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Electrochemical response of carbon paste electrode modified with mixture of titanium dioxide/zirconium dioxide in the detection of heavy metals: Lead and cadmium

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ABSTRACT

A novel carbon modified electrode was developed by incorporating titanium dioxide/zirconium dioxide into the graphite carbon paste electrode to detect heavy metals—cadmium and lead. In this work, the development of the novel titanium dioxide/zirconium dioxide modified carbon paste electrode was studied to determine the optimum synthesis conditions related to the temperature, heating duration, amount and ratio of titanium dioxide/zirconium dioxide, and amount of surfactant, to create the most reproducible results. Using cyclic voltammetric (CV) analysis, this study has proven that the novel titanium dioxide/zirconium dioxide can be utilized to detect heavy metals—lead and cadmium, at relatively low concentrations (7.6×10^{-6} M and 1.1×10^{-5} M for Pb and Cd, respectively) at optimum pH value (pH=3). From analyzing CV data the optimal electrodes surface area was estimated to be 0.028 ($\pm$0.003) cm^2. Also, under the specific experimental conditions, electron transfer coefficients were estimated to be 0.44 and 0.33 along with the heterogeneous electron transfer rate constants of 5.64×10^{-3} and 2.42×10^{-3} (cm/s) for Pb and Cd, respectively.

1. Introduction

With the expanding field of electrochemistry, there are various types of electrodes that have been proposed for heavy metal analysis. Of these many electrodes, carbon paste based sensors have gained a great deal of attention. This is due to the many advantages of carbon paste sensors. Generally, carbon paste electrodes (CPEs) exhibit low background current, large potential window, high conductivity, and long lifetime [1,2]. Furthermore, besides the exceptional mechanical stability, CPE is one of the simplest templates to construct [3]. The bare CPE is made by packing carbon paste (mixture of graphite powder and binding liquids) into a holder, such as a glass tube, which has a metal wire for electrical contact. It is worth mentioning that, unlike other solid electrode templates whose compositions are fixed, CPE can be custom-made by varying the ratio of the paste components for specific packing design [1]. Besides the ease of construction, which is a valuable characteristic in term of mass production suitability, CPEs are also relatively cheap and quick to produce [2,4,5], which are attractive features for commercial utilization. Moreover, CPE represents one of the most flexible substrates for preparing modified electrodes. The modifying reagents can be mixed directly into the carbon paste (most often used technique due to simplicity), mechanically coated onto CPE, or electrochemically deposited onto CPE [1,3]. In this study, the use of a novel titanium dioxide/zirconium dioxide (TiO_2/ZrO_2) carbon paste composite electrode in the detection of lead (Pb) and cadmium (Cd) in aqueous environment will be discussed.

The negative impacts of lead and cadmium in the environment have been well examined and documented. The contamination of these heavy metals in water bodies is a general environmental concern across the world. Lead and cadmium are dispersed in the environment primarily through anthropogenic activities such as mining/smelter, manufacturing of industrial products (mostly batteries), fuel burning, and waste incineration. Short and long-term exposure to lead and cadmium has been linked to cardiovascular disorders, skeletal muscular disorders, respiratory diseases, nervous system disorders, cancers, and other illnesses [6,7].

As mentioned previously, our research group has recently developed a (TiO_2/ZrO_2) carbon paste composite electrode that is capable of quantifying Pb and Cd in aqueous environment. In this study, cyclic voltammetry was utilized to study the electrochemical behavior of the novel working electrode toward quantification of Pb and Cd. In the past, pure titanium dioxide (TiO_2) and pure zirconium dioxide (ZrO_2) have been utilized in developing sol–gel film materials which have been shown to possess good

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electro-catalytic properties, which are beneficial in enhancing electrode sensitivity [8,9]. However, to the best of our knowledge, this is the first time titanium isopropoxy and zirconium propoxy have been chemically incorporated into carbon paste to synthesize a mixed carbon paste composite sensor for the detection of heavy metals. Due to the solid/dry nature of the new TiO_2/ZrO_2 carbon paste composite electrode, this sensor does not need special storage accommodation, as it is not susceptible

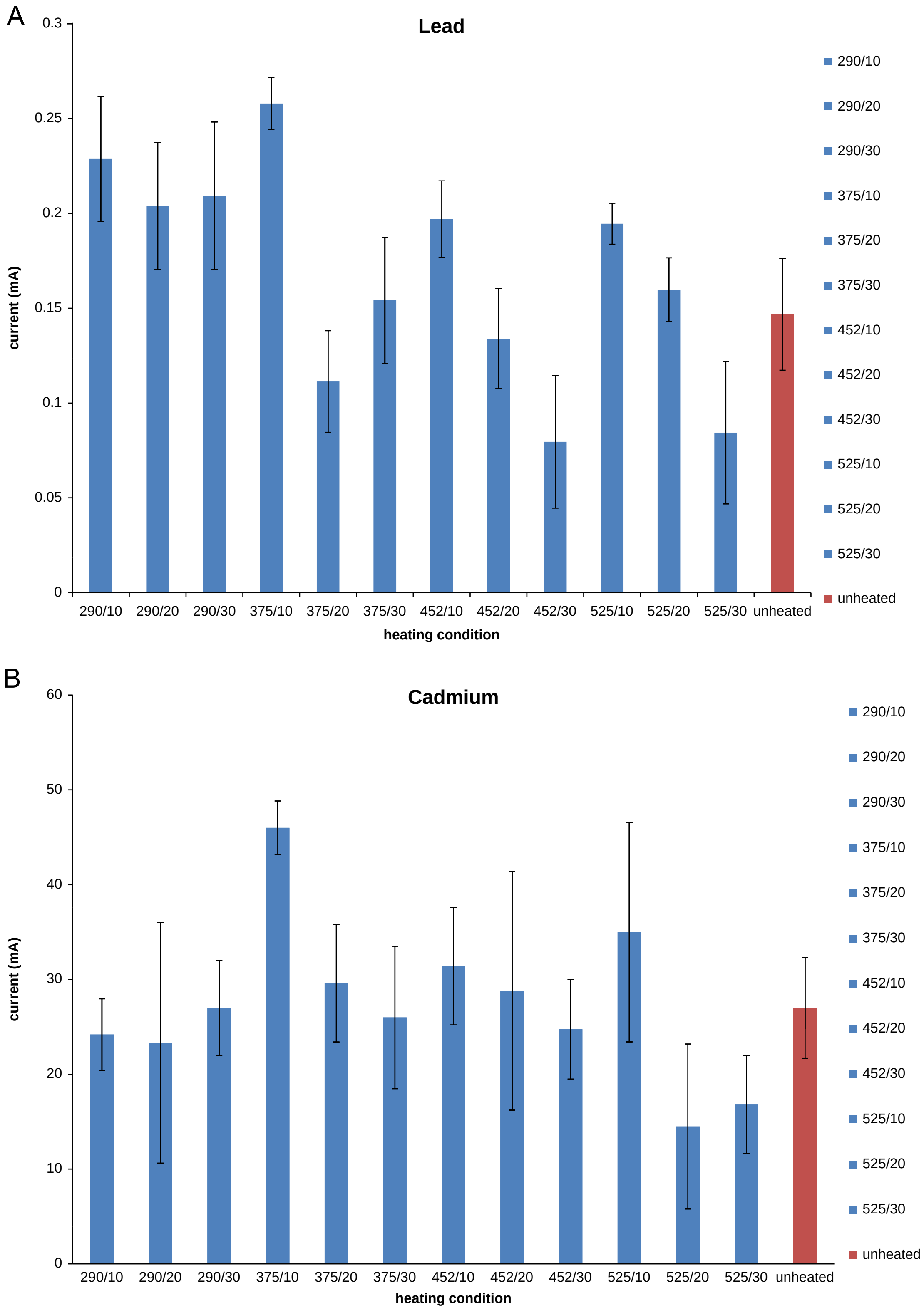

Fig. 1. (A) Heating optimization data for lead (average oxidative current, obtained from CV run in 0.01 M Pb in 0.1 M ATFB) and (B) heating optimization data for cadmium (average oxidative current from multiple independent electrodes, obtained from CV run in 0.01 M Cd in 0.1 M ATFB). Error bar represents ± 1σ.

