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Research paper

Detection of Cadmium by using Ionic Liquid Cellulose based Thin Layer

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Abstract

Ionic liquids have been successfully demonstrated as potential polymer electrolyte with high in conductivity. For sensing application field, ionic liquids based on detection method, performs uniquely with regard to sensing external environments. In this study, ionic liquid cellulose polymer electrolyte was successfully prepared for sensing layer of electrochemical sensor. The ability and sensitivity of the prepared ionic liquid cellulose based thin film as sensing layer on the electrochemical sensor was tested to detect cadmium in wastewater sample by using cyclic voltammetry, (CV). The optimization process was carried out, in which to ensure the electrochemical sensor could detect the cadmium at the best operating conditions. The selection of optimization process involved the effect of pH of the acetate buffer as supporting electrolyte and the effect of scan rate of the electrochemical sensor. The optimum pH of acetate buffer was 6.5 and the optimum scan rate of electrochemical sensor was 0.1 V/s. These optimized conditions were applied in detection of cadmium in the standard and wastewater sample solutions. The amount of cadmium in the wastewater sample was undetectable or below detection level. The sensitivity of the electrochemical sensor was compared to ICP-OES and the result showed that the electrochemical sensor was as applicable as ICP-OES since it can detect the amount of cadmium as low as ppb concentration. The use of ionic liquid cellulose based thin film as sensing layer of electrochemical sensor is a good alternative to detect the cadmium.

Keywords: *Cellulose Polymer Electrolyte; Electrochemical Sensor; Ionic Liquids.*

1. Introduction

Demand for clean and safe drinking water have led scientists to focus on the improvement of design and fabrication of biosensors to detect heavy metal ions in water. Many types of indicators have been suggested for facilitating the detection of heavy metal pollution. Heavy metals are natural component of the Earth's crust however are considered as hazardous compounds even at lower temperature [1]. According to "Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances, ASTDR", heavy metals are ranked in the top 10 in the listings. Thus, the maximum acceptable discharge level into the environment have been regulated by the World Health Organization (WHO) and Environmental Protection Agency (EPA) thereby monitoring the water pollution level [2].

Ionic liquids have been known for a long time a potential for green chemistry application. A typical ionic liquid is made of bulky organic cations and organic anions or inorganic anions which possess various chemical and physical properties [3]. Ionic liquids (ILs) are room temperature molten salts, which have been widely promoted as green solvent with melting points below 100 ^oC [4]. Ionic liquids have many known and potential cations and anions structure, as well as many hundreds of resulting combinations of ionic liquids [5]. The most promising property of ionic liquid is that they have good solvating ability for organic and organometallic compounds. The properties of ionic liquids can be varied over a wide range by the selection of suitable cations and anions which influenced by the properties such as melting point, viscosity and solubility characteristics [6]. Due to unique physicochemical properties of ionic liquids have proved to be essential to the development of electrochemical sensors and biosensors [3, 7].

Recently, it is noted that ionic liquids can dissolve in cellulose and carbohydrates. Basically, cellulose is a colourless, odourless, and nontoxic solid polymer and it have a very good properties, including biocompatible, hydrophilicity, relative, thermos stability, high sorption capacity, and changeable optical appearance, biodegradable, non-toxic, inexpensive natural material and is well soluble in ionic liquids with melting points below 100^{o}C [8]. Based on the structure of cellulose, the hydroxyls groups are reactive and through various reaction such as esterification, halogenation, and oxidation, it can be easily modified [9]. The interaction of ionic liquids and cellulose based-materials have been discussed theoretically in previous studies [10]. Since cellulose is well soluble with ionic liquids, the solubility in it depends on the origin, extent of polymerization, temperature of dissolution and water content. Cellulose can be regenerated in a variety of forms such as films, beads, by adding an anti-solvent for e.g. water to form ionic liquids cellulose solution [7]. Cellulose materials such as cellulose film, containing entrapped analytical reagents suitable for metal ion detection [11].

In the last two decades, ionic liquid based polymer electrolyte have attracted much attention because of their potential application in electrochemical devices [12]. There are prospects of new applications in which combining ionic liquids with polymer electrolyte where they surpass the performance of conventional media, improved safety and a higher operating temperature range. For example, batteries and fuel cells [13]. The field of polymer electrolyte is the study of ionic transport in materials where it made of chain polymers acting as electrolyte solvents or on the other hand the study of polymers that are polyionic and ion conducting themselves [14].

