Research Article

INDONESIAN SCHOLAR SOCIETY

Indones. J. Chem. Stud.
2024, 3(2), 58–65
Available online at journal.solusiriset.com
e-ISSN: 2830-7658; p-ISSN: 2830-778X

Indonesian Journal of Chemical Studies

Carbon Paste Electrode Modified Zeolite-Iron as a Chromium(VI) Detection Medium

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Received: 3 Dec 2024; Revised: 24 Dec 2024; Accepted: 25 Dec 2024;
Published online: 31 Dec 2024; Published regularly: 31 Dec 2024

Abstract—Chromium exists in two dominant species in nature, Cr(III) and Cr(VI). Both are stable; however, Cr(VI) exhibits significantly higher toxicity than Cr(III). Existing measurement methods could not differentiate between these two chromium species. Therefore, a more sensitive and selective measurement method was required for their speciation, particularly for Cr(VI) detection. In this study, a carbon paste electrode modified with zeolite and iron was developed for Cr(VI) measurement using the voltammetry method. The electrode was prepared by mixing graphite, iron-modified zeolite, and liquid paraffin. Measurements were conducted using cyclic voltammetry within a potential range of -1.2 V to 1.2 V. A 0.05 M KCl solution was used as the electrolyte. Electrode characterization was carried out concerning three parameters: the effect of analyte pH, preconcentration time, and the composition of iron-modified zeolite. The optimum Cr(VI) measurement was achieved in a 50 µM Cr(VI) solution at pH 3 using a carbon paste electrode with 20% iron-modified zeolite and a preconcentration time of 25 min. Under these optimal conditions, a cathodic peak current of 5.22 µA was obtained.

Keywords—*Carbon paste electrode; Chromium(VI); Cyclic voltammetry; Iron-modified zeolite*

1. INTRODUCTION

Chromium is a heavy metal naturally found in the environment in the forms of Cr(III) and Cr(VI). Trivalent chromium (Cr(III)) serves as an essential cofactor for insulin, supporting energy, glucose, and lipid metabolism. Additionally, Cr(III) helps regulate blood sugar levels, benefiting individuals with type 2 diabetes and metabolic syndrome while also reducing LDL (bad) cholesterol and increasing HDL (good) cholesterol, contributing to cardiovascular health [1]. In contrast, hexavalent chromium (Cr(VI)) is toxic, mutagenic, carcinogenic, and teratogenic [2]. Cr(VI) can diffuse as chromate anions that penetrate negatively charged cell membranes, inducing oxidation and making it more toxic than Cr(III). This species is highly soluble in water and can enter the human body, causing various health problems, such as dermatitis, respiratory disorders, and cancer due to its carcinogenic nature [3]. Chromium ion contamination in the environment often originates from textile factories, metal plating, and dye industries [4].

Advances in chemical science have developed numerous methods for detecting metal ions like Cr(VI), including UV-Vis spectrophotometry, luminescence, atomic emission spectrometry, X-ray fluorescence spectrometry, and atomic absorption spectrometry [5]. Arif et al. have developed methods for detecting Cr(VI) through optical electrode methods with specific ligan for hexavalent chromium impregnated in the composite membrane of cellulose triacetate, which comes from commercial and lab synthetic [6]. Some of these methods generally require complex instrumentation and are relatively expensive, making them unsuitable for routine analyses and incapable of distinguishing between chromium species [7].

An affordable, simple, sensitive, and specific method for detecting and differentiating chromium species in environmental samples is ion-selective electrodes (ISEs). ISEs are electrochemical sensors widely used due to their numerous advantages, including ease of preparation, simple equipment requirements, selectivity for specific ion species, rapid response times, and cost-effectiveness. These sensors respond explicitly to certain ions, with their surface interacting directly with the measured ions. In this study, carbon paste-based ion-selective electrodes (ISE) were selected due to their cost-effectiveness, significantly lower ohmic resistance, highly stable response, and easily renewable surface [8]

Modified zeolite electrodes can be applied to carbon paste-based ISE to determine chromium in water

