

Full Paper

Selectivity Determination of Pb^{2+} Ion Based on TiO_2 -Ionophores BEK6 as Carbon Paste Electrode Composite

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Abstract- Pb^{2+} ion was investigated by voltammetry selectivity using TiO_2 -Ionophores hexa(p-tert butyl)hexa(ethyl ester)calix[6]arene (BEK6) composite to increase the selectivity and sensitivity of carbon paste electrode (CPE). The BEK6 was synthesized by using hydrolysis method, meanwhile the TiO_2 -P25 and graphite powder were mixed as an electrode composite. The Scanning Electron Microscopy (SEM) shows that the CPE doped TiO_2 -BEK6 (CPE/ TiO_2 -BEK6) have morphology likes a rough, non-porous, composed of fine particles, and homogeneously. The presence of Pb^{2+} ion in pH 5 citrate buffer electrolyte causes the peaks appearance on E_{pa} and E_{pc} were 0.17 V and 0.37 V with the peak potential current

generated of 15.15 μA and -12.0 μA , respectively. The 0.005 g BEK6 was increased significantly the peak current of the Pb^{2+} ion with the LOD value of 0.1756. In addition, the presence of TiO_2 -BEK6 composite shows the measurement current stability by %RSD of 0.83.

Keywords- Pb^{2+} , Ionophore, TiO_2 -BEK6, Cyclic voltammetry, Selectivity

1. INTRODUCTION

The presence of non-biodegradable and persistent Pb^{2+} ion in aquatic environments has been reported as a harmful contaminant for human health, such as brain disorders [1], central nervous system and reproduction [2], increasing blood pressure [3], causing kidney damage and anemia [4]. Several measurement techniques have been used in the determination of Pb^{2+} ion such as AAS, ICP-MS, ICP-OES, and AFS spectroscopy [5-7]. Despite its high selectivity but it requires a long step preparation, complicated instruments operation, and high-cost measurement.

Electrochemical techniques such as voltammetry is an interesting analytical technique to be developed with some considerations such as high sensitivity, good selectivity, fast response, cheaper cost measurement, and simple instrument design allowing for field measurements [8-10]. Various working electrode modifications continue to be achieved in obtaining stable, selective, and sensitive electrodes measurement results for the determination of Pb^{2+} ion in the environment such as modified L-glutamic acid Glassy carbon electrode [11], modified Zinc Oxide-Graphene electrodes [5], Graphene oxide-modified bismuth-modified electrodes [12], montmorillonites-polyaniline nanocomposite glassy carbon electrodes [3], multi-walled carbon modified carbon paste [6], Au nanowire electrodes [13], MWCNTs-nano silica modified carbon paste electrodes [14], and Mn-N codoped by TiO_2 electrode [15]. Other attempts at obtaining electrodes selectively against Pb^{2+} ion are reported with the addition of ionophores [16].

In this work, we report the performance as composite materials in the determination of Pb^{2+} ion. The CPE has some advantages such as easy to update, easy to modify, cheap, and very low current disturbance [17]. The TiO_2 is high conductivity properties, unique physical and chemical properties, different electronic properties, high surface material effectiveness, and is used as a catalyst [18-21]. Its use as a composite material exhibits excellent electrode performance, in which the presence of TiO_2 causes current and electron transfer of electrode surfaces to increase significantly [22-24]. Whereas BEK6 ionophores have been reported to have selective properties of metal ions and have been applied in the development of selective electrode ions [25]. However, the properties of such selectivity have not been reported for the determination of metal ions by voltammetry. So in this work, we specifically study the selectivity properties of BEK6 ionophores to Pb^{2+} ion. Its presence as a new composite

material is expected to have a significant effect both in increasing the oxidation current and reduction of Pb^{2+} ion.

2. EXPERIMENTAL METHODS

2.1. Reagents and apparatus

Ionophore BEK6 synthesized with reference to the method reported Dali et al. [25]. TiO_2 Degussa P25 (Merck, Germany), Graphite powder (Merck, Germany), and paraffin oil ($d=0.88 \text{ g cm}^{-3}$) are used as electrode components. Buffer citrate pH 5 is used as a supporting electrolyte solution. The $\text{Pb}(\text{NO}_3)_2$ standard solutions was used as test solutions, and distilled water used for all solvents.

