

Potentiometric sensor for chromium(VI) using a composite of diphenylcarbazide-natural zeolite-modified membrane electrodes

Rudi Heryanto^{a,b,*}, Eti Rohaeti^a, Laela Wulansari^b, Zulhan Arif^a, Wulan Tri Wahyuni^{a,b}, Budi Riza Putra^c

^a Analytical Chemistry Division, Department of Chemistry, Faculty of Mathematics and Natural Sciences, IPB University, Bogor 16680 Indonesia

^b Tropical Biopharmaca Research Center, Institute of Research and Community Empowerment, IPB University, Bogor 16680 Indonesia

^c National Research and Innovation Agency (BRIN) Republic of Indonesia, Jakarta 10340 Indonesia

*Corresponding author, e-mail: kemometrik@gmail.com

Received 22 Oct 2021, Accepted 9 Feb 2022

Available online 15 Apr 2022

ABSTRACT: The construction and performance of ion selective electrodes (ISEs) for the determination of chromium(VI) based on PVC membranes modified with 1,5-diphenylcarbazide (DPC) and natural zeolite as ionophores are reported in this study. ISE was fabricated in an optimum composition of chromium(VI)-selective membrane consisting of 29 mol% DPC, 43.6 mol% natural zeolite, 25 mol% plasticizer, and 2.2 mol% PVC. The investigation of the performance of the proposed ISE was evaluated in terms of the Nernstian response, range of concentration, limit of detection, response time, and selectivity coefficient. The proposed ISE displayed a linear potential response over a concentration range of 10^{-1} – 10^{-6} M $K_2Cr_2O_7$ with a Nernstian response of -28.8 mV/decade. Adequate sensitivity for chromium(VI) was offered by the proposed ISE with a limit of detection of 2.14×10^{-6} M and a response time of ~ 250 s. The fabricated ISE has also been investigated in selectivity studies in the presence of Cu^{2+} and Fe^{3+} and was found to be more selective in the concentration range of 10^{-1} – 10^{-6} M. Therefore, a novel membrane electrode using a composite of DPC and natural zeolite as an ionophore has shown a satisfactory result for the direct potentiometric measurement of chromium(VI) in the presence of Cu^{2+} and Fe^{3+} , which may have the potential to be used in real sample analysis.

KEYWORDS: ion selective electrode, 1,5-diphenylcarbazide, zeolite, chromium(VI), PVC-based membrane, potentiometry

INTRODUCTION

Ion selective electrodes (ISEs) are one of the classical electrochemical sensors that have been extensively used for analytical purposes due to their simplicity, inexpensiveness, short response time, adequate precision, and accuracy [1]. This type of electrode is commonly used for potentiometric ion sensors with the ability to determine and differentiate metal species in aqueous media, which offers attractive features to be used for practical applications [2]. The response of potentiometric ion sensors depends on the electrode membrane as an electroactive material, testing solution, and the interface of the membrane|solution, which controls their composition, thermodynamics, and kinetic properties [3]. It is also expected that the performance of potentiometric ion sensors must be stable and reliable when they are used for *in situ* measurements. The intention to develop this kind of potentiometric ion sensor is easily achieved when they are based on solid membranes.

Potentiometric measurements based on ISEs for metal ion sensing have been widely developed due to their significant performance such as easy preparation, wide linear operating range with adequate sensitivity and selectivity, portability, quick

response time, and cost-effective approach [4–8]. One of the ISEs that has attracted much attention is ionophores for the detection of chromium(VI) species. In previous studies, various ionophores have been employed to be used for the fabrication of ISEs based on PVC membranes for the sensing of chromium(VI) species such as calix[4]arene [9], C-thiophenecalix[4]resorcinarene [10], quinaldine red [11], Cu(II)-bis(N-4-methylphenyl-salicylidenamino) complex [12], europium β -diketone complex [13], bis(acetylacetonato) Cd(II) [14], *N,N* bis(salicylidene)ethylenediamino cobalt(II) hydrate [15], *N,N,N,N*-tetrakis(3-aminopropyl)-1,4-butadiamine (DABAm4) [16], rhodamine-B [17], charged diaza crown ethers [18], 2-nitrophenyl phenyl ether [19], trioctylphosphine oxide [20], and tricaprylmethyl ammonium [21]. These ionophores have been studied by forming a complex with chromium(VI) within a membrane, so they could be used to fabricate ISEs. However, in addition to unstable responses and short lifetimes, most of the electrodes are still insensitive to chromium(VI) at low concentrations. In addition, some electrodes still have a narrow pH range or narrow working concentration range due to the degradation of the substances (ionophores and plasticizers) that can further diminish the electrode

performance during chromium(VI) measurements. Therefore, it is still interesting to explore another type of ionophore to be used in the fabrication of solid-state membranes for ISE construction. One of the most common reagents for chromium(VI) measurement in 1,5-diphenylcarbazide (DPC) is a chelating agent with a significant affinity and selectivity for Cr(VI) complexation [22,23]. Zeolite as a porous material provides uniformity in terms of shape and pore selectivity, which facilitates ions in accessing its framework for sensing purposes during electroanalytical studies [24,25]. The combination of ionophore and zeolite material results in several applications that have been investigated for analytical purposes [26–28].

In this study, for the reason above, this work aimed to develop a stable measurement of chromium(VI) using the proposed ISEs modified with 3 different ionophores e.g., zeolite, DPC, and DPC:zeolite, at a ratio of 1:1. The performance of each fabricated ISE was evaluated in terms of the Nernstian response, range of measurement, limit of detection, effect of pH, response time, and selectivity coefficient on the interfering ions (Cu^{2+} and Fe^{3+}). The proposed sensor exhibited high sensitivity and adequate selectivity for use in a synthetic solution of chromium(VI) in the presence of Cu^{2+} and Fe^{3+} as interfering ions, which may be possible for use in real applications.

