exposed to perchlorate solution. The effect of the electrode type (Pt, Au, and GC) on the response and sensitivity of perchlorate-CWE was studied. Furthermore, as apparent in Table 2, platinum as electrodes type for perchlorate-CWE resulted in adequate potential responses and subsequently, platinum was adopted as the sensor substrate.

Table 2. Effect of the electrode type on the potential response of perchlorate-CWE

Electrode type	Correlation coefficient	Slope(mV /decade)	Linear range
Platinum	0.9936	-57.4	$6.1\times10^{-2} - 1.6\times10^{-6}$
Gold	0.9936	-46.8	$2.5\times10^{-3} - 7.9\times10^{-6}$
Glassy carbon	0.9917	-44.1	$2.5\times10^{-3} - 1.2\times10^{-5}$

3.2. Calibration graph

The emf response of the perchlorate-CWE (Figure 1) denotes their Nernstian behavior over a wide range of concentrations of perchlorate. The measuring range of a perchlorate-CWE is the linear part of the calibration graph as illustrated in Figure 2. The calibration graph slope of this perchlorate-CWE was -57.84 mV/decade of the perchlorate concentration and a standard deviation of ±1.2 mV after 10 replicate measurements. A linear response regarding the perchlorate concentration was from 1.0×10^{-6} - 6.1×10^{-2} M. DL (detection limit) was assessed according to IUPAC recommendations by the intersection of the extrapolated linear segments of the calibration graph. In this work, the DL of perchlorate-CWE was 5.0×10^{-7} M.

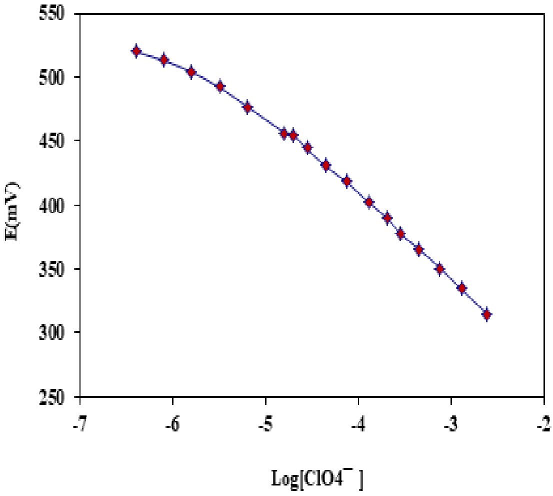


Figure 1. Calibrations curve of the perchlorate-CWE with the composition of the membrane no. 3.

3.3. Dynamic response time

Dynamic response time is a remarkable element for a perchlorate-CWE was described as the elapsed time between the second at which the perchlorate-CWE and a reference electrode are brought into contact with a sample solution and the first second at which the potential of the cell has increased to 90% of the final value. In this study, the practical response time was recorded by varying the concentration of perchlorate in different solutions. The order of measurement was from the lower (1.6×10^{-6} M) to the higher (2.4×10^{-3} M) perchlorate concentration. The actual potential against time for the perchlorate-CWE is displayed in Figure 2(a) and to assess the reversibility of the perchlorate-CWE, an identical procedure conversely was adopted; The resulting potential against time for the perchlorate-CWE obtained across changing the perchlorate concentration from 1.6×10^{-5} to 7.5×10^{-5} M are shown in Figure 2(b).

It was detected that the perchlorate-CWE reaches the steady-state potential in a short time of about 4 s. This is most probably as a result of the quick exchange kinetics of association-dissociation of perchlorate ions with the ionophore.