A potentiostat (DY2100B-Digi-Ivy, Inc.) with three electrode system (CPE/ TiO_2 -BEK6) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl 3.0 M KCl as the reference electrode) was used for electrochemical analysis. The pH meter (Ohaus starter 3000) was used for measurement of pH solution. SEM (JEOL-JSM-6510LV) and Fourier Transform Infra-Red (FTIR) (Shimadzu IRAffinity-1S) were used for characterization of working electrode components.

2.2. Synthesis of Ionophores BEK6

BEK6 was obtained by hydrolysis of BEK6. A 2.0 g of material (0.0019 mol) was mixed with 0.5 g of potassium hydroxide (0.0089 mol), and dissolved in 100 mL of 96% ethanol. Subsequently, it was refluxed for 24 h at a temperature of 78 °C, cooled to ambient temperature, and acidified using 1.0 M HCl. The white precipitate formed was filtered off and washed with 1.0 M HCl, followed by distilled water. The precipitate obtained is then dried in a desiccator and recrystallized.

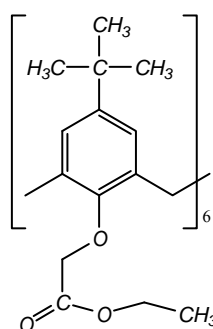


Fig. 1. BEK6 ionophore structure

2.3. Synthesis of CPE/ TiO_2 -BEK6 Composite

Graphite powder, TiO_2 -P25 anatase, and BEK6 were mechanically mashed and sieved using 200 mesh. The powder is homogenized in hot paraffin oil with a temperature ranging

from 80 °C. The paste formed was inserted in a 3 mm diameter glass tube that connected with a copper wire. The BEK6 ionophore was mixed into graphite and TiO₂-P25 anatase are 0.005 g, 0.010 g, and 0.015 g, respectively. The reference electrode was prepared by mixing TiO₂ anatase, graphite, and paraffin oil with the ratio of mass (w/w) 2:3:5. The composites are homogenized at 80 °C.

3. RESULTS AND DISCUSSION

3.1. Characterization of CPE/TiO₂-BEK6 electrode

The addition of BEK6 ionophores (Fig. 2A) causes the specific absorption of IR-carbon pastes (C-H) at 2854.65 cm⁻¹ and 2924.09 cm⁻¹ wave numbers to decrease in intensity. This reduction is expected due to stretching vibration of the BEK6 ionophore aliphatic C-H group [25]. In addition, the presence of BEK6 ionophores also affects the specific absorption of Ti-O vibrations that occur at 663.51 cm⁻¹ [26-28]. The wavenumber absorption at the 1751.36 cm⁻¹ is the specific absorption of the C=O group of BEK6 ionophores [25]. The presence of 2368.59 cm⁻¹ indicated the C-O bond from ester group.

Fig. 2B is SEM analysis result to identify the surface morphology of CPE/TiO₂-BEK6 electrode. Based on the figure, it is seen that CPE/TiO₂-BEK6 has a rough surface, not porous, and homogeneously mixed. At 10 μm magnification it is seen that the electrode composite consists of fine particles.

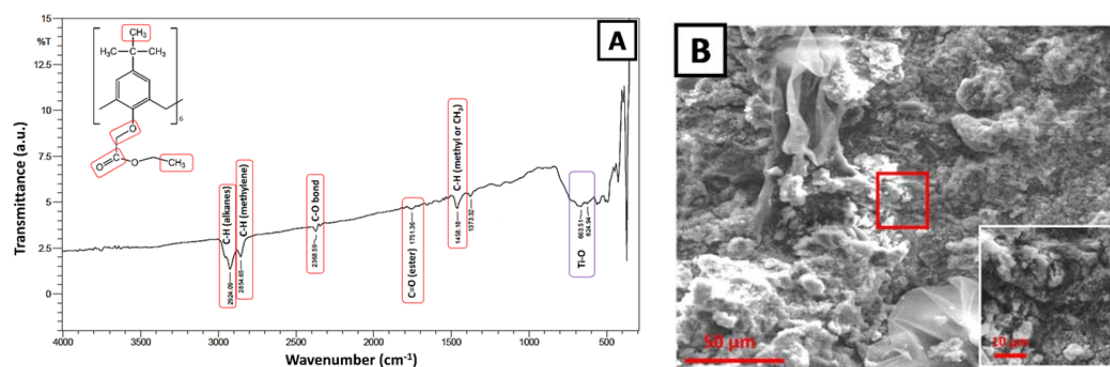


Fig. 2. Characterization of CPE/TiO₂-BEK6 electrode, (A) IR spectra of CPE/TiO₂-BEK6 electrode, and (B) Morphology of CPE/TiO₂-BEK6 electrode