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DOI: 10.55749/ijcs.v3i2.64

samples. These modified zeolite electrodes exhibit unique shapes and sizes, charge selectivity, and a high ion exchange capacity, making them more advantageous than traditional chemically modified electrodes. Zeolites are considered the most significant ion exchangers among various materials, such as silica-alumina gels and activated carbon. Therefore, applying zeolite electrodes as electrochemical sensors leverages the principle of ion exchange [9]. Zeolites modified with $Fe(OH)_3$ have improved anion exchange capacity by enabling Fe(III) ions to infiltrate the zeolite cavities and replace the balancing cations. Thereby, neutralizing the negative charge of the zeolite structure and allowing it to adsorb anions [10]. This remarkable characteristic can be applied to develop specific purposes for detecting hexavalent chromium, and new electrodes can be prepared with new material combinations.

In this study, natural zeolites from Tasikmalaya, West Java, were used. These zeolites were modified with iron, fabricated into carbon paste-based electrodes, and then characterised through performance testing. The performance evaluation includes examining the influence of analyte pH, preconcentration time, and the composition of iron-modified zeolite on the cathodic current measurement of Cr(VI) using cyclic voltammetry. According to several previously published studies, using zeolite-iron as a modifier for carbon paste electrodes is new and improves its sensitivity for anion detection.

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used included natural zeolite from Tasikmalaya, West Java, $Fe(NO_3)_3$ (CAS 10421-48-4), HNO_3 (CAS 7697-37-2), H_2SO_4 (CAS 7697-37-2), H_3PO_4 (CAS 7664-38-2), 1,5-diphenylcarbazide (DPC) (CAS 140-22-7), $K_2Cr_2O_7$ (CAS 7778-50-9), HCl (CAS 7647-01-0), NaOH (CAS 1310-73-2), KCl (CAS 7447-40-7), graphite (7782-42-5), and liquid paraffin (CAS 8002-74-2). All materials were purchased from Merck, Darmstadt, Germay with Analytical Grade Reagent quality.

2.2. Instrumentation

The instruments used included a mortar, 200 mesh sieve, magnetic stirrer (MG-78-1), centrifuge (M400D), UV-Vis spectrophotometer (Thermo Spectronic Genesys 10UV), AAS (Shimadzu AA-7000), electrode tubes, voltammetry (eDAQ), XRD (Shimadzu XRD-7000), SEM (JEOL JSM-6510), EChem v2.1 software, and Origin 7 software.

2.3. Zeolite Preparation

The natural zeolite from Tasikmalaya, West Java, was ground and sieved to obtain particles passing through a 200-mesh sieve. Subsequently, the zeolite was washed with distilled water and dried in an oven at 105 °C for 24 h.

2.4. Zeolite Activation

The activation of zeolite was performed chemically (acid treatment) and physically (heating). 100 g of zeolite sample was mixed with 250 mL of 3 M HCl solution. The mixture was stirred for 60 min, then filtered and rinsed with distilled water until reaching a pH of 5–6. The zeolite was then dried in a furnace at 300 °C for 3 h. The washing process was complete when no precipitate formed in the filtrate after adding $AgNO_3$.

2.5. Iron-Modified Zeolite Fabrication

The iron solution was prepared by mixing 50 mL of 0.075 M NaOH solution with 50 mL of 0.05 M $Fe(NO_3)_3$ solution. The NaOH solution was added dropwise to the iron solution under slow stirring. After the solution was mixed entirely, its pH was checked, and 75 mL of the solution was added to 1 g of zeolite. The mixture was shaken for 12 h, rinsed with water, and dried in an oven at 40 °C.

2.6. Determination of Iron Content in Iron-Modified Zeolite

The Fe content in the iron-modified zeolite was determined using Atomic Absorption Spectroscopy (AAS). Samples of both unmodified and modified zeolite, weighing 50 mg, were treated with 10 mL of 5% HNO_3 solution and allowed to stand for 60 min. The mixture was filtered, and the filtrate was diluted to a final volume of 50 mL in a volumetric flask. The solution was subsequently analyzed using AAS.