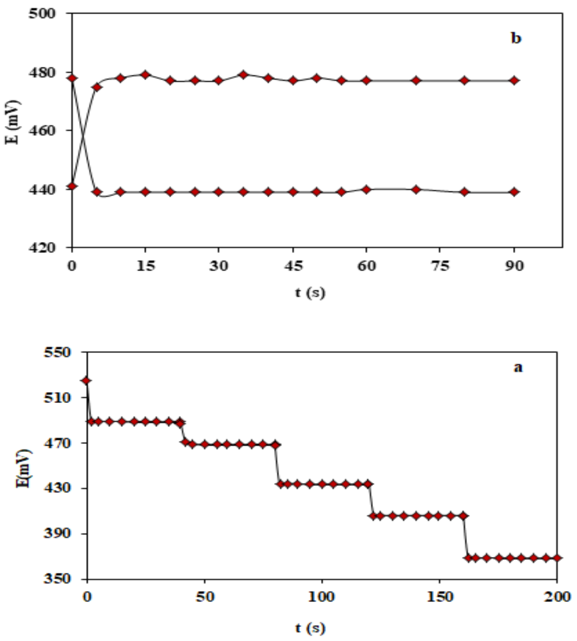


Figure 2. (a) Dynamic response time of ISE for step changes in the concentration of perchlorate in the range of $1.6\times10{-6}$, 6.4×10^{-6}, 2.8×10^{-5}, 1.8×10^{-4}, 4.4×10^{-4} and 2.4×10^{-3} M (in the sequence of left to right in figure (a)). (b) Static response time for the ISE

3.4. Effect of pH

The pH of the sample solution is a key element, generally affecting the response of the perchlorate-CWE considering its effect on the activity of the active analyte especially in the existence of the hydrolysis reaction. In this work, hydrolysis is the insignificant cause of the low affinity of perchlorate to hydrolysis, but pH can influence the stability of the electrode. To investigate the effect of pH on perchlorate-CWE responses, the potential was recorded at a particular concentration of the perchlorate solution (1.0×10^{-4} M) from the pH value of 1.5 up to 11.0 (concentrated HCl or NaOH solutions were used for the pH adoption), and results were shown in Figure 3. As it is apparent from Figure 3, the potential remained constant regardless the pH shifts in the range of 3.0 to 8.5, which can be settled as the working pH range of the perchlorate-CWE and out of this domain, the potential displays sharp alteration. The alteration of the potential at pH < 3.0 could be associated with protonation or removal of the ionophore in the membrane phase of perchlorate-CWE, which causes in lack of its capability to interact with perchlorate ions. At pH>8.0 the potential fall may be correlated with the interference of hydroxide ions.

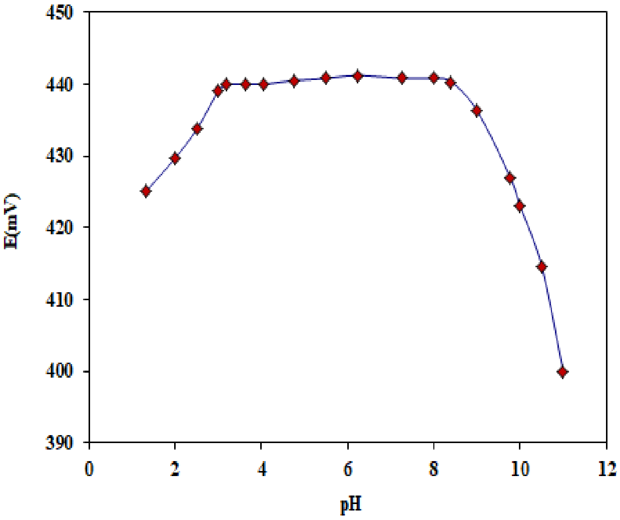


Figure 3. Influence of pH on the potential response of the perchlorate-CWE to 7.5 ×10-5 M of perchlorate ion.

3.5. Stability and Lifetime.

The stability and lifetime of the perchlorate-CWE were also examined. The long-time stability of the perchlorate-CWE was investigated by measuring the response of the perchlorate-CWE throughout a period of 18 h. The perchlorate-CWE reserved its full activity during this period of time. Lifetime studies were based on monitoring the change in perchlorate-CWE slope and linear response range with time. The perchlorate-CWE prepared could be employed for at least 70 days free from significant change in potential of the perchlorate-CWE (Table 3).

Table 3. Lifetime study of perchlorate-CWE

Day	Slope (mV per decade)	Linear range (M)	R^2
10	-57.2	5.3×10^{-2} – 3.6×10^{-6}	0.9986
20	-58.5	6.2×10^{-2} – 4.0×10^{-6}	0.9989
40	-57.4	5.5×10^{-2} – 3.9×10^{-6}	0.9985
70	-57.7	6.9×10^{-2} – 4.6×10^{-6}	0.9903