3.2. Electrochemical properties of CPE/TiO₂-BEK6 electrode

The electrochemical properties determination of CPE/TiO₂-BEK6 composite was carried out in a 1.0 ppm Pb²⁺ ion solution containing citrate buffer pH 5 as the supporting electrolyte. The presence of TiO₂-BEK6 as a CPE composite material exhibits an increase in both oxidation and reduction currents of Pb²⁺ ion (Fig. 3C) rather than only TiO₂ (Fig. 3B). Where the current occurs at the oxidation potential (E_{pa}) and reduction (E_{pc}) are 0.17 V and 0.37 V,

respectively. This potential is a redox potential for Pb^{2+} ion, this is supported by the absence of peak current in the citrate buffer pH 5 solution (Fig. 3A). The presence of BEK6 also causes the peak current to be sharp and narrow and shows the redox process of Pb^{2+} ion on the electrode surface is reversible with the ratio of $I_{pa}/I_{pc} = 1.0$.

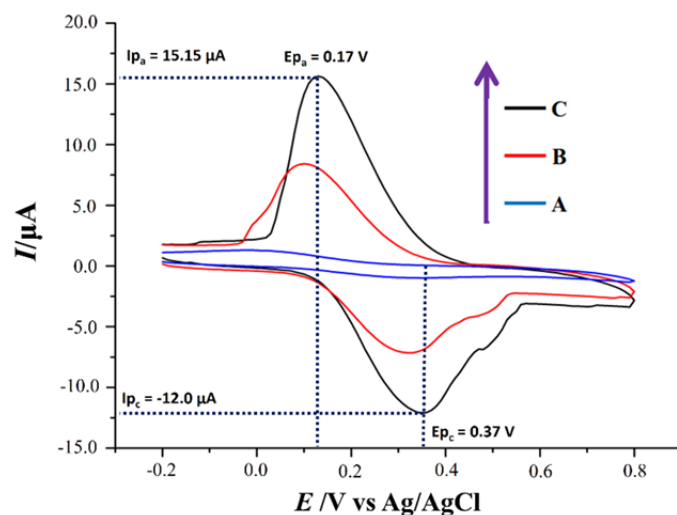


Fig. 3. Cyclic Voltammogram: (A) citrate buffer pH 5; (B) Pb^{2+} ion using CPE/ TiO_2 ; (C) Pb^{2+} ion using CPE/ TiO_2 -BEK6

Table 1. Effect of BEK6 mass variation on oxidation current and reduction of Pb^{2+} ion

Working electrode	Mass of BEK6 (g)	I_{pa} (μA)	I_{pc} (μA)
	0.005	15.15	-12.0
CPE/ TiO_2 -BEK6	0.010	11.89	-8.18
	0.015	11.29	-7.58