2.7. Chromium Adsorption Testing

Adsorption tests were carried out using a standard Cr(VI) solution with concentrations ranging from 1.5 to 250 µM at pH 3. 50 mg of iron-modified zeolite was added to 5 mL of the standard Cr(VI) solution and shaken for 6 h. The final pH of the solution was measured, and the solution was separated from the precipitate using a centrifuge at 1500 rpm.

To the supernatant, 0.1 mL of concentrated H_2SO_4 and 0.03 mL of concentrated H_3PO_4 were added, followed by stirring and allowing the solution to stand for 5 min. Subsequently, 0.1 mL of 1% DPC (1,5-diphenylcarbazide) in acetone was added, and the solution was mixed thoroughly. After 10 min, the absorbance of the solution was measured using a UV-Vis spectrophotometer at a wavelength of 543 nm.

2.8. Electrode Fabrication

The carbon paste electrode (CPE) was prepared by mixing graphite and liquid paraffin. In contrast, the modified zeolite-iron carbon paste electrode (CPE-ZB) was prepared by mixing graphite, modified zeolite-iron, and liquid paraffin (**Fig. 1**).

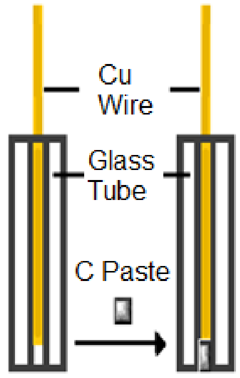

Fig. 1. Scheme of carbon paste electrode fabrication

All materials were combined to form a homogeneous paste. A glass tube with a diameter of 2.5 mm was used as the electrode body. A copper wire, a connector between the electrode and the power source, was inserted into the tube, leaving approximately 3 mm of space at the tube's tip. The paste was then packed tightly into the tip of the tube until filled. The surface of the electrode was polished using oil paper.

2.9. Electrode Performance Testing using Voltammetry Method

A 50 µM Cr(VI) analyte solution in 0.05 M KCl was prepared at several pH levels ranging from 1 to 6. The solution was placed into a voltammetric cell containing the Cr(VI) analyte solution, and the current response was observed using cyclic voltammetry over a potential range of -1.2 V to 1.2 V.

2.10. Effect of Pre-concentration Time

The Cr(VI) 50 µM solution with the best pH was determined by optimizing the pre-concentration time through stirring at room temperature. The time varied between 5–35 min with 5 min intervals. After stirring, the electrode was rinsed with distilled water and placed in the voltammetric cell containing the electrolyte solution. The current response was observed using cyclic voltammetry within the potential range of -1.2 V to 1.2 V.

2.11. Effect of Zeolite-Iron Composition

CPE-ZB was made by mixing graphite, iron-modified zeolite, and liquid paraffin in various compositions to observe the effect of the zeolite-iron composition on the CPE performance (**Table 1**). Pre-concentration on the electrode was first carried out with the Cr(VI) analytical solution having optimum pH at the best pre-concentration time. The current response was then observed using cyclic voltammetry within the potential range of -1.2 V to 1.2 V.

Table 1. Materials and composition of the electrode

Electrode	Composition		
	Graphite (mg)	Zeolite-iron (mg)	Paraffine (mg)
CPE-ZB 10	60	10	30
CPE-ZB 20	50	20	30
CPE-ZB 30	40	30	30
CPE-ZB 40	30	40	30
CPE-ZB 50	20	50	30

2.12. XRD Analysis

Identification with XRD was performed to identify the types of minerals present in the zeolite. Approximately 200 mg of the sample was directly mounted on a 2×2.5 cm^2 aluminium plate. The sample was characterized using Cu radiation in the 2θ range of 5–80°.

2.13. SEM Analysis

Characterization with SEM was performed to determine the morphology of the zeolite sample. The characterization was conducted on Tasikmalaya zeolite before modification and iron-modified zeolite.