MATERIALS AND METHODS

Reagents and apparatus

Powder of natural zeolite was obtained from Cikembar Region (West Java, Indonesia), and 1,5 diphenylcarbazide (DPC), poly(vinyl chloride) (PVC), acetophenone, oleic acid, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), potassium chloride (KCl), tetrahydrofuran (THF), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) were obtained from Merck (Darmstadt, Germany) and used without further purification.

Electrochemical measurements were carried out using a potentiometer (EUTECH Instrument pH 510), silver/silver chloride (Ag/AgCl) wire obtained from dipping Ag wire into saturated KCl solution, shaker K Model VRN-360, PSA Nanoplus Delsa, SEM JEOL-836, XRD Shimadzu-7000, infrared spectrophotometer (Infrared Bruker Tensor 37), and mesh filter in sieving sizes of 200 and 325 mesh. Standard apparatuses in the laboratory such as glassware, centrifuges, and analytical balances were also used in the experiments.

Preparation and characterization of natural zeolite

The natural zeolite used in the fabrication of the electrode membrane originated from the Cikembar Region, West Java, Indonesia. This zeolite was initially ground using a mortar and sieved into a particle size

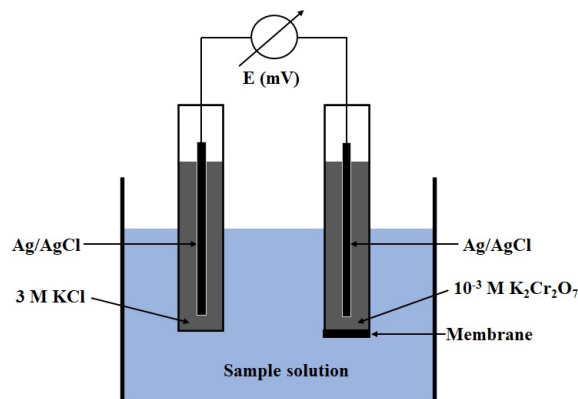


Fig. 1 The potentiometric cell used for the determination of chromium(VI) using the proposed ion selective electrode method.

of 200 mesh. The zeolite powder was then activated in HCl for 3 h. After 3 h, the zeolite powder was neutralized and rinsed with distilled water until the filtrate obtained was neutral pH and free of chloride ions. Then, the zeolite powder was dried in an oven at $300\text{ }^\circ\text{C}$ for 3 h and subsequently sieved to a particle size of 325 mesh. The cation exchange capacity (CEC) of the activated zeolite was then determined using the method published by the Indonesian Soil Research Institute [29]. The obtained zeolite powder was also characterized with PSA, SEM, and XRD.

Fabrication of electrode membrane-modified ionophore

Membrane fabrication was performed using 3 types of ionophores: DPC, natural zeolite powder, and a mixture of DPC:natural zeolite powder at a ratio of 1:1. The coating solution for the membrane was prepared by mixing PVC (0.033 g), acetophenone (0.057 ml), oleic acid (0.005 g), THF (6 ml), acetone (1 ml), and each ionophore (0.005 g). The solution of the resulting mixture was stirred for 15 min and then transferred into a glass petri dish 2 cm in diameter. The glass petri dish was then covered with filter paper, and the mixture was evaporated slowly in open air for 3 days. After 3 days, a thin film was obtained on the PVC-based membrane and subsequently conditioned by soaking them in 10^{-3} M $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Construction of ISE for chromium(VI) using a membrane-modified ionophore

Before construction of ISE, a modified membrane was prepared based on 3 types of ionophores: (1) DPC, (2) natural zeolite, and (3) a mixture of DPC:natural zeolite for chromium(VI) detection. Initially, a silver wire was cleaned with fine filter paper and rinsed with distilled water. Then, the part of silver wire was coated into 0.1 M HCl and passed with 10 mA/cm^2

for 1 min using a Pt wire as a cathode. After the electrolysis process, a black deposit (AgCl) was obtained on the silver wire. The obtained silver wire was then rinsed with pure water and inserted into the glass tube compartment. The membrane-modified ionophore was placed at the end of the glass tube compartment, and the glass tube was filled with 10^{-3} M $K_2Cr_2O_7$. During the insertion of Ag/AgCl wire into the body electrode, the wire was dipped into 10^{-3} M $K_2Cr_2O_7$ without any bubble formation or leaking solution out of the electrode. A schematic diagram of the potentiometric cell used in this proposed ion selective electrode method for chromium(VI) detection was shown in Fig. 1. Characterization of membrane-modified ionophores was performed using scanning electron microscopy and infrared spectroscopy.

Determination of measurement range and limit of detection from ISE

The observation of potential (E) in the ISE with different ionophores was performed in the stock solution of $K_2Cr_2O_7$ in the concentration range of 10^{-1} – 10^{-6} M. The potential measurement was conducted in the electrochemical cell consisting of ISE for chromium(VI) as the cathode, Ag/AgCl electrode as the anode, and potentiometer (EUTECH Instrument pH 510) as the potential readout. Each potential value obtained from ISE for chromium(VI) was plotted in the curve of E (mV) as y-axis and negative logarithmic of $Cr_2O_7^{2-}$ concentration as x-axis and processed using regression linear formula. The limit of detection was determined by making an intersection point between linear and nonlinear curves in the curve of potential measurement of $K_2Cr_2O_7$ standard solution using ISE. The intersection point was then extrapolated into the x-abcissa to obtain the value of the detection limit from each ISE.

Response time for ISE

The response time for ISE was evaluated by measuring the potential (E) using $K_2Cr_2O_7$ in the concentration range of 10^{-1} – 10^{-6} M until a stable value was obtained.

pH effect in ISE measurement

The pH dependence of the electrode potential was examined by measuring 10^{-3} M $K_2Cr_2O_7$ in the pH range of 2–14. Each solution was measured using 3 ISEs with different ionophores to obtain its potential value (E) related to the stability readout in a certain pH range. After obtaining the optimum pH range for chromium(VI) measurement, the potential was measured using $K_2Cr_2O_7$ solution in the range of 10^{-1} – 10^{-6} M.