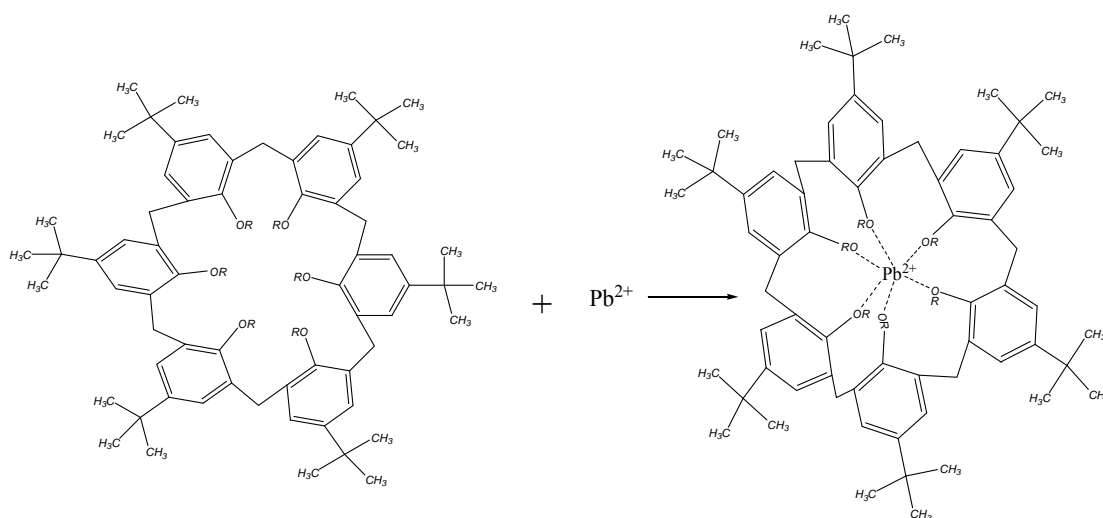


Fig. 4. Mechanism propose the BEK6 as chelate agent of Pb^{2+} ion in the electrochemical system

The effect of BEK6 ionophores on the CPE/TiO₂-BEK6 performance specifically was studied by varying the mass of BEK6 as a composite electrode. Table 1 shows that the three mass variations tested, the 0.015 g BEK6 causes the redox currents of Pb²⁺ ion to decrease, indicating that excess BEK6 mass will slow the electron transfer process on the electrode surface. This phenomenon causes the some Pb²⁺ ions interact strongly to trap on the BEK6 surface. The mass of 0.005 g BEK6 shows a high peak current so that the mass is used in the subsequent Pb²⁺ ion tests.