The accelerating urbanization and industrialization in developing countries with an enormous and rising in demand for heavy metals causes a high anthropogenic emission of the pollutants into the environment. Cadmium has been chosen as one of the heavy metals to be detected in this study since cadmium is a trace heavy metals and highly toxic elements. This is not only threatening human health through contamination of drinking water, but also aquatic ecosystem. Most heavy metals are well-known toxic and carcinogenic agents. Therefore, fast and accurate detection of metal ions is a critical issue [15]

Electrode of electrochemical sensor have been chosen for heavy metals trace analysis. The detection limits of the electrode determine the efficiency of the heavy metal trace analysis. Various factors such as poor electron transfer and low electrical conductivity could lead to poor detection levels. Thus, in enhancing the sensitivity of detection limits of the electrode, a few alternatives have been widely developed. Developing and modifying a good composite is one of the well-known alternatives. Shiddiky and Torriero research, suggested combining ionic liquid and cellulose, form stable composite materials [16]. This can be seen in stripping voltammetry that use carbon nanotubes with improved triphenylphosphine-ionic liquids composite shows detection of heavy metals have better analysis [17]. Screen Printed Carbon Electrode (SPCE) have been used widely by some researchers, with several different composites. Based on the previous studies, the composite mixture of ionic liquid is the most effective which produce better peaks and good analysis in detection of heavy metals analysis [18]. Better peaks produced narrow and sharp voltammogram in which will make detection of metal ions easier.

Nowadays, detection of heavy metals has been significant for environmental monitoring. Heavy metals pollution indicates serious health problems to humans as well as flora and fauna. In response to this problem, this study proposed ionic liquid polymer electrolyte as alternative method analysis in sensing layer of electrochemical sensor to detect heavy metals in wastewater. The present of the ionic liquid increase the conductivity, holding a very good thermal stability and wide potential window. Therefore, ionic liquid cellulose based thin film is synthesized and used to detect to the presence of heavy metals in trace for natural waters. Cellulose-based thin film is one of the matrices or solid support bearing immobilized analytical reagent. It also suitable for metal ion detection owing to its properties, inexpensive, readily available and widespread. Hence, this study then proceeds the sensing application field in detection of heavy metals of wastewater sample.

2. Method and Materials

2.1. Material

Ionic liquid of 1-methyl-1-propyl pyrrolidinium triflate [C_3C_1Pyrr] [OTf], methyl cellulose, deionized water, standard solutions of cadmium, standard solutions of lead and standard solutions of mercury, 0.2M acetic acid, 0.1M sodium acetate (0.01M acetate buffer), 0.1M nitric acid, 0.01M hydrochloric acid, 0.01M sodium hydroxide, 1% nitric acid.

2.2. Standard Preparation to Check Sensitivity of Electrode

0.2M Acetic acid and 0.1M sodium acetate were prepared to make acetate buffer solution. Acetate buffer was used as supporting electrolyte. 1000 ppm standard cadmium solution was diluted to 4 ppb, 3 ppb, 2 ppb, 1 ppb and 0.5 ppb in volumetric flask by using acetate buffer using a series of dilution.

2.3. Collection and Preparation of Sample

The wastewater sample was retrieved from lake located at section 7, Shah Alam Selangor. The sample was collected by using 500 mL plastic bottle. Then, it was stored in the laboratory. The wastewater sample was acidified with nitric acid (HNO_3). After that, it was filtered using Whatman filter paper (125 mm) by applying vacuum pump. The filtered sample was placed into 100 mL beaker and was evaporated at 60 ^oC using hotplate in the fume hood until the volumes remained 20 mL to 50 mL. Next, 1 mL of evaporated sample was diluted with 1% nitric acid and proceeded for the analysis of ICP-OES [19].

2.4. Preparation of Ionic Liquids Polymer Electrolyte

The ionic liquid polymer electrolyte films were prepared by weighing 1 g of methyl cellulose and dissolved in deionized water. The mixture solution was then stirred until homogenous solution formed. Next, 2.0 g of 1-methyl-1-propyl pyrrolidinium triflate [C_3C_1Pyrr] [OTf] was added to the methyl cellulose solution and stirred at room temperature until homogeneous solution formed. The solution was casted in the petri dish and dried at 60 ^oC for 10 minutes.

2.5. Preparation of Ionic Liquid Polymer Electrolyte On Screen Printed Carbon Electrode, SPCE

About 2 microliter of ionic liquid cellulose based thin film was dropped on the working electrode of SPCE using micropipette. Next, the electrode dried for 10 minutes at room temperature. The modified SPCE is ready for experiment.