3. RESULT AND DISCUSSION

3.1. Results of Preparation, Activation, and Identification of Zeolite

The natural zeolite used was from Tasikmalaya, West Java. Generally, this zeolite was in chunks with a white-green to grey colour. The zeolite was prepared by crushing and sieving it to obtain grains that pass through a 200-mesh sieve. After that, the zeolite was activated to remove impurities (contaminating minerals) from nature that cover the pores, thus maximizing its adsorption capacity. This activation was carried out chemically and physically. Chemically, certain solvents were added to clean the pore surface, remove contaminating compounds, and rearrange the position of exchangeable atoms. Meanwhile, physical activation was performed by heating at temperatures of 200-400 °C for several h, aimed at removing water trapped in the zeolite pores, thereby increasing the surface area of the zeolite [11].

Chemical activation in this study was carried out by acidification using 3 M HCl for 1 h. Zeolite activation with HCl at this concentration causes the zeolite to undergo dealumination and denationalization, which means the release of Al and cations from the zeolite pores [12]. An example of the Al release reaction from the zeolite framework by HCl is illustrated in **Fig 2.** Acid activation results in an increase in the surface area of the zeolite due to the reduction of impurities that cover the zeolite pores. This increase in surface area is expected to enhance its adsorption capacity [13].

XRD then identified the mineral type. The principle is that when an X-ray beam is directed at a crystal sample, the crystal planes will diffract the X-rays, and the diffracted rays will be detected and translated as diffraction peaks. The more crystal planes in the sample, the stronger the diffraction intensity. Each peak in the XRD pattern represents a crystal plane with a specific orientation in three-dimensional axes. Identification is done by comparing the 2θ peaks from the sample with standard 2θ peaks [11].

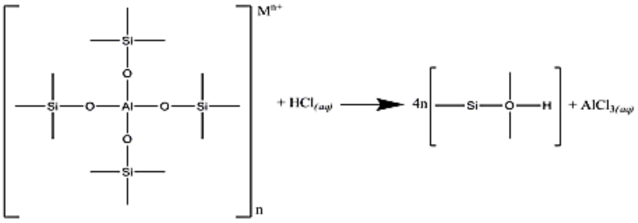

Fig. 2. Example of the reaction of Al release from the zeolite framework by HCl

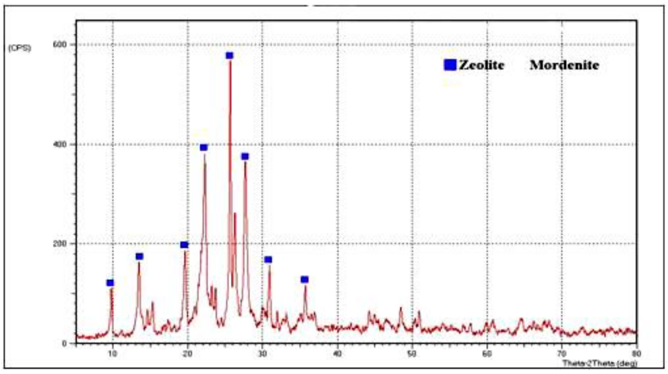

Fig. 3. Diffractogram of natural type of Mordenite zeolite

Fig. 3 shows the diffractogram of natural zeolite, mordernite type. The 2θ values of the sample match the standard data from the Joint Committee on Powder Diffraction Standards (JCPDS) archive number 49-0924, corresponding to mordenite zeolite. This indicates that the natural zeolite from Tasikmalaya has the mineral type of mordenite. This result is consistent with several previous studies, which reported that the natural zeolite from Tasikmalaya has only one dominant mineral type, mordenite, with impurities in the form of quartz [14,15]. A comparison of the highest 2θ values from the sample and standard is shown in **Table 2**.

Table 2. 2θ's peak of mordenite natural zeolite after activation

Natural Zeolite (mordenite) JCPDS 49-0924	Cikalong natural zeolite after activation
19.681	19.6635
22.381	22.2860
25.779	25.6992
26.402	26.2913
27.742	27.7334

3.2. Preparation of Iron-Modified Zeolite and Adsorption Test

Zeolite is a hydrated aluminosilicate mineral composed of tetrahedral units of SiO_4 and AlO_4, with a hollow framework structure filled with water molecules and cations [16]. These cations can move freely, allowing ion exchange without damaging the zeolite structure [17]. The zeolite crystal structure forms a three-dimensional tetrahedral framework (**Fig. 4a**), where Si and Al atoms occupy the central atoms in the tetrahedron. Meanwhile, oxygen atoms are located at the corners (**Fig. 4b**).