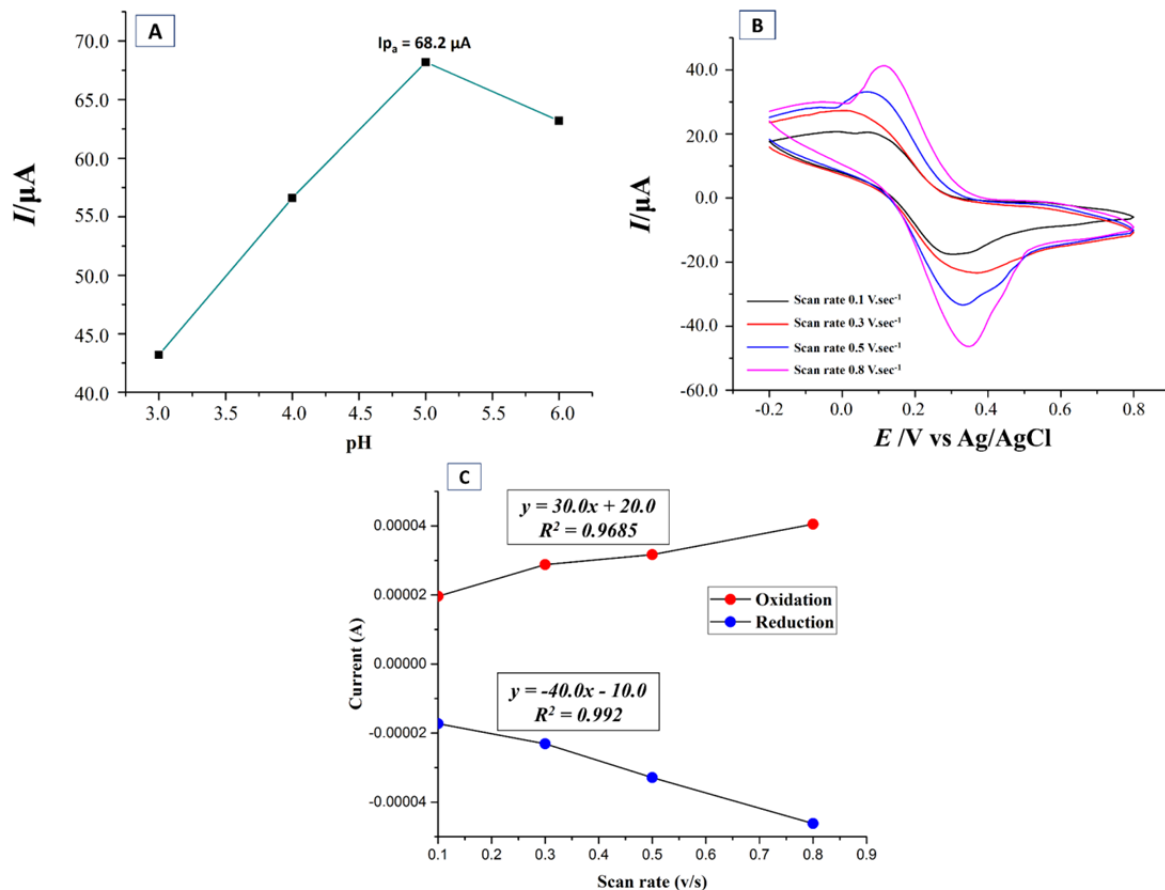


Fig. 5. (A) Effect of electrolyte supporting pH; (B) Voltammogram profile with different scan rate, and (C) Scan rate variation of CPE/TiO₂-BEK6 electrode

Fig. 4. explained that the BEK6 role as chelate agent to incarcerate Pb²⁺ ion so the ions distribution and electron convenient in the electrochemical system. Subsequently, the electron transfer forwarded on a working electrode was containing the CPE/TiO₂ to high electron energy and electron stability to the Potentiostat detected [29].

3.3. Effect of pH and scan rate variation

The pH range of 3-6 was chosen in studying the pH effect of supporting electrolyte on the performance of CPE/TiO₂-BEK6 in detecting Pb²⁺ ion. Fig. 5A shows the effect of pH on I_{pa}

of Pb^{2+} ion, where the citrate buffer pH 5 gives the highest I_{pa} of $\pm 68.2 \mu\text{A}$. The use of $\text{pH} > 5$ causes the peak current decrease. This is because at the pH near to base cause Pb^{2+} ion start to settle in the form of hydroxide compound $\text{Pb}(\text{OH})_2$ that will reduce the number of Pb^{2+} ion moving on the surface of the electrode.

Based on the scan rate variation (Fig. 5B,C), it is seen that the scan rate potential has a linear relationship to the peak current of the Pb^{2+} ion, where the greater the scan rate potential the movement of Pb^{2+} ion from the bulk solution to the electrode surface becomes so rapid the peak current is also higher. In addition, the increased scan rate potential causes E_{pa} and E_{pc} shifted towards a more positive direction. The plot of I_{pa} and I_{pc} to the scan rate potential shows the linear relationship with the equations were $I_{pa} = 30.0x + 20.0$ ($R^2 = 0.96$) and $I_{pc} = -40.0 \times 10.0$ ($R^2 = 0.99$). These results suggest that the redox process on the electrode surface is affected by diffusion controlled [30].

3.4. Selectivity BEK6

The selectivity of BEK6 studied in a solution containing 0.1 ppm Pb^{2+} ion in the presence of Ni^{2+} as disturbing ions whose concentrations varied.

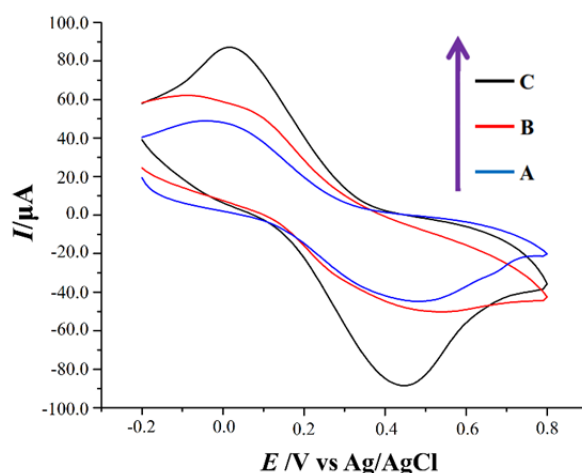


Fig. 6. Selectivity of BEK6 in a solution containing Pb^{2+} ion in the presence of Ni^{2+} ions : (A) 0.1 ppm; (B) 0.05 ppm; and (C) 0.01 ppm

The presence of Ni^{2+} ion gives a significant effect on the potential and current values of the Pb^{2+} ion (Fig. 6). In addition, the presence of Ni^{2+} ion was decreased the peak currents causes the electron transfer become longer and electrochemical properties turn towards reversible quasi. Fig. 6 shows that determination of selectivity using CPE/ TiO_2 -BEK6 composite with increasing concentration of Ni^{2+} as interfering ion causes the peak current was decreasing of Pb^{2+} ion. This condition due to Ni^{2+} as interfering ion attached on the working electrode surface so the number of Pb^{2+} ion on the electrode surface is reduced.