to shrinking, swelling, and leaching like polymer films and metal films modified electrodes [10,11]. Our goal is to create an eco-friendly sensor that not only has the catalytic properties for detecting Pb and Cd, but also has the characteristics suitable for mass product and commercial usage (affordability, selectivity, mechanical stability, and physical rigidity).

2. Experimental

2.1. Chemicals and materials

Methyltrimethoxysilane (MTMOS), Ti(IV) isopropoxy, Zr(IV) propoxy, Tween 80, Tween 20, Ammonium Tetraflouroborate (ATFB)

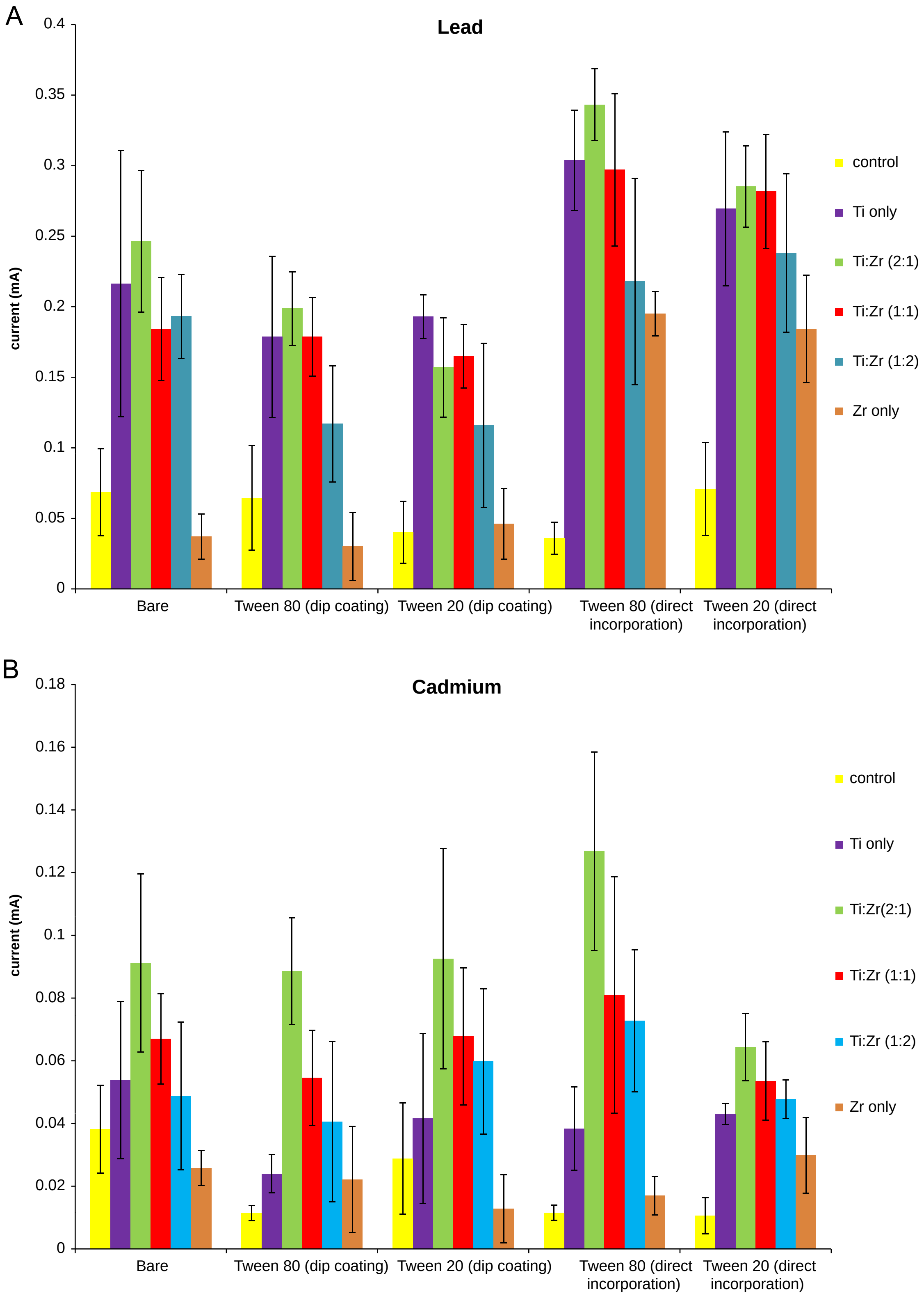

Fig. 2. (A) TiO_2/ZrO_2 ratio and surfactant application optimization data for lead and (B) TiO_2/ZrO_2 ratio and surfactant application optimization data for cadmium (average oxidative current from multiple independent electrodes obtained from CV run in 0.01 M Pb and 0.01 M Cd in 0.1 M ATFB solution). Error bar represents $\pm 1\sigma$.

(99+%), $Pb(NO_3)_2$, $Cd(NO_3)_2\cdot 4H_20$, $K_2Fe(CN)_6$ were purchased from Sigma-Aldrich. Capillary tubes (1.5–1.8 mm I.D., 10 cm, borosilicate glass opened both ends) were from Kimble Chase. Graphite powder (7–11 μm, 99%) was from Alfa Aesar. Acetate buffers (made by titrating appropriate volume of 0.1 M sodium acetate into 0.1 M acetic acid) and 1 M HNO_3 were used for pH adjustment (pH range 1–7).