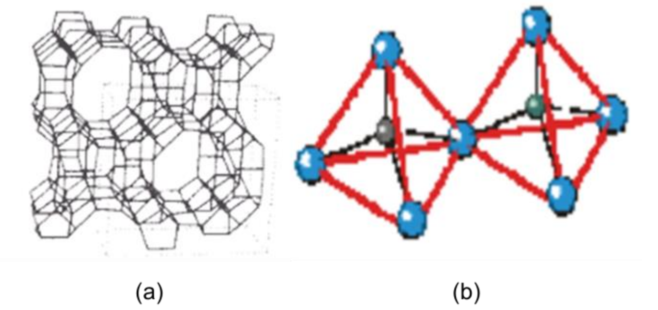

Fig 4. Framework of (a) 3D mordenite zeolite and (b) tetrahedral structure of zeolite; Si atoms (●), Al atoms (●), O atoms (●)

Fig. 5. Iron modified zeolite

Some Si atoms in the zeolite are replaced by Al atoms, resulting in a negatively charged structure due to the charge difference between the tetrahedrons $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$. This negative charge causes zeolite to have low or no anion adsorption capability. The function of zeolite as a detection medium for anionic species such as Cr(VI) can be enhanced by modifying the zeolite with iron cations. The modification involves the reaction of $Fe(NO_3)_3$ with NaOH, carried out slowly to prevent the formation of $Fe(OH)_3$ precipitates, resulting in a red solution containing iron cations. The modified zeolite appears orange, and its iron content is measured using AAS. The iron content analysis shows a significant increase, from 0.2200 to 5.0013 ppm (95.6%), proving the success of the modification. **(Fig. 5)**.

Morphological analysis using SEM was performed on the surface of the zeolite before and after modification with iron. The analysis results are presented in **Fig. 6**. Morphological analysis using SEM showed that the surface of the zeolite after modification had more pores with a more uniform sizes than before modification. This makes iron-modified zeolite a potential medium for Cr(VI) adsorption and as a selective ion electrode.

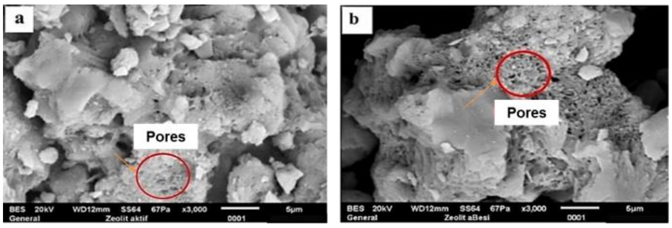

Fig. 6. Surface morphology of (a) zeolite before modification and (b) iron-modified zeolite at 3000× magnification

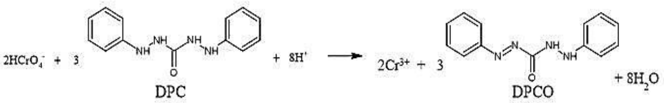

Fig 7. Reaction of Cr(VI) with DPC

Adsorption test of Cr(VI) using the DPC method on zeolite before and after modification [18]. The DPC method is based on measuring the absorption of a reddish-purple solution, indicating the formation of a complex between 1,5-diphenylcarbazide [$(C_6H_5NHNH)_2CO$ (DPC)] and Cr(VI) (**Fig 7**). The wavelength of this complex was determined in the range of 500–600 nm, with a result of 543 nm. The DPC-Cr(VI) complex on unmodified zeolite forms a reddish-purple colour, showing a very low adsorption capacity of zeolite for Cr(VI). Meanwhile, the adsorption capacity of the modified zeolite for Cr(VI) is significantly higher, as indicated by the reduced intensity of the reddish-purple colour in the solution after reacting with DPC.