Based on the above results indicated by the addition of Ni²⁺ interfering ion can impair the performance of CPE/TiO₂-BEK6 in Pb²⁺ metal analysis.

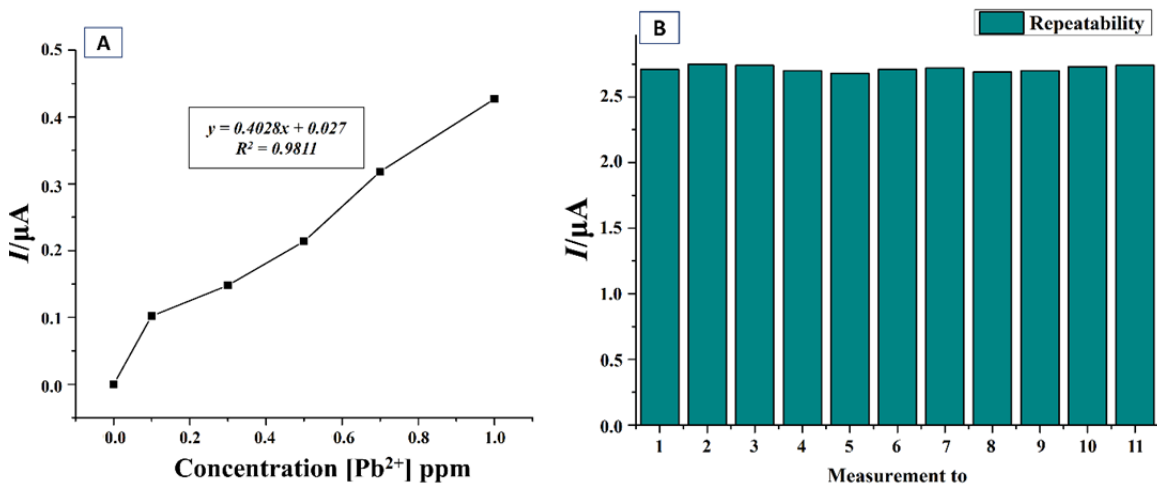


Fig. 7. (A) I_{pa} ion value Pb^{2+} on various concentration variations; (B) current stability of CPE/TiO₂-BEK6 to Pb^{2+} ion

Table 2. LOD determination of CPE/TiO₂-BEK6 against Pb^{2+} ion

Concentration [Pb^{2+}] ppm	Current (μA) (y)	y_1	$(y-y_1)$	$(y-y_1)^2$
0.0	0.0	0.027	-0.027	0.000729
0.1	0.102	0.068	0.033	0.001150
0.3	0.148	0.086	0.061	0.003768
0.5	0.214	0.113	0.100	0.010162
0.7	0.318	0.155	0.162	0.026539
1.0	0.427	0.198	0.228	0.051988
SUM				0.094339
Standard Deviation (STD)				0.023584
Slope				0.4028
Intercept				0.027
LOD				0.17565

3.5. Limit Detection and Stability of CPE/TiO₂-BEK6

Limit detection is determined by varying the concentration of Pb^{2+} ion in the range 0.1-1.0 ppm. Measurements in the concentration range produce linear curve I_{pa} with value $R=0.98$ and LOD value 0.17565. The stability of CPE/TiO₂-BEK6 was determined by measuring I_{pa} Pb^{2+} ion using 11 electrodes. Based on the histogram of Fig. 7B, CPE/TiO₂-BEK6 has good stability in Pb^{2+} ion measurements with RSD% value of 0.83. Table 2 shows the results of current measurements in detecting Pb^{2+} ion in different concentration variations. This condition inhibits the probability of measurement accuracy with STD data of

0.02. It is a good accuracy and precision performance of CPE/TiO₂-BEK6 electrode for determining metal ion.

4. CONCLUSION

The presence of CPE/TiO₂-BEK6 composite significantly increases the current of oxidation peak and the Pb²⁺ ion reduction. The combination of CPE/TiO₂-BEK6 composite shows excellent performance in facilitating the electron transfer process at the electrode surface. The high-stability has shown the CPE/TiO₂-BEK6 with value R=0.98; LOD value 0.17565; and RSD% value of 0.83. It is used in the determination of Pb²⁺ ion by using voltammetry method as an early stage in obtaining a new composite material with high sensitivity and selectivity.

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