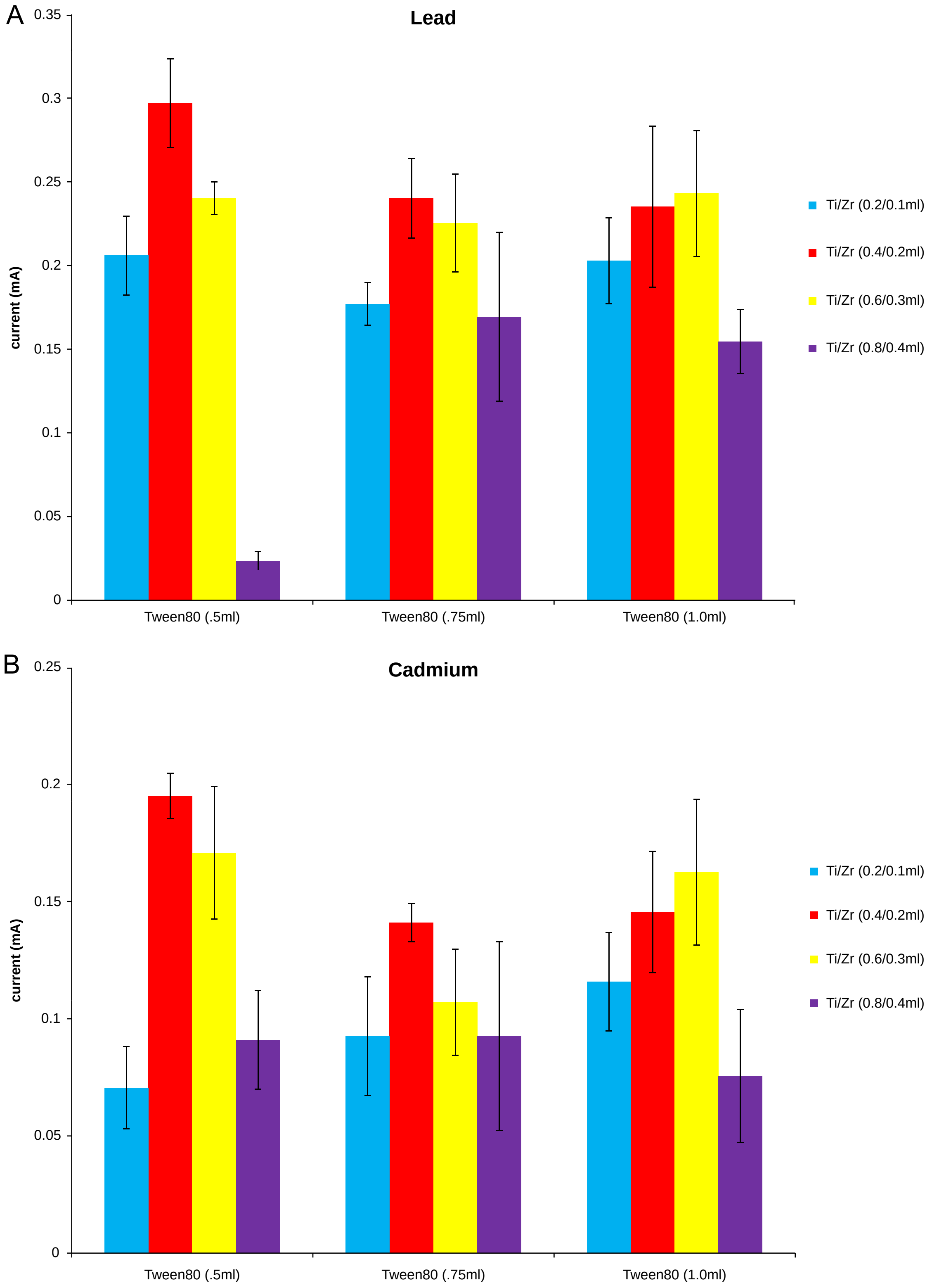

Fig. 3. (A) TiO_2/ZrO_2/Tween 80 volume loading optimization data for lead and (B) TiO_2/ZrO_2/Tween 80 volume loading optimization data for cadmium (average oxidative current from multiple electrodes, obtained from CV run in 0.01 M Pb and 0.01 M Cd in 0.1 M ATFB). Error bar represents $\pm 1\sigma$.

2.2. Apparatus

All cyclic voltammetric measurements were carried out on Bioanalytical System Epsilon, utilizing three electrodes electrochemical cell with TiO_2/ZrO_2 carbon paste composite electrode as working electrode, Ag/AgCl (3 M NaCl) as reference electrode, and platinum wire as auxiliary electrode. All cyclic voltammetric experiments were carried out at room temperature.

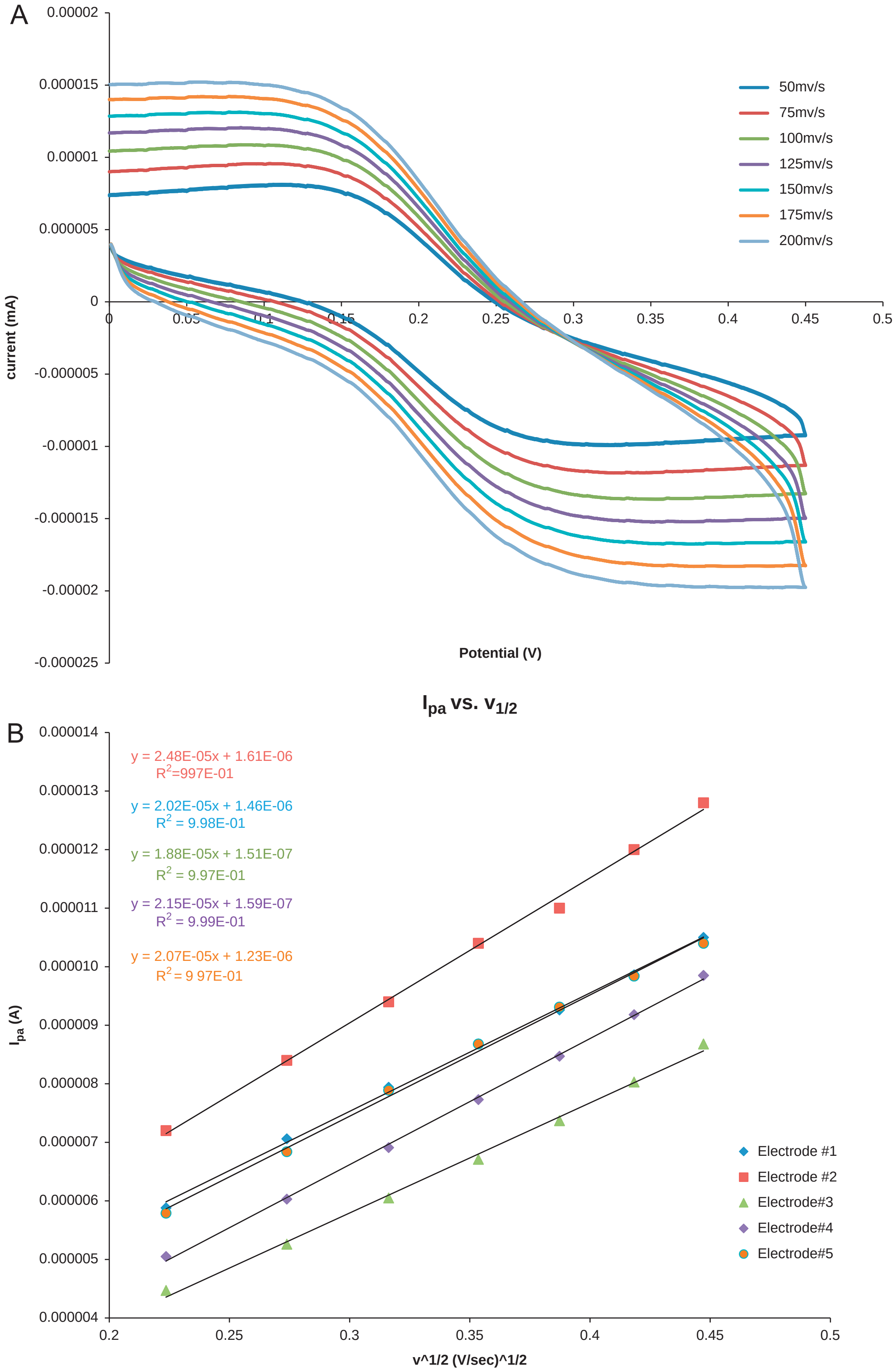

Fig. 4. (A) CV of 1 mM $Fe(CN)_6^{4-}$ (in 0.1 M ATFB) at various scan rates (50–200 mV/s) and (B) Plot of I_{pa} vs. $v^{1/2}$.