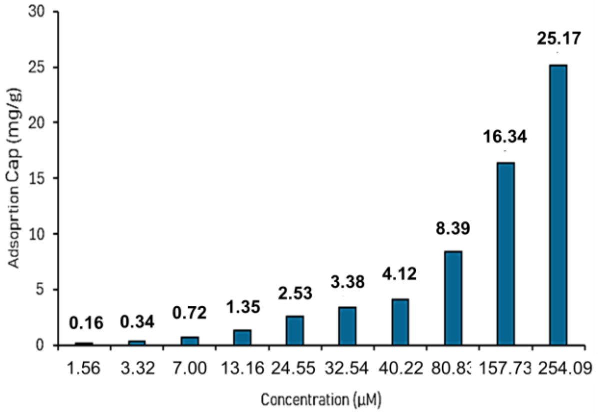

Fig. 8. Adsorption of Cr(VI) profile on zeolite-iron

The adsorption capacity was determined for Cr(VI) concentrations ranging from 1.5 to 250 µM, using a constant amount of iron-modified zeolite (±0.05 g) and shaking time (**Fig. 8**). The results showed a positive linear relationship between Cr(VI) concentration and adsorption capacity: the higher the Cr(VI) concentration, the greater the adsorption capacity. This increase occurs because higher concentrations enhance the number of adsorbate ions that can be adsorbed by the adsorbent if the active sites are available [13].

The results indicate that the active sites of iron-modified zeolite can still adsorb Cr(VI) within the concentration range used, suggesting that higher concentrations might yield higher adsorption capacities. The maximum adsorption capacity was obtained at a Cr(VI) concentration of 254.0952 µM, amounting to 25.1674 mg/g.

3.3. Electrode Fabrication and Performance Test with Voltammetry

Electrochemical analysis using voltammetry was performed with a 3-electrode system consisting of CPE and CPE-ZB as the working electrode, an Ag/AgCl reference electrode, and a Pt auxiliary electrode. 0.05 M KCl solution was used as the electrolyte for Cr(VI) measurements. The electrolyte solution reduces the electrostatic attraction between the electrode charges and the analyte ions and maintains the ionic strength [19].

Fig. 9 shows the voltammograms of CPE and CPE-ZB in 0.05 M KCl electrolyte solution. From -1.2 V to 1.2 V, the KCl solution did not produce a peak current response on either CPE or CPE-ZB. This result indicates that KCl is suitable as an electrolyte solution because it does not undergo oxidation or reduction reactions within the potential range used.

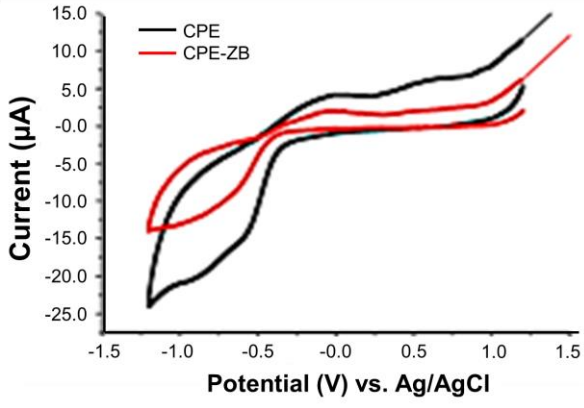

Fig. 9. CPE and CPE-ZB voltammogram in KCl 0.05 M electrolyte solution.

Nitrogen gas was bubbled into the electrolyte solution for 20 sec prior to measurement. This is done to remove dissolved oxygen from the solution. Dissolved oxygen can cause redox reactions on the electrode surface, leading to oxygen peaks on the voltammogram. These peaks can interfere with the analysis, especially if oxygen has peaks at potentials similar to the analyte [8]. The standard reduction potential of oxygen in water at 25 °C is +0.40 V (versus the standard hydrogen electrode (SHE)). The reduction reaction is as follows (**Eq. 1**) [18,19]:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \quad (1)$$

The performance of CPE and CPE-ZB electrodes in Cr(VI) solution was tested with three parameters: the impact of analyte pH, preconcentration time, and zeolite-iron composition. The effect of analyte pH on the cathodic current signal was studied in the pH range of 1–6 in a 50 µM Cr(VI) solution in 0.05 M KCl. The highest peak current was observed at pH 3, measuring 4.87 µA (**Fig. 10**). This current corresponds to the response generated during the reduction of Cr(VI) at the electrode. The reduction of Cr(VI) to Cr(III) occurred at a potential of +1.33 V (vs. SHE), while the decline of Fe^{3+} to Fe^{2+} occurred at a potential of +0.77 V (vs. SHE) [20]. In this study, the reduction current of Cr(VI) appeared at a potential of -0.62 V (vs. Ag/AgCl). Chromium ions can exist in polyvalent states, with their electrical charge dependent on the pH of the system. The fraction of dominant Cr(VI) species based on the pH of the solution is presented in **Fig. 11**.