2.6. Analysis of Standards and Sample Solutions Using Electrochemical Sensor

The analysis of standards and sample solutions using electrochemical sensor was carried out by using screen printed carbon electrode (SPCE). The wastewater samples that was prepared earlier, was measured using micropipette and placed on the surface of SPCE which covered all three working, counter and reference electrodes and the voltammogram was observed.

2.7. Analysis of Standards and Sample Solutions Using ICP-OES

The same standard and sample solutions used in the electrochemical sensor for ICP-OES analysis to detect cadmium and compare between standard and samples. The calibration units of each standard solutions were inserted according to the concentration of standard solution that was prepared. The identification and positions of standard and sample solutions for the wavelength of cadmium at 228.802 nm has selected. The analysis was started by analysing blanks, followed by standard solutions and finally sample solutions. The replication of measurement will be set for triplicate measurement.

3. Results and Discussions

3.1. Optimization of Electrochemical Sensor

3.1.1. Effect of pH of acetate buffer

The effect of pH of acetate buffer is the first parameter of optimization process in this experiment. 0.01M acetate buffer was used as supporting electrolyte of the electrochemical sensor in which made up of 0.1M sodium acetate and 0.2M acetic acid. 0.01M Sodium hydroxide and 0.01M hydrochloric acid were used as a pH adjuster. The pH used in this experiment is from the most acidic to the most basic to see how sensitive the electrode to the solution with different pH.

The use of acetate buffer is necessary to increase the conductivity of the solution. The sensitivity of the electrochemical sensor towards cadmium detection could be enhanced by maintain the pH of the buffer whereby the buffer functioning as in facilitating the migration of cadmium ion towards the sensor. The solution; standard cadmium and wastewater sample solutions are naturally resist to charge transfer. However, when cadmium ions are transferred at the electrode, acetate buffer would help to migrate the transfer electron to balance the charge and complete the circuit. The different in pH values of acetate buffer which tested from 3, 6.4, 7.4, 8 and 11 gives different of conductivity of the solution.

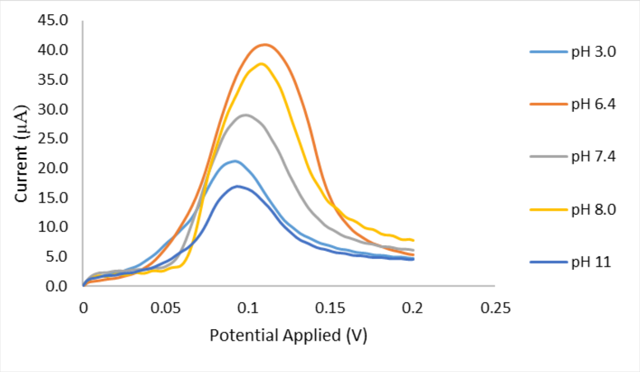

Fig. 1: Voltammogram of 0.5 ppb standard Cadmium solution in acetate buffer with different pH values n=3.

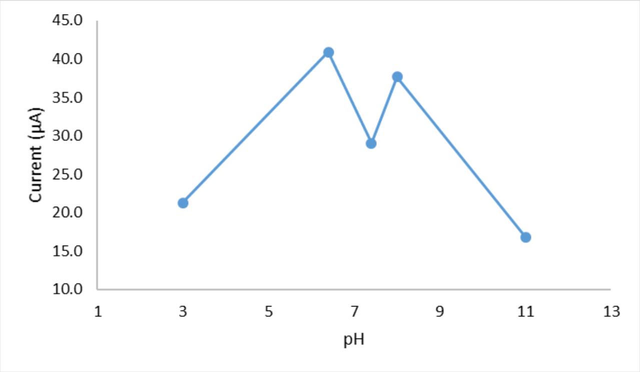

Fig. 2: Effect of pH on 0.5 ppb standard Cadmium solution in acetate buffer with different pH.

Based on Fig. 1, we can see that the optimized pH for acetate buffer was at 6.4. This was shown in the graph in which the pH at 6.4, the current was at highest compared to other pH. As for pH 3.0 of acetate buffer, the acidity is too high. It means that there is higher concentration of H^+ at the electrode surface, and it tends to reduce to H_2 molecule instead of reduced Cd^{2+} to Cd. The higher concentration of H^+ was blocked the cadmium ions to be reduced (Fig. 2). Therefore, the detection current produced was low. As for pH above 6.4, the current produced also decreased.