Selectivity Coefficient for ISE

The value of the selectivity coefficient was determined using a mixed solution with a fixed primary method

(FPM). A solution containing primary ions, 10^{-3} M $K_2Cr_2O_7$, was initially used to determine its potential value (E). Then, the potential value was measured using a mixed solution of 10^{-3} M $K_2Cr_2O_7$ with a solution containing interference ions ($CuSO_4$ and $FeCl_3$) with a volume ratio of 1:1. Both solutions containing these 2 interference ions were prepared in the concentration range of 10^{-1} – 10^{-6} M. The value of the selectivity coefficient can be calculated using Eq. (1):

$$K = (10^{\Delta E/S} - 1)[K^+]/[X^{+m}]^{1/m} \quad (1)$$

where K is the selectivity coefficient, ΔE is the potential difference between primary ions and mixed ions in the solution, S is the Nernstian response, $[K^+]$ is the concentration of primary ions, $[X^{+m}]$ is the concentration of interference ions, and m is the charge of interference ions.

RESULTS AND DISCUSSION

Membrane composition

The sensitivity and selectivity of ISE depend not only on the ionophore but also on the percentage composition of the materials used in the membrane preparation. It has been reported that generally, the optimum membrane composition consists of 1–7% ionophores, 28–33% PVCs, 60–69% plasticizers, and 0.03–2% lipophilic anions [30]. PVC was used as the polymeric matrix, THF as the membrane solvent, acetophenone and oleic acid as the plasticizer, and acetone as the ionophore solvent. In this study, ionophores such as DPC, zeolite, and composites of DPC and zeolite were used to modify the electrode membrane for ISE. Acetophenone and oleic acid play a crucial role in membrane fabrication due to their ability to form ion-selective channels and expand ion mobility to the ionophores inside the membrane [16]. In addition, a thin film will be produced when these plasticizers are mixed with PVC, resulting in an increased ion diffusion ability towards the membrane. However, if the composition percentage of PVC is increased, the membrane would be thicker and stiffer, leading to a smaller porosity. In the case of a higher ion density, it would be difficult for these ions to diffuse to the electrode membrane, leading to a lower Nernstian response and linearity [31]. In general, the purpose of adding these plasticizers into the composition was to reduce the value of the glass transition (T_g) to obtain a flexible membrane with low viscosity.

Surface characterization of the modified membrane using PSA, XRD, and SEM

Fig. 2 showed typical SEM images of natural zeolite, membrane-modified DPC, zeolite, and a mixture of DPC and zeolite. From the SEM image (Fig. 2A) in the HCl-activated natural zeolite, there were some cavities in the zeolite particles (indicated by circle lines) that

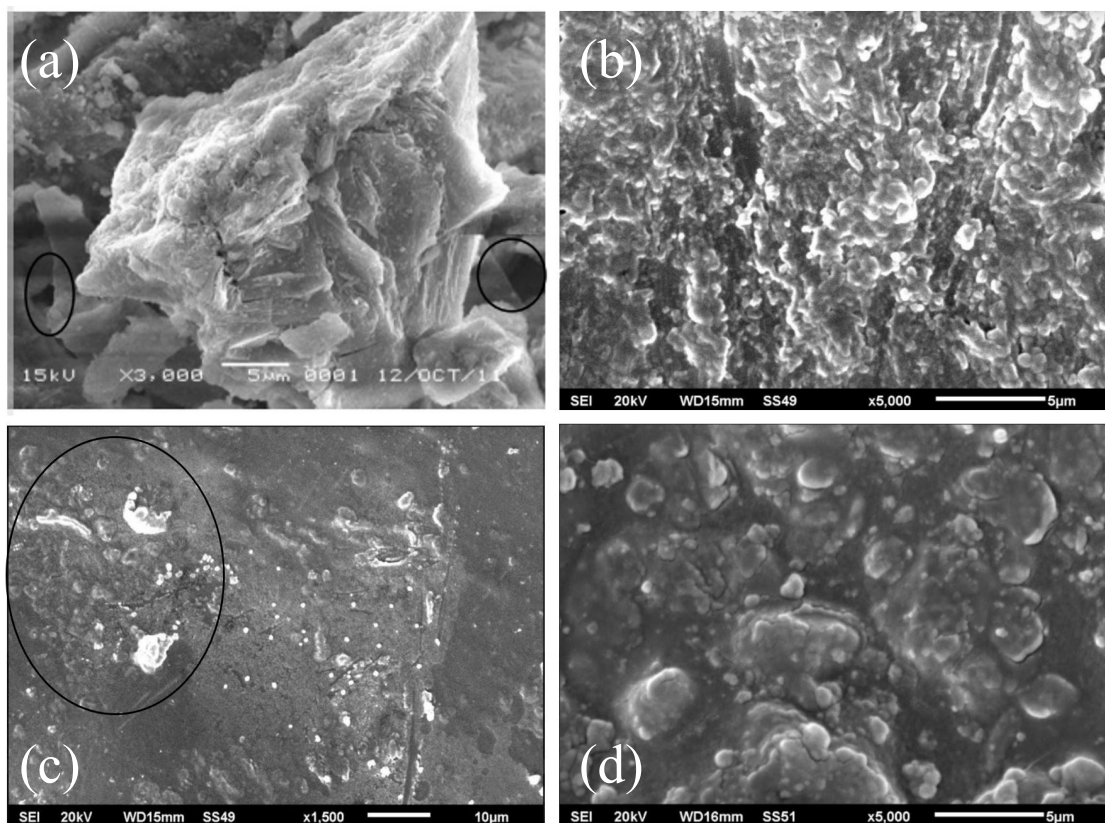


Fig. 2 Scanning electron microscopy images showing the surface morphology of (a) natural zeolite after HCl treatment, (b) membrane-modified DPC, (c) membrane-modified zeolite, and (d) membrane-modified composite of DPC and zeolite.