2.3. *Preparation of the optimal TiO_2/ZrO_2 carbon paste composite electrode.*

3 g of graphite powder was added into a mixture of 1.5 mL MTMOS, 0.3 mL 1 M H_2SO_4, 0.5 mL isopropanol, 0.4 mL Ti(IV) isopropoxy, 0.2 mL Zr(IV) propoxy, and 0.5 mL Tween 80. This mixture is thoroughly mixed in a borosilicate glass vial to form a homogenous carbon paste material. A copper wire (0.5 mm O.D., 12.5 cm long) is inserted into the capillary tube, the copper wire serves as the electrical contact component. The carbon paste mixture above was manually packed into the capillary tube with the copper wire and allowed to be set at room temperature. After 15 min of setting time, the carbon paste electrode was heated for optimized results at 10 min at 375 °C and allowed to be cooled and set naturally at room temperature for 24 h before utilized. Other heating temperatures tested were 290 °C, 452 °C, and 525 °C at varied times of 20 and 30 min as well.

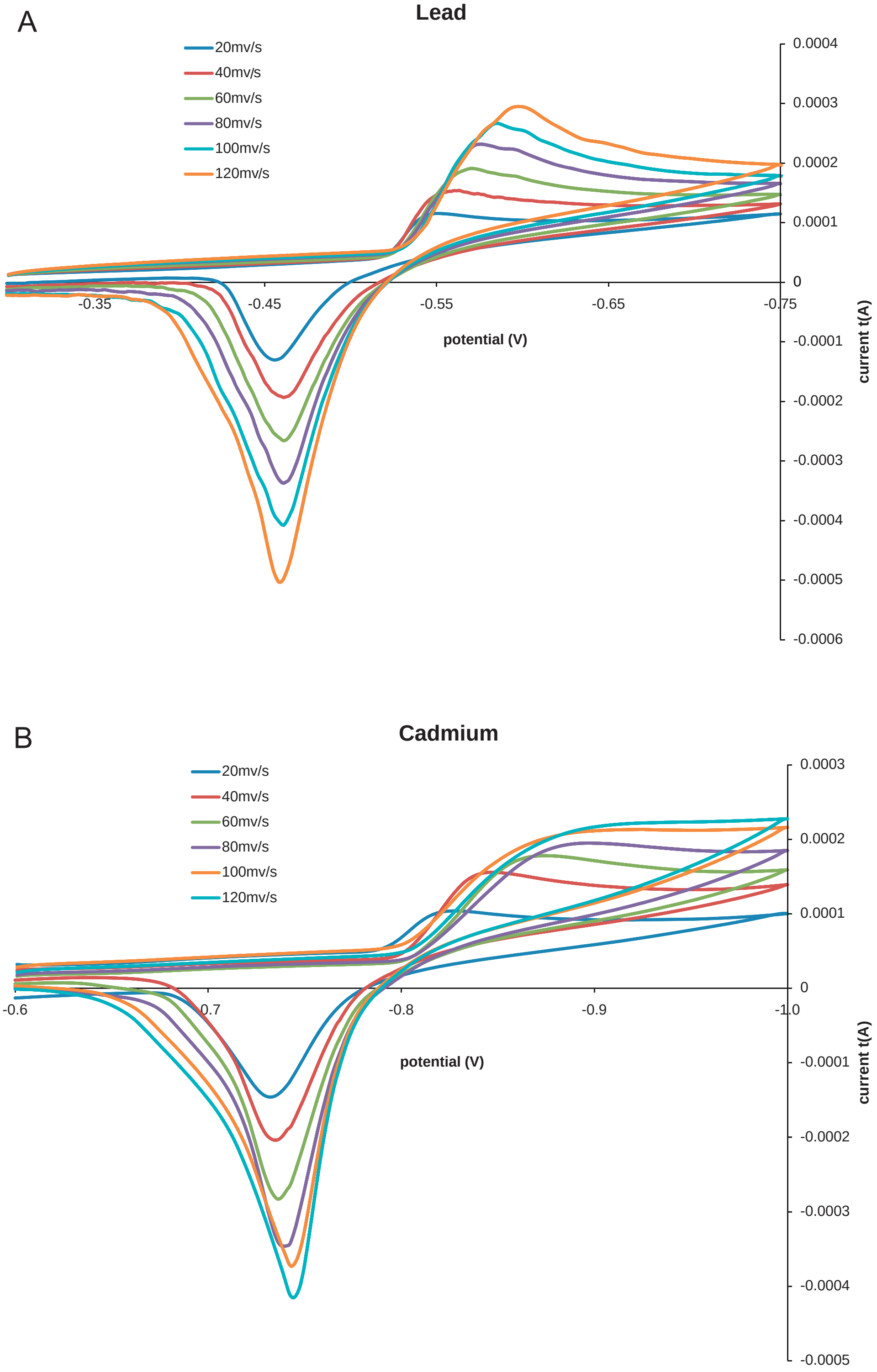

Fig. 5. CV of 0.01 M Pb (A) and 0.01 M Cd (B) (in 0.1 M ATFB) at various scan rates (20–120 mV/s).

3. Results and discussion

3.1. Optimization of electrode synthesis parameters

3.1.1. Optimization of heating temperature and duration

For optimization of heating conditions, the following temperatures were chosen: 290 °C, 375 °C, 452 °C, and 525 °C, and the selected heating durations were: 10, 20, and 30 min. The electrode carbon paste used for heating optimization had the following composition: 1.5 mL MTMOS+0.3 mL 1 M H_2SO_4+0.5 mL isopropanol +Ti isopropoxy/Zr propoxy (0.3 mL each)+3 g carbon. Heating is known to help with the annealing process as well as developing the electrode crystalline surface structure [12–15]. The range of heating temperature above was selected because too low temperature would not be sufficient to develop the surface structure, while too high temperature would lead to surface cracking thus