3.1.2. Effect of scan rate

The effect of scan rate is the second parameter in this experiment. Scan rate of cyclic voltammetry control the speed of the applied potential was scanned. Scan rate with higher speed causes the size of the diffusion layer to be decreased. As a result, higher current is observed. For electrochemically reversible electron transfer processes involving freely diffusing redox species. The scan rate was tested from the low speed to high speed rate that is 0.02, 0.05, 0.1, 0.3 and 0.5V/s (Fig. 3).

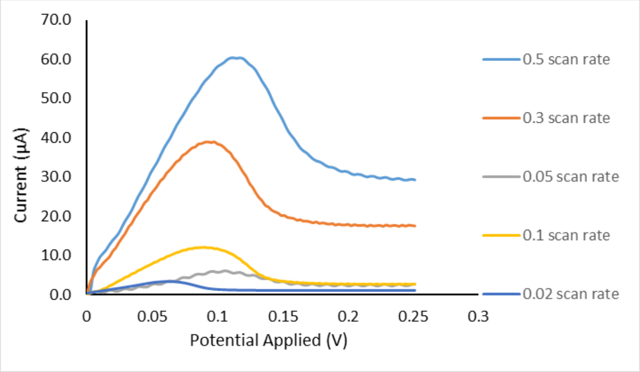

Fig. 3: Voltammogramm of 0.5 ppb standard Cadmium solution in acetate buffer with different scan rate values n=3.

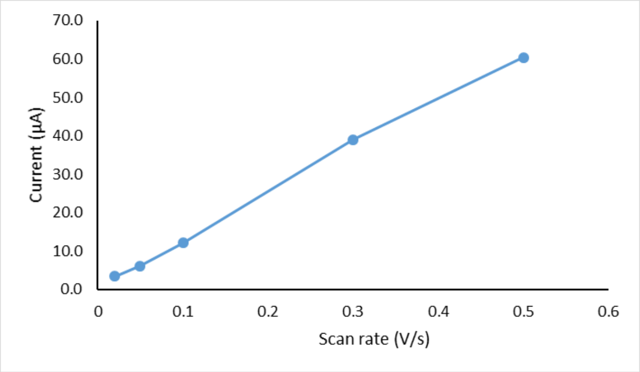

Fig. 4: Effect of pH on 0.5 ppb standard Cadmium solution in acetate buffer with different scan rate.

From Fig. 4, it showed the effect of pH on 0.5 ppb standard cadmium solution in acetate buffer with different scan rate. The result showed the increase the scan rates the higher the current produced. The first curve shows the oxidation rates are very fast, however when the scan rate decreased the curve shift to reduce the current. This may be rationalized in terms of equilibrium at the surface is no longer establishing rapidly. However, when the scan rate is too high, there will be less number of electroactive species covered or adsorped the electrode surface that makes less current because less chance for the electroactive species can undergo reduction and oxidation. Hence, this could affect sensitivity of electrode. In contrast, the slow reaction would produce lower current or less conductivity. Therefore, the optimum scan rate was at 0.1V/s that is between the range, it was not too high and too low to produced sharp and better voltammogram.

3.2. Effect of ionic liquid cellulose based thin film as sensing layer on SPCE

Ionic liquid cellulose based thin film was introduced as the sensing layer of the electrochemical sensor. The ionic liquid cellulose was placed on the surface of screen printed carbon electrode of the electrochemical sensor via drop casting method. The cellulose was also used and placed on the surface to compare the results with ionic liquid cellulose voltammogram. This is to see the differences conductivity of cellulose without ionic liquid.

The ionic liquid used was 1-methyl-1-propyl pyrrolidinium triflate [C_3C_1Pyrr] [OTf], in which has high ionic conductivity to enhance the electrical conductivity between working electrode of SPCE and the cadmium ion in the sample and standard solution. This surface modification by using ionic liquid cellulose is prior to enhance the surface detection of electrochemical sensor, SPCE effect towards cadmium ions. It helps the electrochemical sensor to detect cadmium ion in a very low concentration (ppb). In this part, comparison was made by testing cadmium standard series of dilution ranging from 4 ppb to 0.5 ppb using bare SPCE (Fig. 5), modified with ionic liquid cellulose (Fig. 9) and modified with cellulose (Fig. 7).