can be filled by ionophores in its framework structures. In addition, the average particle size of natural zeolite after the sieving process using a 325-mesh filter was 414.3 nm from PSA analysis. Further analysis of the natural zeolite using XRD (figure not shown) also confirmed that the mordenite-type zeolite is suitable for the fabrication of electrode membranes. The XRD analysis of natural zeolite showed 4 main peaks at 2θ angles of 9.785, 19.647, 22.049, and 27.692, which are similar in mordenite-type natural zeolite according to the database of PCPDFWIN 29-1257 at 2θ angles of 9.754, 19.579, 22.205, and 27.680. After HCl treatment, the obtained CEC value for natural zeolite was 46.22 $\text{cmol}_{(+)}/\text{kg}$, which indicates that this material has a greater ability to absorb anion species than cationic species. Meanwhile, membrane-modified DPC (Fig. 2B) showed an uneven surface with several fine and wider lumps, while membrane-modified zeolite (Fig. 2C) produced a flatter surface. Fig. 2C also revealed the collection of zeolite particles on the left part of the image, and other particles were unevenly spread on the membrane surface. Furthermore, Fig. 2D showed the image of the membrane-modified composite of DPC and zeolite, indicating some uneven lumps on the surface that looked similar to membrane-

modified DPC (Fig. 2B). Hence, the lumps shown on both membrane-modified DPC and the composite may be associated with DPC deposits on the surface.

Surface characterization of the modified membrane using infrared spectrophotometer (IR)

In general, Fig. 3 showed the number of characteristic peaks, indicating several functional groups from each ionophore in the modified membrane. Fig. 3A displayed that the IR spectra of membrane-modified DPC produce some absorption peaks at 3362.68 and 3277.09 cm^{-1} , indicating N–H asymmetric stretching, which are close to what was reported by El-Kabbany et al [32] at 3359 and 3276 cm^{-1} . The presence of absorption peaks in the infrared areas of 1654.32 and 1603.56 cm^{-1} indicated absorption for C=O stretching and N–H bending, respectively. These peaks are usually expressed as a band of amide I with 80% C=O stretching in its character and amide II, which is a strong interaction between N–H bending and C–N stretching. In addition, C=C stretching from aromatic structures was indicated by an absorption peak in the area of 1538.13 cm^{-1} . The peak of N–N stretching was also seen at 1493.87 cm^{-1} , which is close to the area reported by El-Kabbany et al [32] at

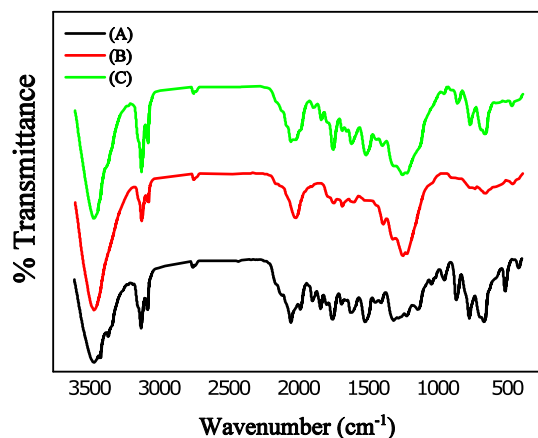


Fig. 3 Infrared spectrum of (A) membrane-modified DPC, (B) membrane-modified natural zeolite, and (C) membrane-modified composite of zeolite with DPC.

approximately 1486 cm^{-1} , while the absorption peak at 1254.85 cm^{-1} revealed the occurrence of aromatic C–H bending. Furthermore, the peak for monosubstituted benzene was displayed in the 763.95 cm^{-1} region, which also corresponds to previous report [32]. Based on the infrared spectrum results, it can be concluded that the functional groups for DPC compounds as ionophores are shown in the membrane-modified DPC.

The IR spectrum from membrane-modified zeolite (Fig. 3B) showed the characteristic peaks of functional groups for zeolite. The presence of absorption peaks at 1100 cm^{-1} and 700 cm^{-1} , which are typical for zeolite, indicated the vibration of Si–O and Al–O, respectively. Meanwhile, the characteristic peak at 1057.69 cm^{-1} showed the internal region of asymmetric vibration of Si–O and Al–O [33]. Furthermore, the symmetric vibration of Si–O and Al–O stretching appeared in the absorption region at 669.53 cm^{-1} and is in accordance with the range of regions reported [34]. The appearance of an absorption peak at 615.52 cm^{-1} suggests the formation of a double ring, which is an external link between zeolite layers. The absorption peak at 468.13 cm^{-1} is attributed to the bending vibration of Si–O and Al–O, which is close to that previously reported [33]. The appearance of an absorption peak at 3433 cm^{-1} is attributed to O–H stretching in the membrane-modified DPC, zeolite, and composite of DPC with zeolite. In particular, the membrane-modified zeolite was strengthened with an absorption peak at 1635.36 cm^{-1} , which is attributed to O–H bending from H_2O deformation. In addition, the absorption peak at approximately $3000\text{--}2800\text{ cm}^{-1}$ reflects the presence of an aliphatic C–H group due to the vibration of C–H stretching [35]. These functional groups presumably come from the impurities of organic compounds entrapped in the zeolite frame-

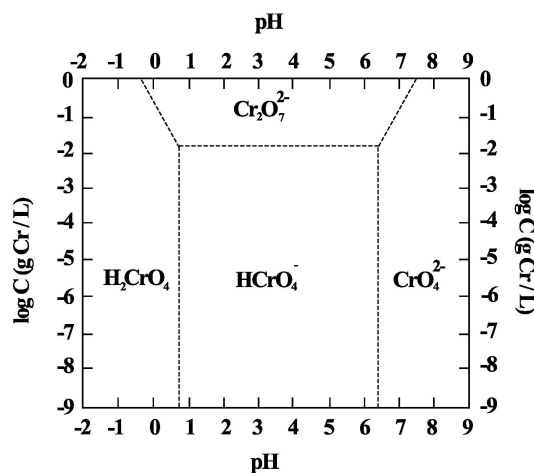


Fig. 4 Pourbaix diagram for Cr(VI) species at $25\text{ }^\circ\text{C}$ [31].

work or are derived from solvent and hydrocarbon compounds in the membrane.