When the solution pH ranges from 1 to 6, chromium exists in equilibrium as $HCrO_4^-$ and $Cr_2O_7^{2-}$ species. At pH levels above 6, Cr(VI) predominantly exists as CrO_4^{2-} ions, while at pH levels below 1, the primary species is H_2CrO_4. In the pH range of 0.75–6.25, two dominant Cr(VI) species could be observed: $HCrO_4^-$ at low concentrations (below 0.01 g/L) and $Cr_2O_7^{2-}$ at high concentrations (above 0.01 g/L). Given that the optimum pH was 3.0 and the $K_2Cr_2O_7$ solution used for this analysis had a concentration of 50 µM, equivalent to 0.0147 g/L, the dominant Cr(VI) species in the solution was $Cr_2O_7^{2-}$.

The subsequent parameter studied was preconcentration time. Preconcentration involves accumulating the analyte on the electrode surface and can significantly influence the measured current response on the working electrode. The effect of preconcentration time on cathodic current was evaluated using a Cr(VI) solution at pH 3. Preconcentration was performed by immersing the electrode in the Cr(VI) solution while stirring magnetically at room temperature. The preconcentration times tested ranged from 3 to 35 min, in 5-min intervals.

The optimum preconcentration time for Cr(VI) measurement was determined to be 25 min, producing a current of 5.52 µA (**Fig. 12**). At shorter preconcentration times (5–20 min), the resulting currents were low. This is likely due to incomplete adsorption of Cr(VI) onto the electrode surface. Conversely, at longer preconcentration times, the electrode surface became oversaturated with adsorbed Cr(VI), causing desorption and a subsequent decrease in the measured current [14,21].

The final parameter evaluated in this study was the composition of the iron-modified zeolite. This test identifies the optimal zeolite-iron composition for the best signal response in Cr(VI) analysis. Cr(VI) solution with pH 3.0 and a preconcentration time of 25 min was used. The proportions of zeolite-iron were varied relative to graphite. The tested compositions were 10, 20, 30, 40, and 50%. The optimum composition was found to be 20% (CPE-ZB 20), yielding a peak current of 5.22 µA (**Fig. 13**). Other compositions—CPE-ZB 10, CPE-ZB 30, CPE-ZB 40, and CPE-ZB 50—produced peak currents of 2.85, 2.52, 2.00, and 1.09 µA, respectively.

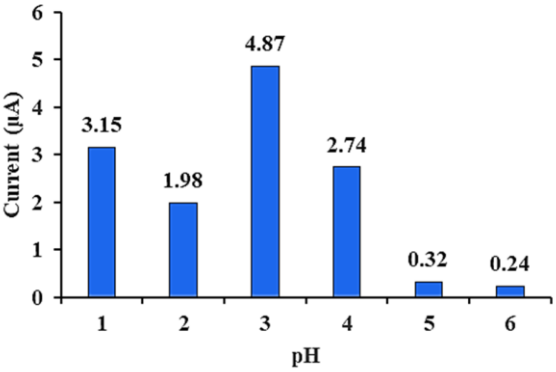

Fig. 10. Peak current values of CPE-ZB in 50 µM Cr(VI) solution at pH 1–6.