3.6. Selectivity

The selectivity is apparently one of the most important characteristics of a perchlorate-CWE that indicates the superiority of a perchlorate-CWE to respond to the target ion along with the interference ions, which are present in the measuring solution. The experimental selectivity coefficients depend on the activity and the method of their determination. Several procedures have been reported in the literature for selectivity determination. Ion-exchanger-based membranes electrodes are exhibit the Hofmeister selectivity sequence based on the anions lipophilicity; and show the same selectivity pattern that follows the solvation energies of the ions, but ionophore-based membranes electrode may show very different selectivity's. This is achieved by the formation of strong complexes between the extracted anion and the ionophore in the membrane electrodes that exhibit non-Hofmeister selectivity patterns, i.e., selectivity's that are not based solely on the anion lipophilicity. Complex formation constants have been determined in the membrane phase in the range of ~10^8 for monovalent to ~10^{25} for divalent ions. With ionophore-based membranes electrode, the selectivity is now dictated by the free energy of transfer of the ions from the aqueous to the membrane phase, the complex formation constants between the extracted ions and the ionophore, and the concentrations of the active membrane components in the membrane. selectivity coefficients For this study were calculated with Matched Potential Method (MPM) and the Mixed Solution Method (MSM). Based on the IUPAC suggestions [49, 50], in the MPM, the potentiometric coefficients $K^{pot}_{ClO_4^-,X}$ values were evaluated graphically from potential measurements of a solution containing a fixed concentration of perchlorate ion (1×10^{-4} M) and varying amounts of different interfering ions based on the equation (1).

$$K^{pot}_{ClO_4^{-1},X} \times a_X^{1/n} = a_{ClO_4^{-1}}\left\{\exp\left[\left(E_2 - E_1\right)\frac{F}{RT}\right]\right\} - a'_{ClO_4^{-1}} \qquad (1)$$

E$_1$ and E$_2$ are the electrode potentials for the solution just containing perchlorate and for the solution containing interfering ions and perchlorate ions, respectively. According to Eq. (1), the $K^{pot}_{ClO_4^-,X}$ values for ions can be evaluated from the slope of the graph of $\left\{a_{ClO_4^{-1}}\left\{\exp\left[\left(E_2 - E_1\right)\frac{F}{RT}\right]\right\} - a'_{ClO_4^{-1}}\right\}$ versus $a_X^{1/n}$. According to the MPM method, the potentiometric selectivity coefficient is described as the activity ratio of target and interfering ions that give the same potential change under the same conditions. At first, a known activity ($a_{ClO_4^{-1}}$) of the target ion solution is added into the reference solution that contained a fixed activity ($a'_{ClO_4^{-1}}$) of target ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of interfering ion (X) is added to the reference solution until the same potential change (ΔE) is recorded. based on this method, equation (2) defined the selectivity coefficient ($K_{ClO4^-, X}$).

$$K^{pot}_{ClO_4^{-1},M} = \frac{\left(a'_{ClO_4^{-1}} - a_{ClO_4^{-1}}\right)}{a_M} \qquad (2)$$

It is important to note that in this method, a very low concentration of the perchlorate (target ion) (2.0×10^{-5} M) was used as a primary solution

($a'_{ClO_4^{-1}}$). The value of $K_{ClO4^-, X}$ for several common anions was measured. The emf values obtained are plotted against the logarithm of the activity of the interfering ion (Figure 4). The intersection of the extrapolated linear fragments of this plot indicates the value of the interfering ion that is to be applied to evaluated selectivity.

The finding values of the selectivity coefficients are displayed in Table 4. Interferences were negligible in the performance of the electrode preparation. The selectivity coefficients were reported for the perchlorate-CWE in the presence of many common lipophilic anions such as SCN^-, I^-, ClO_3^-, NO_3^-. These anions are usually investigated by other perchlorate ISEs and in this research; they were also considered and investigated. These anions usually present in water samples. The characteristics of the studied perchlorate-CWE were much better than those reported for other sensors. Of special interest was the selectivity attained for chlorate, which provided a determination of perchlorate in the presence of a much higher chlorate concentration.

Some response properties of the proposed electrode in comparison with other perchlorate-CWE and the obtained results are recited in Table 5. The high degree of selectivity with respect to most other anions was attained. As can be observed, the selectivity coefficients of the present perchlorate-CWE for a variety of common anions, including those found in water samples, were superior to those reported for the other electrodes exclude that of references of [35] which provided similar values. As can be seen in Table 4, common reductive anions such as $S_2O_3^{2-}$, I^-, $C_2O_4^{2-}$ & CN^- have been used to investigate the response of the prepared Perchlorate-CWE and as a result, the use of these anions with reductive properties ,do not cause a noticeable change in the response of the Perchlorate-CWE.