ISE characterization of the Nernstian response and range of measurement

In this study, each ISE was treated in a similar way that was fabricated in 6 replicates, and its Nernstian response and correlation coefficient were determined. Initially, the electrolysis of Ag wire was performed in saturated KCl solution to form a thin layer of AgCl on its wire. Then, the Nernstian response of the Ag/AgCl wire was determined by measuring the potential (E) in KCl solution in the concentration range of 10^{-1} – 10^{-5} M. The value of the Nernstian response of the Ag/AgCl wire should be close to the theoretical value for monovalent ions because Ag has a +1 charge. Fig. 4 showed the Pourbaix diagram [34] describing the dependence of pH and ion concentration of chromate species in $\text{K}_2\text{Cr}_2\text{O}_7$ solution. In the pH range of 0.75–6.45, there were 2 dominant species of chromate: HCrO_4^- (if the concentration of Cr(VI) was less than 0.01 g/l) and $\text{Cr}_2\text{O}_7^{2-}$ (if the concentration of Cr(VI) was high). In this study, $\text{K}_2\text{Cr}_2\text{O}_7$ solution was used in the concentration range of 10^{-1} – 10^{-6} M with a pH range of 4–6. Therefore, the dominant species in $\text{K}_2\text{Cr}_2\text{O}_7$ in this pH range is HCrO_4^- , as previously reported [21, 37]. In ISE 1 using membrane-modified zeolite, the best electrode showed the highest correlation coefficient of 0.9954 with a Nernst factor of -18.4 mV/decade . The value of the Nernstian response for the transfer process of monovalent ions was 59.2 mV/decade . However, the curve slope in Fig. 5A indicates the Nernstian response for trivalent ions. This is due to ion exchange occurring from the aqueous phase via complexation of DPC as an ionophore and the predominant ion, HCrO_4^- , into the organic phase and spontaneously reduced to chromium(III).

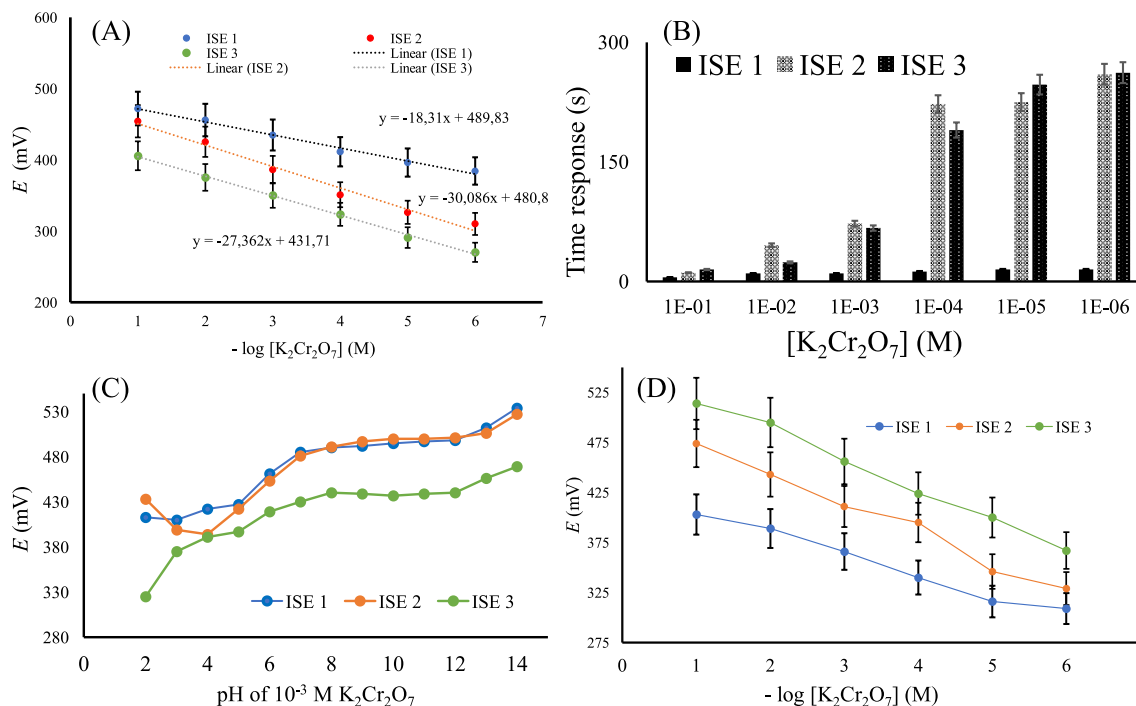


Fig. 5 (A) Relationship between $K_2Cr_2O_7$ in the concentration range of 10^{-1} – 10^{-6} M and the potential response (mV), (B) time response, (C) relationship between pH of 10^{-3} M $K_2Cr_2O_7$ and potential response (mV), and (D) relationship between $K_2Cr_2O_7$ in the concentration range of 10^{-1} – 10^{-6} M and the potential response (mV) measured at pH 9 obtained from 3 different ISEs: ISE 1 for membrane-modified DPC, ISE 2 for membrane-modified zeolite, and ISE 3 for membrane-modified composite of DPC and zeolite.