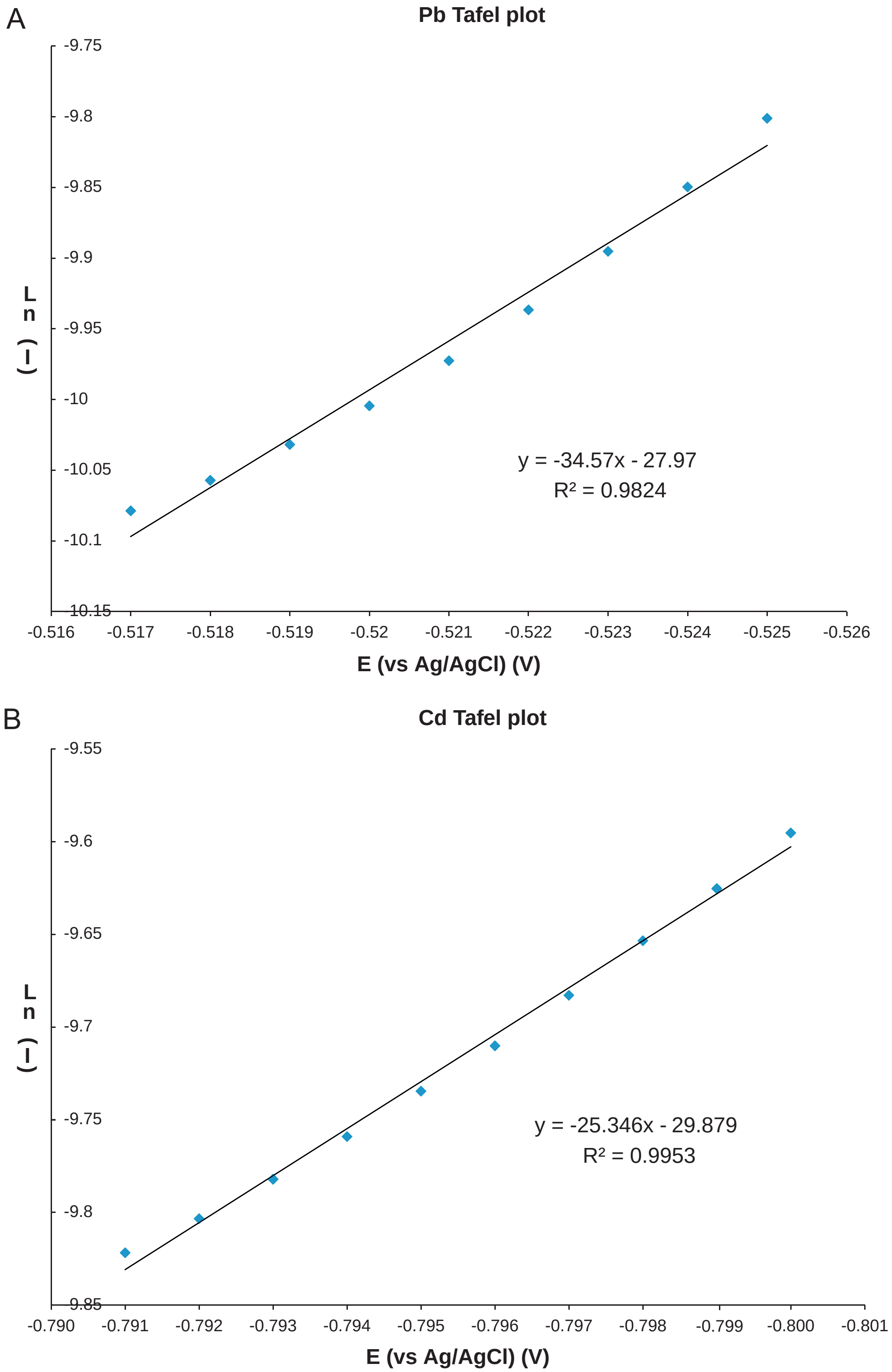

Fig. 6. Tafel plot of Pb (A) and Cd (B) (plot of ln(I) vs. E of rising portion of cathodic branch at 20 mV/s).

damaging the electrode surface [16,17]. For the same reasons, the heating durations above were selected. By running cyclic voltammogram (CV) of the different electrodes heated at different temperature/duration combinations in 0.01 M Pb and 0.01 M Cd solutions (in 0.1 M ATFB supporting electrolyte), the oxidative current magnitudes were collected and compared. For each heating condition combination, data from multiple different electrodes were collected.

Fig. 1 illustrates that, for both heavy metals, the overall trend appeared to be increasing heating time meant lower response (this can be understood as the result of overheating). Furthermore, at the heating combination of 375 °C/10 min, the electrode response appeared to be optimum for both heavy metals, but for cadmium it was much more obvious compared to lead. Therefore, 375 °C/10 min was selected to be the optimal heating condition combination for the TiO_2/ZrO_2 carbon paste composite working electrode.

3.1.2. *Optimization of TiO_2/ZrO_2 ratio and surfactant application*

The next parameter of optimization was the ratio of TiO_2 and ZrO_2. For this step the following TiO_2/ZrO_2 ratios (volume:volume) were chosen: (2:1), (1:1), (1:2), only TiO_2, and only ZrO_2 (constant total volume of 0.6 mL). For the control electrode, 0.6 mL of high-quality water is used instead of TiO_2 or ZrO_2. For surfactant variability, two surfactants were chosen (Tween 20 and Tween 80), which are both polysorbate surfactants. These surfactants were found to improve the crystalline process of TiO_2 and ZrO_2 after heating and help homogenizing the sensor surface thus enhancing the electrocatalytic activity of the electrode surface [8,9,18]. For applications of these surfactants, two different methods of applications were tested. The first method was dipping of the electrode into the surfactants before heating, and the second method was direct incorporation of the surfactants (0.5 mL) into the carbon paste composite. The electrodes prepared via dipping into surfactants appear to be burned at the surface after heating. All electrodes were heated at optimal heating conditions previously established (375 °C for 10 min). Similar to optimization of heating condition, the oxidative current magnitude data from multiple independent different electrodes were collected and compared by running CV in 0.01 M Pb and 0.01 M Cd (in 0.1 M ATFB) solutions.

From data in Fig. 2, it is observed that, for lead and cadmium, the electrodes that were modified with TiO_2 and (or) ZrO_2 appeared to be more sensitive than the control ones (control—without TiO_2 or ZrO_2; bare—no Tween 80 or Tween 20). Furthermore, the general trend, with a few exceptions, was that the sensitivity appeared to be best for TiO_2/ZrO_2 (2:1) compared to other ratios of (1:1), (1:2), only TiO_2, then lastly only ZrO_2, regardless of surfactant application. For Pb, it was more apparent that surfactant application via direct incorporation into carbon paste was better, but the same conclusion cannot be drawn for Cd data (Fig. 2B). Overall, the electrode made with TiO_2/ZrO_2 (2:1) and Tween 80 (0.5 mL) directly incorporated appeared to be most sensitive for both metals. Therefore, 2:1 TiO_2/ZrO_2 ratio and Tween 80 (0.5 mL) direct incorporation was selected as the optimal modification quantity.

3.1.3. *Optimization of TiO_2/ZrO_2 Tween 80 volume loading*

Once the TiO_2/ZrO_2 ratio as well as surfactant type and surfactant application method were optimized, the total volume of TiO_2, ZrO_2 and loading volume of Tween 80 would be the next parameters to be optimized. Using the optimal ratio of TiO_2/ZrO_2 (2:1) the total volumes were varied from 0.3 mL to 1.2 mL (increasing at 0.3 mL increment). Also, the volume loading of Tween 80 were varied from 0.5 mL to 1 mL (increasing at 0.25 mL increment). Using CV, the oxidative current magnitude data were collected and compared (0.01 M Pb and 0.01 M Cd (in 0.1 M ATFB) solutions).