Table 4. Selectivity coefficients of various interfering ions with perchlorate-CWE

Interferent anion	MSM	MPM
KCl	^{a}	2.33×10^{-3}
Na_2SO_4	^{a}	1.84×10^{-3}
KNO_3	^{a}	3.45×10^{-3}
KIO_3	3.51×10^{-5}	1.51×10^{-3}
NaN_3	2.01×10^{-5}	1.84×10^{-3}
KI	7.04×10^{-5}	4.04×10^{-3}
NaF	4.45×10^{-6}	1.54×10^{-3}
$KClO_3$	3.00×10^{-5}	1.55×10^{-3}
KSCN	3.16×10^{-5}	6.16×10^{-2}
$Na_2C_2O_4$	9.10×10^{-7}	2.10×10^{-3}
NaBr	6.86×10^{-8}	2.66×10^{-3}
CH_3COONa	3.56×10^{-5}	2.88×10^{-2}
NaCN	5.18×10^{-5}	3.39×10^{-2}
$NaNO_2$	5.10×10^{-7}	4.41×10^{-3}
Na_2SO_3	6.21×10^{-7}	2.74×10^{-2}
$KHCO_3$	3.51×10^{-5}	1.12×10^{-2}
Na_2CO_3	1.00×10^{-6}	2.32×10^{-2}
KH_2PO_4	3.45×10^{-5}	2.00×10^{-3}
Na_2HPO_4	1.00×10^{-6}	2.60×10^{-2}
$Na_2S_2O_3$	3.31×10^{-7}	7.31×10^{-3}
KIO_4	1.00×10^{-3}	4.43×10^{-1}

^{a} No detection

As it is apparent, in all cases in Table 5, Comparison of the proposed electrode with other comparable electrodes, response time for the proposed perchlorate-CWE are shorter than those reported in the literature. Furthermore, in some instances, the selectivity coefficient, response range independent from pH, DL, and dynamic linear range of the perchlorate-CWE are superior and comparable to those reported for other perchlorate-CWE constructed on a variety of different ionophores. Another advantage of the proposed perchlorate-CWE is the high stability of the electrode that causes an increase in precision.

Table 5. Response characteristics of proposed perchlorate-CWE in comparison to some other perchlorate-ISEs

Ref.	Slope (mV)	Response time (s)	Working pH	Linear range (M)	DL(M)	Interfering ion with $k^{pot}\geq1.0\times10^{-2}$
[30]	59.7	≤10	1.7-9.5	7.9×10^{-6}-8.0×10^{-2}	4.1×10^{-7}	I^-, SCN^-, IO_4^-
[33]	48.3	≤10	2.0-10.0	1.0×10^{-5}-1.0×10^{-2}	5.6×10^{-6}	SO_4^{2-}, SO_3^{2-}, Cl^-, F^-, Br^-, NO_3^-, ClO_3^-, HCO_3^-
[34]	60.3	≤5	2.0-9.0	8.0×10^{-7}-1.0×10^{-1}	5.6×10^{-7}	SCN^-, IO_4^-, I^-, NO_3^-
[35]	59.5	≤10	4.0-12.0	4.0×10^{-7}-1.0×10^{-1}	2.0×10^{-7}	MnO_4^-
[36]	60.0	≤5	1.2-12.5	1.0×10^{-6}-1.0×10^{-1}	6.6×10^{-7}	SO_4^{2-}, SO_3^{2-}, Cl^-,F^-,BrO_3^{2-}, $C_2O_4^{2-}$, HCO_3^-,NO_2^-
[37]	57.8	≤10	4.0-10.0	8.0×10^{-6}-1.6×10^{-1}	5.0×10^{-6}	F^-, Cl^-, SCN^-, Br^-, SO_4^{2-}, NO_3^-, CN^-, NO_2^-
[38]	56.8	≤5	3.0-10.0	1.0×10^{-6}-1.0×10^{-1}	8.3×10^{-7}	SCN^-, CO_3^{2-}, SO_4^{2-}, NO_2^-, $C_2O_4^{2-}$, Cl^-
[39]	60.6	≤10	3.5-12.0	1.0×10^{-6}-1.0	8.0×10^{-7}	CrO_4^{2-}, $C_2O_4^{2-}$, NO_3^-, CO_3^{2-}, IO_3^-, CN^-, I^-, Br^-, SCN^-
[40]	54.1	≤60	3.5-11.0	1.24×10^{-7}-1.0×10^{-3}	7.66×10^{-8}	IO_4^-, I^-
[28]	59.3	9	2.5-9.0	1.0×10^{-7}-1.0×10^{-2}	8.4×10^{-8}	SCN^-, I^-, Br^-, NO_3^-, SO_4^{2-}, F^-,
[31]	59.24	9	2.0-4.0	1.0×10^{-7}-1.0×10^{-1}	5.45×10^{-5}	I^-, IO_3^-, Cl^-, PO_4^{3-}, SO_3^{2-}, BO_3^{3-},
[This work]	57.4	≤4	3.0-8.5	1.6×10^{-6} - 6.1×10^{-2}	5.0×10^{-7}	IO_4^-