Meanwhile, at ISE 2 using membrane-modified zeolite, the best electrode exhibited the highest correlation coefficient of 0.9938 with a Nernstian response of -29.11 mV/decade, which indicates that the predominant ion during measurement was $Cr_2O_7^{2-}$. This value is in accordance with Welch et al [34] and Hassan et al [15], who reported that $HCrO_4^-$ and $Cr_2O_7^{2-}$ are the predominant ions and exist together in $K_2Cr_2O_7$ solution in a pH range of 2–6. However, in this study, the mechanism of $Cr_2O_7^{2-}$ selectivity over $HCrO_4^-$ in membrane-modified zeolites was not investigated. In addition, at ISE 3 using membrane modification, the composite of DPC and zeolite showed the highest correlation coefficient of 0.9946 with a Nernstian response of -28.8 mV/decade. This value is close to the Nernstian response for divalent ions, which is 29.6 mV/decade. Thus, it can be concluded that the predominant ion during the measurement of Cr(VI) solution was $Cr_2O_7^{2-}$.

Limit of detection and response time at 3 different ISEs during Cr(VI) measurements

The limit of detection for chromium(VI) measurements using 3 different ISEs could be directly determined by the extrapolation of an intersection point towards the x-axis from the curve of the logarithmic concentra-

tion of $K_2Cr_2O_7$ against the potential of the solution (E). Limit of detection obtained as 1.44×10^{-6} M for membrane-modified DPC (ISE 1), 1.91×10^{-6} M for membrane-modified zeolite (ISE 2), and 2.14×10^{-6} M for membrane-modified composite of DPC and zeolite (ISE 3) with ISE 1 showing the highest sensitivity for chromium(VI) measurement. Meanwhile, the response time for 3 different ISEs when measuring $K_2Cr_2O_7$ was shown in Fig. 5B. The reference electrode and the proposed electrode were immersed into $K_2Cr_2O_7$ in the concentration range of 10^{-1} – 10^{-6} M, and their response times were recorded after reaching a stable potential at a certain time. From Fig. 5B, ISE 1 showed the shortest response time compared to ISE 2 and ISE 3. In general, the electrodes took a longer time to respond to chromium(VI) species in diluted solutions (10^{-4} – 10^{-6} M) and a faster time in concentrated solutions (10^{-1} – 10^{-3} M).

Influence of pH in ISE measurement

The pH dependence of the ISE potential on the response of the membrane electrode was investigated, and a relationship curve between the pH of the chromium(VI) solution (x-axis) and potential (y-axis) was constructed. The dependence of the potential response of the proposed electrode was studied over

Table 1 Selectivity coefficient of 3 different ISEs ISE 1 for membrane-modified DPC, ISE 2 for membrane-modified zeolite, and ISE 3 for membrane-modified composite of DPC and zeolite) towards Cu^{2+} and Fe^{3+} as interference ions.

B	A	$K_{A,B}^{\text{pot}}$		
		ISE 1	ISE 2	ISE 3
Cu^{2+}	10^{-1}	0.1160	0.0717	0.0184
	10^{-2}	0.0739	0.0203	0.0581
	10^{-3}	0.0936	0.0381	0.1248
	10^{-4}	0.1721	0.0268	0.0616
	10^{-5}	0.2749	0.0260	0.1192
	10^{-6}	0.6496	0.0822	0.1733
Fe^{3+}	10^{-1}	1.4304	0.4994	0.1345
	10^{-2}	6.6358	0.7342	0.0557
	10^{-3}	2.7800	0.1766	0.1542
	10^{-4}	0.0299	0.0607	0.0262
	10^{-5}	0.0455	0.5676	0.0491
	10^{-6}	0.0455	0.5676	0.0491

[A] = concentration of interference ion.

a wide range of pH values of 2–14 using a 10^{-3} M $\text{K}_2\text{Cr}_2\text{O}_7$ solution. The pH of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution was adjusted by the addition of diluted HCl and/or NaOH and was displayed in Fig. 5C. Based on Fig. 5B, the electrode potential for 3 different ISEs was independent of pH in the range of 8–12. This result is similar to that previously reported [14], who found that the potentiometric sensor for chromium(VI) species works suitably in alkaline media (pH range of 8–12). At pH values above 12, hydroxyl ions probably compete chromium(VI) species for the binding process to the electrode membrane, while at pH values lower than 8, the lowered potential value may be due to the reduction of chromate into dichromate species or ionophore instability.

Next, pH 9 was selected as the optimum pH for measuring the potential of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in a concentration range of 10^{-1} – 10^{-6} M to investigate the Nernstian response and correlation coefficient. The relationship curve between the negative logarithm of $\text{K}_2\text{Cr}_2\text{O}_7$ concentration and the measured potential at pH 9 was displayed in Fig. 5D. Based on the Pourbaix diagram in Fig. 4, the predominant species in $\text{K}_2\text{Cr}_2\text{O}_7$ solution at pH values above 7 are CrO_4^{2-} species. These species may be sensed by ISE 2 and ISE 3 due to their Nernstian response close to the divalent ion. Meanwhile, the obtained Nernstian response for ISE 1 was close to the trivalent ion with the predominant species at the solution being CrO_4^{2-} . However, these species might be allegedly extracted into the organic phase and spontaneously reduced into Cr(III) and sensed by ISE 1.