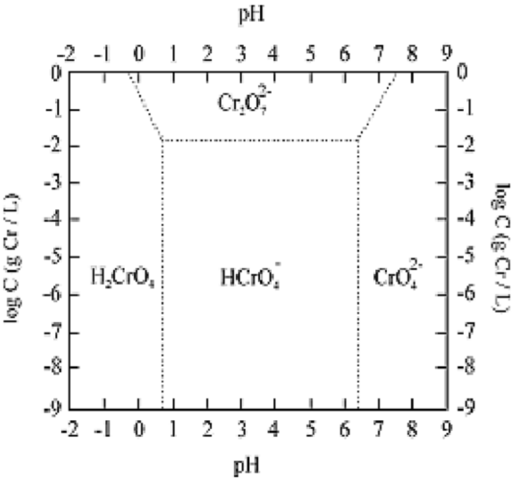

Fig. 11. Pourbaix diagram of Cr(VI) ion species at 25 °C

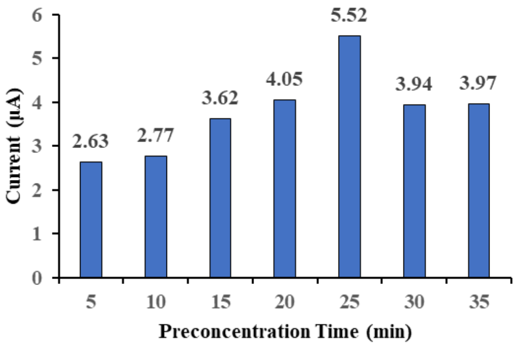

Fig. 12. Effect of preconcentration time on the reduction current of Cr(VI).

Higher proportions of zeolite-iron do not correlate positively with the measured peak current (**Fig. 13**). As the proportion of zeolite-iron increased, the graphite content in the electrode decreased. Graphite functions as the conductor in the electrode [21]. In 10% zeolite-iron composition, the measured current was low despite the high graphite content. This is likely because the zeolite-iron is insufficiently optimized to adsorb Cr(VI). Meanwhile, at 30–50%compositions, the reduced graphite content limits electrical conductivity, resulting in lower currents. These findings are in good agreement with the previous studies [22,23].

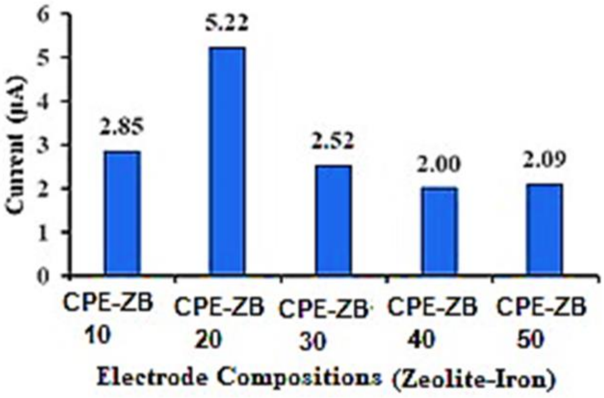

Fig. 13. Effect of zeolite-iron composition on the reduction current of Cr(VI)

CONCLUSION

The natural zeolite from Tasikmalaya primarily consisted of the mineral mordenite. Iron-modified zeolite demonstrated an enhanced adsorption capacity for Cr(VI) with increasing Cr(VI) concentration. The maximum adsorption capacity recorded was 25.1674 mg/g at a Cr(VI) concentration of 254.0952 µM. Zeolite-Iron could be used as a modification material in carbon paste electrodes (CPE) for Cr(VI) measurement using cyclic voltammetry with a 0.05 M KCl electrolyte solution over a potential range of -1.2 V to 1.2 V. Optimal Cr(VI) measurement was achieved using a 50 µM Cr(VI) solution at pH 3.0, with CPE modified with 20% zeolite-iron and a preconcentration time of 25 min. Under these conditions, the peak cathodic current was 5.22 µA.

SUPPORTING INFORMATION

There is no supporting information in this paper. The data that support the findings of this study are available on request from the corresponding author (ZA)

ACKNOWLEDGEMENTS

The authors would like to thank the Analytical Chemistry Division and Joint Laboratory of the Department of Chemistry, IPB University.

CONFLICT OF INTEREST

The authors have no conflict of interest in this publication.

AUTHOR CONTRIBUTIONS

ZA, RIA, and ER conducted the experiment and analyzed data. NAA and HR wrote and revised the manuscript. ZA finalized the manuscript. All authors agreed to the final version of this manuscript.

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