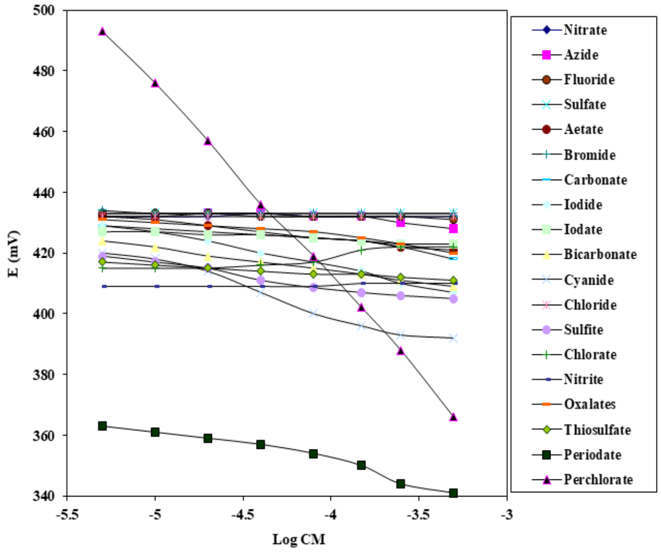


Figure 4. The potential response of the perchlorate-CWE is plotted vs. the logarithm of the activity of the different interfering ion.

3.7. Analytical Applications

To evaluate the applicability of the perchlorate-CWE for real samples, some efforts were made determining perchlorate ions concentration in environmental samples; the proposed perchlorate-CWE was employed to recover perchlorate ions in tap water and mineral water samples. The analysis was performed by direct potentiometers using the standard addition technique by adding defined amounts of perchlorate to samples containing no perchlorate ion. The results and the recovery percent of analysis in these prepared samples are given in Table 6. Recoveries obtained in two samples were satisfactory. As can be seen, the proposed perchlorate-CWE can be successfully applied to determine perchlorate in different water samples.

Table 6. Determination of perchlorate concentration in different water samples

Sample	**Perchlorate concentrations**		**Recovery %**
	added(M)	**perchlorate-CWE (Found) [a]**	
mineral water (koohrang)	6.95×10-6	6.94×10-6±1.57×10-6	99.85
	3.65×10-5	3.52×10-5±7.04×10-6	96.43
tap water	6.95×10-6	7.04×10-6±1.47×10-6	101.29
	3.65×10-5	3.57×10-5±7.49×10-6	97.80

4. Conclusion

The findings obtained from the aforementioned study exhibit that perchlorate-CWE based on “Dixanthylinum dye” is excellent perchlorate-CWE and can be utilized for the determination of this ion in the company of concentrations of common interfering ions in tap water and mineral water with no requirement for pretreatment steps and with negligible interactions from other anionic species exist in the samples. It is very easy to assemble with a fast response time and shows high selectivity, a lower detection limit of 5.0× 10^{-7} M, the dynamic range of 1.0×10^{-6} to 6.1×10^{-2} M, response time of ~4 s, and a pH range of 3.0–8.0. The RSD of about 1.2% indicated that the results are reproducible. The optimum composition was 30.0% of powdered PVC, 66.0% of a plasticizer (*o*-NPOE) and 1.0% of the corresponding ionophore (dixanthylinum dye).

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