Influence of interfering ions

It is also necessary to evaluate the influence of interfering ions on chromium(VI) selectivity when measured

using ISE with DPC, zeolite, and its composite as ionophores. In this study, the effect of Cu^{2+} and Fe^{3+} as interfering ions on the proposed chromium(VI) selective response was investigated. The selectivity coefficient ($K_{A,B}^{\text{pot}}$) for chromium(VI) species over interfering ions was determined by the fixed interference method (FIM), which is recommended by IUPAC [38]. The concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ solution was fixed at 1.0×10^{-3} M, while the concentration of interfering ions (Cu^{2+} and Fe^{3+}) was varied in the concentration range of 10^{-1} – 10^{-6} M. The values of selectivity coefficients were summarized in Table 1. From Table 1, it was clearly seen that Cu^{2+} has small effects on the chromium(VI) measurement using all the proposed electrodes (ISEs 1, 2, and 3) due to its coefficient selectivity being lower than 1. This indicates that all the proposed electrodes are more selective towards chromium(VI) than Cu^{2+} as similarly reported by Sanchez-Moreno et al [39], who explained that the presence of Cu^{2+} does not interfere with the performance of electrode membranes modified with DPC. Meanwhile, the existence of Fe^{3+} gives a small interference effect only at high concentrations of chromium(VI) (above 10^{-3} M) when measured with ISE 1 but not with ISEs 2 and 3. Therefore, it can be concluded from Table 1 that the selectivity coefficients for the interfering ions (Cu^{2+} and Fe^{3+}) are small enough and would not significantly affect the functioning of the proposed sensor for chromium(VI) detection.

CONCLUSION

We employed natural zeolite and DPC as ionophores, resulting in a stable membrane for electrode fabrication and showing good analytical performance for potentiometric chromium(VI) sensing. The Nernstian response for membrane-modified DPC, zeolite, and composite of DPC and zeolite (ISEs 1, 2, and 3) at $\text{K}_2\text{Cr}_2\text{O}_7$ in the concentration range of 10^{-1} – 10^{-6} M was determined to be -18.4 , -29.11 , and 28.8 mV/decade, respectively. The limit of detection for ISEs 1, 2, and 3 also showed good sensitivity for chromium(VI) measurement with values of 1.44×10^{-6} , 1.91×10^{-6} , and 2.14×10^{-6} M, respectively. The proposed sensor also showed good selectivity towards Cu^{2+} and Fe^{3+} as interfering ions as indicated by a selectivity coefficient lower than 1. Therefore, it can be concluded that this potentiometric sensor for chromium(VI) based on DPC and zeolite has the potential to be used in real sample analysis.

Acknowledgements: This work is supported by the research funding in the scheme funding of Penelitian Dasar Unggulan Perguruan Tinggi, The Ministry of Research and Technology, National Research and Innovation Agency of the Republic of Indonesia with the contract number 1927/IT3.L1/PN/2021 the fiscal year 2021.