According to data presented in Fig. 3, it is observed that, for both Pb and Cd, at Tween 80 volume of 0.5 mL and 0.75 mL, the response was best for TiO_2/ZrO_2 total volume of 0.6 mL. While at Tween 80 volume of 1 mL, the response appeared to be best at

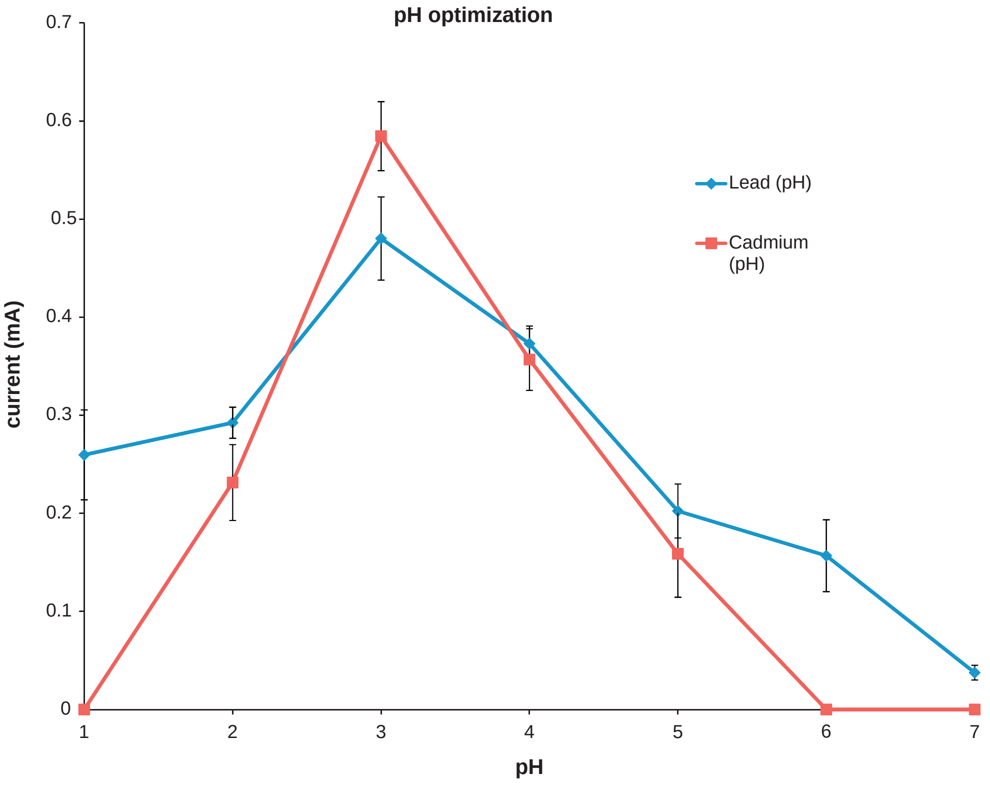

Fig. 7. Oxidative current variation with pH (CV ran in 0.01 M Pb and 0.01 M Cd); pH adjusted using acetate buffers and 1 M HNO_3.

TiO_2/ZrO_2 total volume of 0.9 mL. One important factor to note was that, for increasing TiO_2/ZrO_2 total volume, the carbon paste became much thicker and harder to pack. Overall, the electrodes made with total TiO_2/ZrO_2 volume of 0.6 mL and 0.5 mL Tween 80 were the most sensitive for both metals; therefore, this combination of TiO_2/ZrO_2/Tween 80 volume loading was chosen for subsequent electrode synthesis.

3.2. Estimation of electrode surface area

The electrode surface was estimated using the Randles–Sevcik equation [19–21]

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

In which I_p represents peak current, n is the number of electron transfer, C is the solution concentration, A is the electrode surface area, D is the diffusion coefficient, and v is the scan rate. Using the reference compound potassium hexacyanoferrate (II) at 0.001 M, CV's of this solution were obtained at various scan rates (from 50 to 200 mV/s, at 25 mV/s increment increase). By measuring the anodic peak current, which reflected the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$, at various scan rates and by plotting these peak current magnitude vs. square root of the scan rate, a linear fit with the electrode surface area equal to slope/$(269 \times n^{3/2} \times D^{1/2} \times C)$ was obtained.

From the data presented in Fig. 4, the average estimated electrode surface area is calculated to be 0.028 ± 0.003 cm^2 ($D = 7.6E-6$ cm^2/s [22], $n = 1$). This value is acceptable because with the assumption of a flat surface, the average electrode area

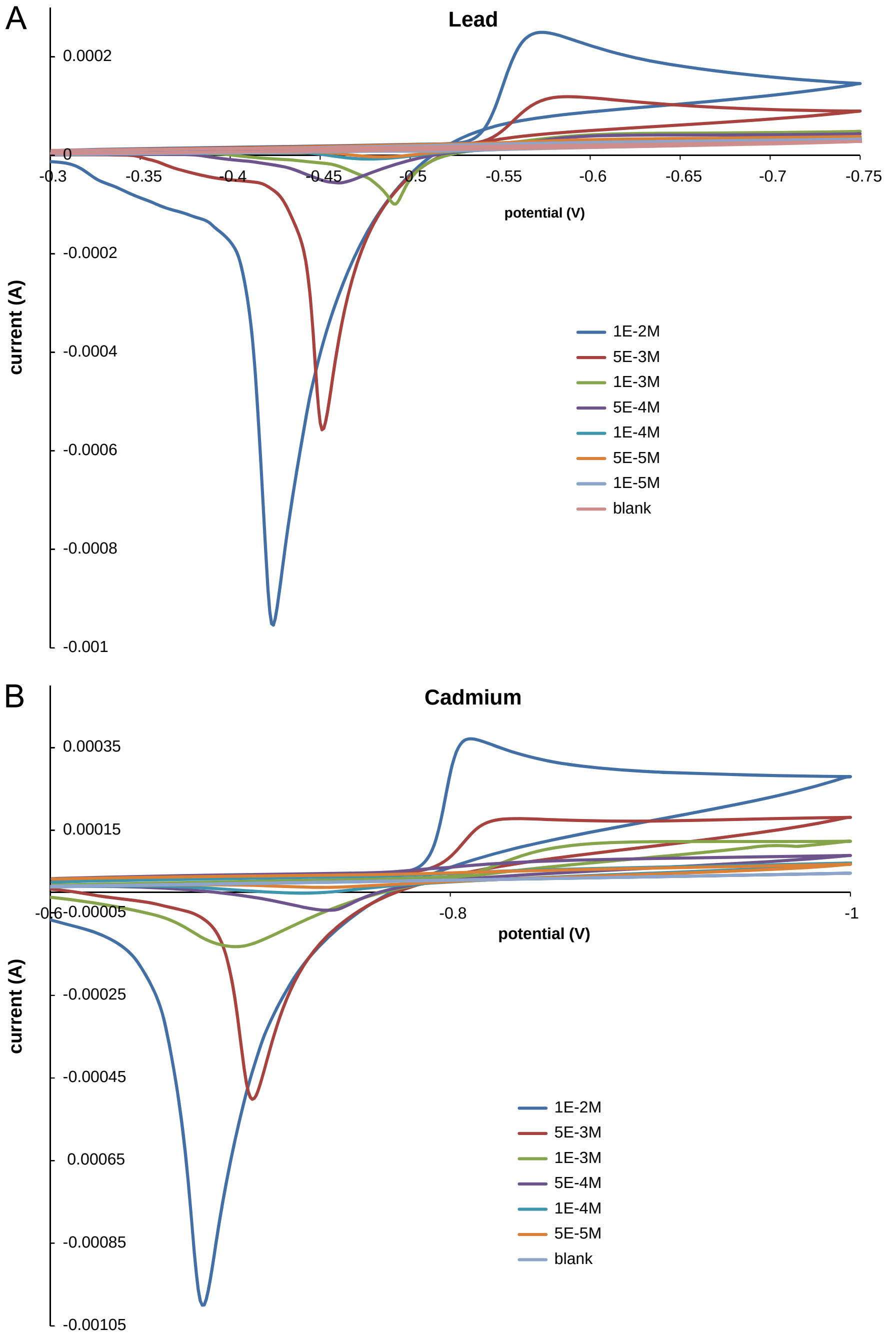

Fig. 8. CV of Pb (A) and Cd (B) at different concentrations, pH = 3.

would be approximately 0.021 cm^2 (assuming the average opening diameter of the capillary tube to be 0.165 cm). The increase in electrode surface area could be accounted for the presence of surface micro-structures.