REFERENCES

- Korany MA, Mahmoud RK (2021) A new approach for determination of water-soluble hexavalent chromium in real cement and industrial water samples using Ni-Fe layered double hydroxides/urea/glycerol nanocomposite based potentiometric sensor. *Microchem J* **171**, ID 106890.
- Mukherjee S, Bhattacharya S, Ghosh K, Pal S, Halder A, Naseri M, Mohammadniaei M, Sarkar S, et al (2021) Sensory development for heavy metal detection: A review on translation from conventional analysis to field-portable sensor. *Trends Food Sci Technol* **109**, 674–689.
- Bobacka J, Ivaska A, Lewenstam A (2008) Potentiometric ion sensors. *Chem Rev* **108**, 329–351.
- Rezayi M, Heng LY, Kassim A, Ahmadzadeh S, Abdollahi Y, Jahangirian H (2012) Immobilization of tris(2 pyridyl) methylamine in a PVC-membrane sensor and characterization of the membrane properties. *Chem Cent J* **6**, ID 40.
- Ahmadzadeh S, Rezayi M, Karimi-Maleh H, Alias Y (2015) Conductometric measurements of complexation study between 4-isopropylcalix[4]arene and Cr³⁺ cation in THF-DMSO binary solvents. *Measurement* **70**, 214–224.
- Ahmadzadeh S, Yoosefian M, Rezayi M (2021) Comprehensive experimental and theoretical investigations on chromium(III) trace detection in biological and environmental samples using polymeric membrane sensor. *Int J Environ Anal Chem* **101**, 1461–1476.
- Badakhsan S, Ahmadzadeh S, Mohseni-Bandpei A, Aghasi M, Basiri A (2019) Potentiometric sensor for iron (III) quantitative determination: experimental and computational approaches. *BMC Chem* **13**, ID 131.
- Ahmadzadeh S, Kassim A, Rezayi M, Abdollahi Y, Rounaghi GH (2011) A conductometric study of complexation reaction between meso-octamethylcalix[4]pyrrole with titanium cation in acetonitrile-ethanol binary mixtures. *Int J Electrochem Sci* **6**, 4749–4759.
- Dalkiran B, Ertürün HEK, Özel AD, Canel E, Özkinali S, Kiliç E (2017) Chromate-selective electrodes prepared by using calix[4]arenes for the speciation of Cr(VI) and Cr(III). *Ionics* **23**, 2509–2519.
- Jain AK, Gupta VK, Singh LP, Srivastava P, Raisoni JR (2005) Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions. *Talanta* **65**, 716–721.
- Yari A, Bagheri H (2013) Determination of Cr(VI) with selective sensing of Cr(VI) anions by a PVC-membrane electrode based on quinaldine red. *J Chin Chem Soc* **56**, 289–295.
- Benvidi A, Elahizadeh M, Zare HR, Vafazadeh R (2008) Highly sensitive membrane electrode based on a copper(II)-bis(N-4-methylphenyl-salicylidenaminato) complex for the determination of chromate. *Anal Lett* **44**, 595–606.
- Ganjali MR, Eshraghi MH, Ghadimi S, Moosavi SM, Hosseini M, Haji-Hashemi H, Norouzi P (2011) Novel chromate sensor based on MWCNTs/nanosilica/ionic liquid/Eu complex/graphite as a new nanocomposite and its application for determination of chromate ion concentration in waste water of chromium electroplating. *Int J Electrochem Sci* **6**, 739–748.
- Ardakani MM, Dastanpour A, Salavati-Niasari M (2005) Novel coated-wire membrane sensor based on bis(acetylacetonato) cadmium(II) for the determination of chromate ions. *Microchim Acta* **150**, 67–72.
- Rezayi M, Ghasemi M, Karazhian R, Sookhakian M, Alias Y (2014) Potentiometric chromate anion detection based on Co(SALEN)₂ ionophore in a PVC-membrane sensor. *J Electrochem Soc* **161**, B129.
- Choi Y-W, Minoura N, Moon S-H (2005) Potentiometric Cr(VI) selective electrode based on novel ionophore-immobilized PVC membranes. *Talanta* **66**, 1254–1263.
- Hassan SSM, El-Shahawi, Othman AM, Mosaad MA (2005) A potentiometric rhodamine-B based membrane sensor selective determination of chromium ions in wastewater. *Anal Sci* **21**, 673–678.
- Singh LP, Bhatnagar JM, Tanaka S, Tsue H, Mori M (2005) Selective anion recognition: charged diaza crown ethers based electrochemical sensors for chromate ions. *Anal Chim Acta* **546**, 199–205.
- Hassan SSM, Abbas MN, Moustafa GAE (1996) Hydrogen chromate PVC matrix membrane sensor for potentiometric determination of chromium(III) and chromium(VI) ions. *Talanta* **43**, 797–804.
- Choi Y-W, Moon S-H (2001) A study on hexachromic ion selective electrode based on supported liquid membranes. *Environ Monit Assess* **70**, 167–180.
- Choi Y-W, Moon S-H (2004) Determination of Cr(VI) using an ion selective electrode with SLMs containing Aliquat336. *Environ Monit Assess* **92**, 163–178.
- Mumtaz K, Iqbal S, Shahida S, Shafique MA, Wasim M, Ahmad B (2021) Synthesis and performance evaluation of diphenylcarbazide functionalized mesoporous silica for selective removal of Cr(VI). *Micropor Mesopor Mater* **326**, ID 111361.
- Uzunboylu S, Karakas Ö, Demirci-Çekiçi, Apak R (2021) Sulfate radical formation by Cr(III) activation of peroxydisulfate – Diphenylcarbazide spectrophotometric determination of sulfate radical and its scavenging activity. *Spectrochim Acta A Biomol Spectrosc* **260**, ID 119941.
- Danesh-Khorasgani M, Nezamzadeh-Ejehieh A (2016) PVC-zeolite nanoparticle-surfactant anion exchanger membrane: preparation, characterization, and its application in development of ion-selective electrode for detection of sulfate. *J Solid State Electrochem* **20**, 2827–2833.
- Nosuhi M, Nezamzadeh-Ejehieh A (2018) An indirect application aspect of zeolite modified electrodes for voltammetric determination of iodate. *J Electroanal Chem* **810**, 119–128.
- Putra BR, Darusman LK, Rohaeti E (2013) Carbon paste electrode hexadecyltrimethylammonium bromide modified natural zeolite for chromium(VI) detection. *Indo J Chem* **13**, 122–128.
- Porada R, Fendrych K, Baś B (2021) Electrochemical sensor based on Ni-exchanged natural zeolite/carbon black hybrid nanocomposite for determination of vitamin B₆. *Microchim Acta* **188**, ID 323.
- Fekry AM, Abdel-Gawad SA, Azab SM, Walcarius A (2020) A sensitive electrochemical sensor for moxifloxacin hydrochloride based on nafion/graphene oxide/zeolite modified carbon paste electrode. *Electroanalysis* **33**, 964–974.

29. Indonesian Soil Research Institute (2005) *Chemical Analysis for Soil, Plants, and Fertilizers*. Bogor: Research Center for Agricultural Development, Ministry of Agricultural of Indonesia.
30. Ertürün HEK, Yılmaz M, Kiliç E (2007) Construction of an anion-selective electrode: Dichromate-selective electrode. *Sens Actuators B Chem* **127**, 497–504.
31. Zahran EM, New A, Gavalas V, Bachas LG (2014) Polymeric plasticizer extends the lifetime of PVC-membrane ion-selective electrodes. *Analyst* **139**, 753–763.
32. El-Kabbany F, Taha S, Hafez M (2011) IR spectroscopic analysis of polymorphism in diphenyl carbazide. *Spectrochim Acta A Mol Biomol Spectrosc* **78**, 981–988.
33. Shirazi L, Jamshidi E, Ghasemi MR (2008) The effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size. *Cryst Res Technol* **43**, 1300–1306.
34. Wuntu DA, Tangkuman HD (2008) Degree of crystallization as a function of ageing and crystallization time on zeolite A synthesis using microwave radiation. *Chem Prog* **1**, 19–24.
35. Utubira Y, Wijaya K, Triyono T, Sugiharto E (2006) Preparation and characterization of TiO₂-zeolite and its application to degrade textile wastewater by photocatalytic method. *Indo J Chem* **6**, 231–237.
36. Welch CM, Nekrassova O, Compton RG (2005) Reduction of hexavalent chromium at solid electrodes in acidic media: reaction mechanism and analytical applications. *Talanta* **65**, 74–80.
37. Yari A, Bagheri H (2013) Determination of Cr(VI) with selective sensing of Cr(VI) anions by a PVC-membrane electrode based on quinaldine red. *J Chin Chem Soc* **56**, 289–295.
38. Buck RP, Lindner E (1994) Recommendations for nomenclature of ion-selective electrodes (IUPAC recommendations 1994). *Pure Appl Chem* **66**, 2527–2536.
39. Sánchez-Moreno RA, Gismera MJ, Sevilla MJ, Procopio JR (2010) Evaluation of solid-state platforms for chromium(VI) potentiometric sensor development. *Sens Actuators B Chem* **143**, 716–723.