3.3. *Estimation of kinetic parameters—electron transfer coefficient (α) and heterogeneous electron transfer rate constant (k_0).*

The simple Tafel plots (Fig. 6) were constructed by plotting the potential vs. natural log of current in the rising portion of the cathodic branch. These plots would be approximately linear with the slope equal to $-\alpha nF/RT$, in which alpha is a kinetic parameter known as the electron transfer coefficient. From this relationship, the electron transfer coefficients for Pb and Cd redox systems ($n=2$), using the optimal TiO_2/ZrO_2 carbon paste composite electrode were estimated to be 0.44 and 0.33, respectively. These results were reasonable as visual inspection of the voltammogram indicated that the cathodic branch of the voltammogram was much broader compared to the anodic branch. The slow scan rate of 20 mV/s was chosen because at this scan rate the redox process would still be predominantly kinetic dependent, while at higher scan rates, the redox process would become more diffusion control as indicated by the broadening of both the anodic and cathodic peaks (Fig. 5).

Using the method described by Nicholson [23], the heterogeneous electron transfer rate constant of a redox couple can be estimated. This parameter reflected the rate of electron transfer between the redox system and the electrode surface (at formal potential). Furthermore, this parameter would be quite useful in determining the reversibility of a redox couple under specific conditions. Nicholson had published the relationship between the electron transfer rate constant and the function psi (Ψ). Working curve of this function psi relates to ΔEp has been published [23,24] to be used for estimation of k_0 by measuring ΔEp and relating that to psi at various scan rates. Using the optimal TiO_2/ZrO_2 carbon paste composite working electrode, k_0 values were estimated to be 2.42×10^{-3} and 5.64×10^{-3} cm/s for Cd and Pb, respectively. The diffusion coefficients used for k_0 calculations for Pb and Cd ions were from Valente et al. [25] and Macero and Rulfs [26]. These results indicated that both Pb and Cd redox systems at the new electrode surface were quasireversible under the current experimental setup/conditions as redox couples with k_0 values between 2×10^{-2} and 3×10^{-5} cm/s would be classified as quasireversible [27].

3.4. *Optimization of pH*

From Fig. 7, it was observed that, at pH of 1, 6, and 7, the electrode did not respond for detection of Cd. This could be due to hydrogen and hydroxide ion activity at large negative potential, which resulted in sufficiently large charging background current that masked the oxidation peak current. This problem, however, was not as severe for Pb as the potential range for redox of Pb is not as negative compared to that of Cd. Overall, it was observed an increase in peak current magnitude as pH increases from 1 to 3, at pH of 3, the electrode appeared to be most sensitive. Furthermore, beyond pH of 3, the peak current magnitude decreased gradually with increasing pH. From these results, the functional pH range of the novel working electrode for detection of Pb would be between 1 and 7, while the functional pH range for Cd would be between 2 and 5, with the optimal pH appeared at 3 for both metals.

3.5. *Linear response range and detection limit of Pb and Cd using CV*

Figs. 8 and 9 illustrates the range of linear detectability for these heavy metals with the TiO_2/ZrO_2 carbon paste composite electrodes. Thus, using the optimal TiO_2/ZrO_2 carbon paste composite electrode,

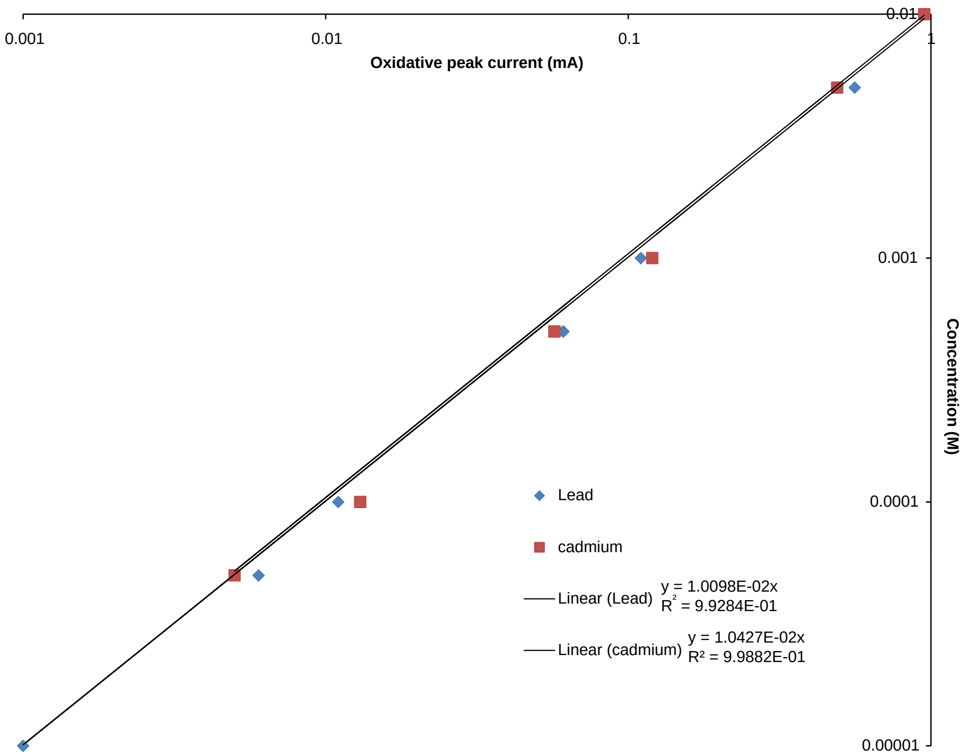

Fig. 9. Linear response plot of Pb and Cd (oxidative peak current vs. metal ion concentration) in log–log scale.

the linear response ranges were found to be from 1×10^{-2} M to 1×10^{-5} M for Pb and from 1×10^{-2} M to 5×10^{-5} M for Cd via cyclic voltammetric analysis. Moreover, from 10 independent blanks, the detection limit of Pb and Cd were estimated to be 7.6×10^{-6} M and 1.1×10^{-5} M, respectively. The detection limits were estimated using 3 sigma method, which the detection limit equal to blank signal plus 3 times the blank standard deviation.

3.6. Performance/sensitivity comparison between the optimal TiO_2/ZrO_2 carbon paste composite electrode and the unmodified carbon paste electrode (CPE).

From Fig. 10, it can be seen that the sensitivity, for both metals, of the optimal TiO_2/ZrO_2 carbon paste composite electrode is much higher compared to that of the unmodified CPE. Furthermore, when

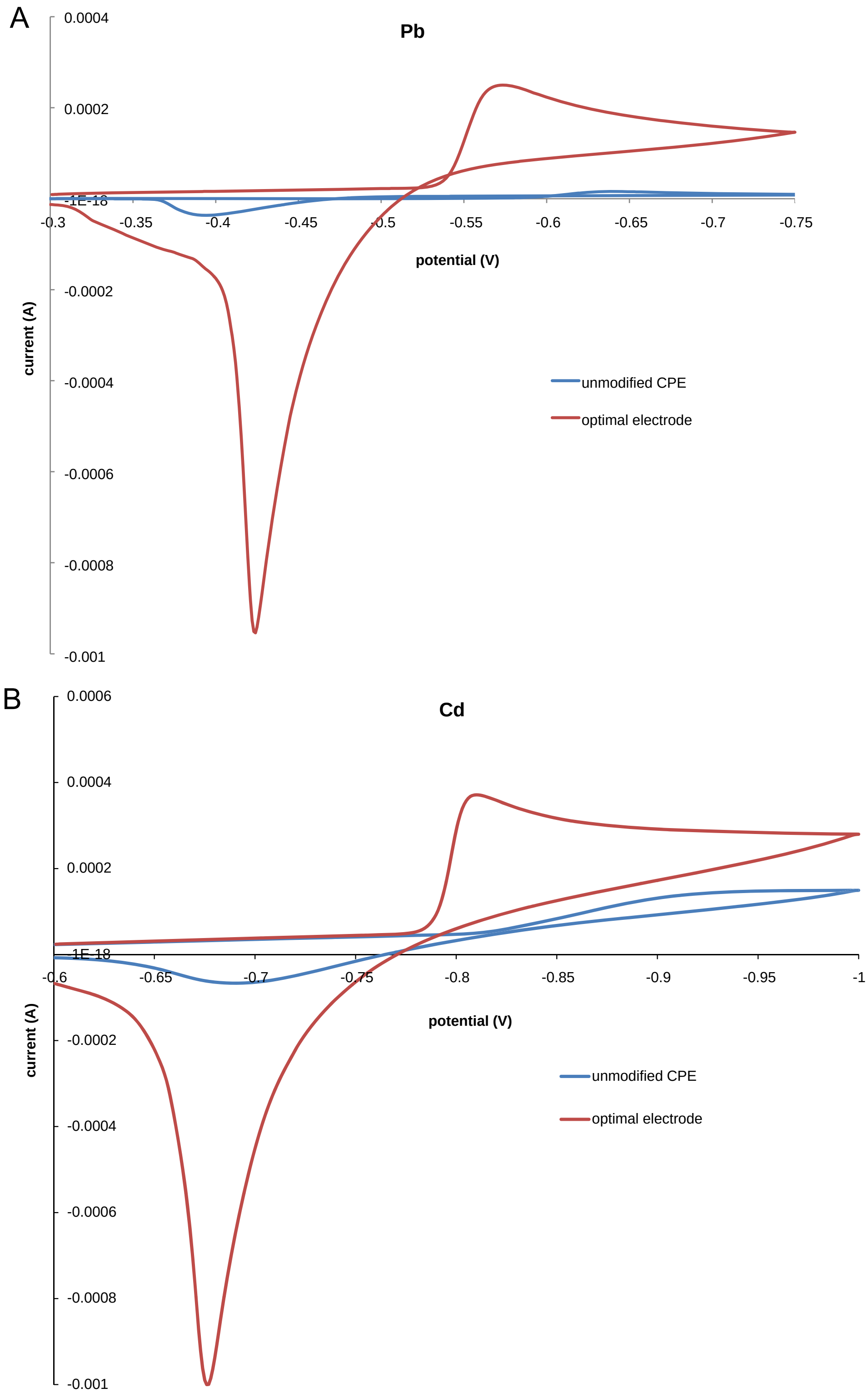

Fig. 10. Comparison between optimal TiO_2/ZrO_2 carbon paste composite electrode and unmodified CPE, Pb (A) and Cd (B) (CV ran in 0.01 M Pb and 0.01 M Cd, pH=3).

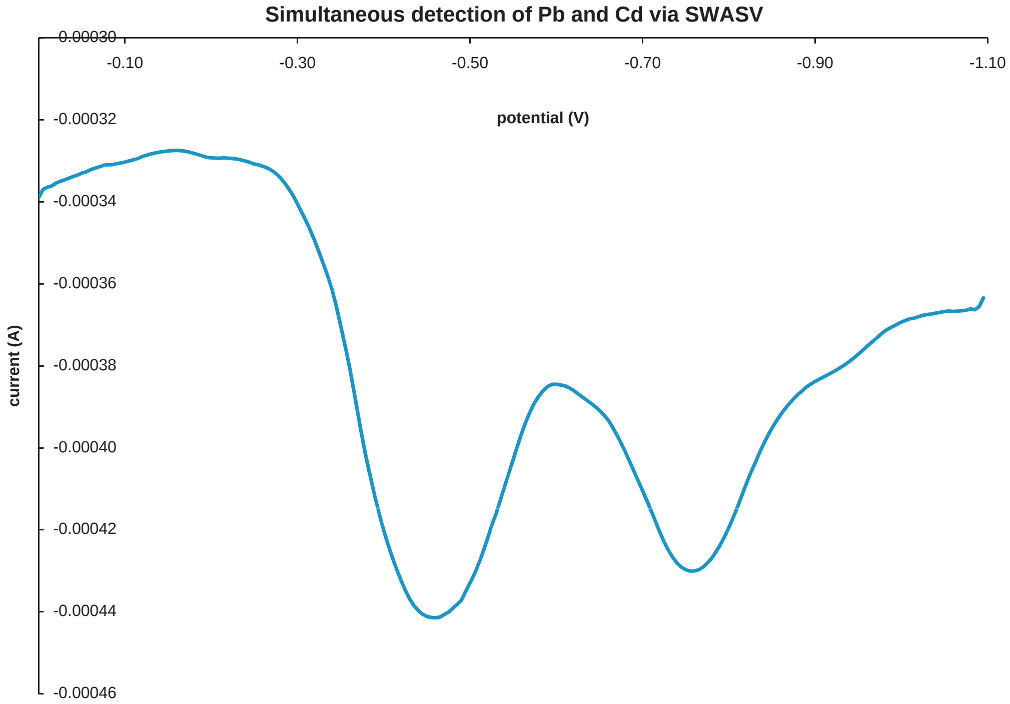

Fig. 11. Preliminary SWASV of Pb and Cd (at 1x10^{-6} M) using optimal TiO_2/ZrO_2 carbon paste composite electrode (deposition time = 120 s, deposition potential = −1.1 V, SW amplitude = 25 mV, SW frequency = 25 Hz, E step = 5 mV).

the optimal electrode was used, reversibility of both redox couples (Pb and Cd) appeared to be significantly improved (smaller peak potential separations) compared to when the unmodified CPE was employed. This data supported our hypothesis that the presence of TiO_2/ZrO_2/Tween 80 helped improve the electrode performance/sensitivity by enhancing the electrocatalytic activity of the modified electrode surface.

4. Conclusion

In this study, the novel electrode successfully developed TiO_2/ZrO_2 carbon paste composite electrode proved to be suitable for the detection and quantification of Pb and Cd in aqueous solution. It was found that by using cyclic voltammetry, the detection limits for Pb and Cd were estimated to be 7.6×10^{-6} M and 1.1×10^{-5} M, respectively, for this new working electrode. Since the sensitivity of cyclic voltammetry is limited by charging current, further study utilizing square-wave anodic stripping voltammetry to quantify Pb and Cd simultaneously will be conducted (preliminary result is shown in Fig. 11), along with analysis of real water samples. Additionally, in the future, analysis of the novel working electrode surface will be studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) to better understand the electrode surface morphology and chemical composition.

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