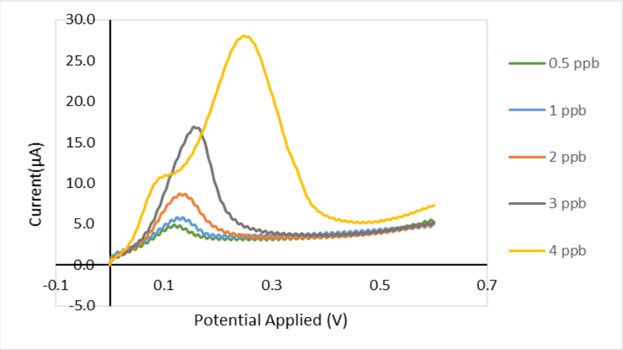

Fig. 5: Voltammogram for series of standard Cadmium solution in acetate buffer pH 6.4, scan rate 0.1V/s tested on bare SPCE electrochemical sensor.

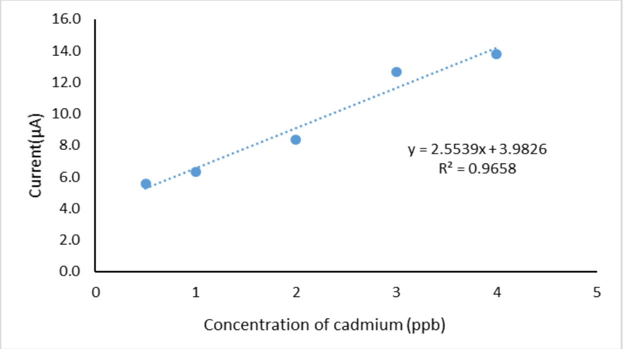

Fig. 6: Standard calibration graph for series of standard Cadmium solution in acetate buffer pH 6.4, scan rate 0.1V/s tested on bare SPCE of electrochemical sensor.

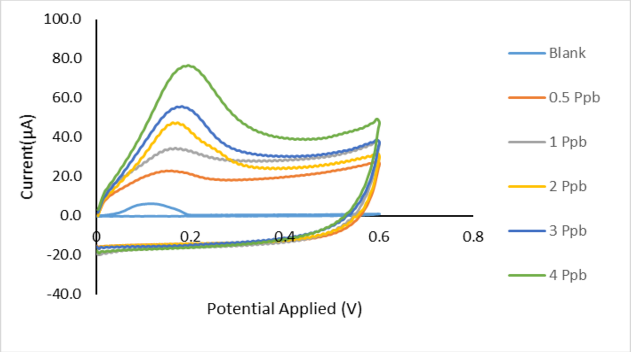

Fig. 7: Voltammogram for series of standard Cadmium solution in acetate buffer pH 6.4, scan rate 0.1V/s tested on cellulose SPCE of electrochemical sensor.

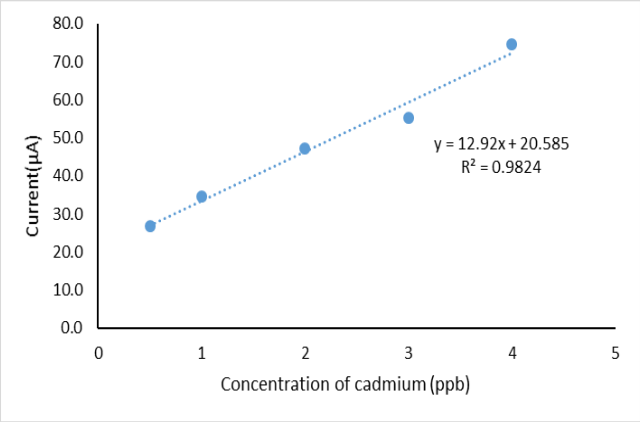

Fig. 8: Standard calibration graph for series of standard Cadmium solution in acetate buffer pH 6.4, scan rate 0.1V/s tested on cellulose SPCE of electrochemical sensor.

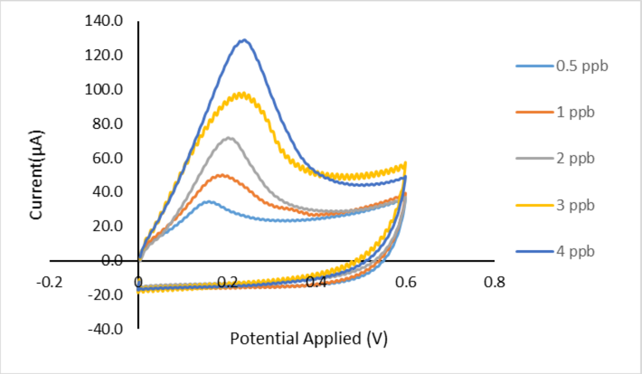

Fig. 9: Voltammogram for series of standard Cadmium solution in acetate buffer pH 6.4, scan rate 0.1V/s tested on ionic liquid cellulose based thin film SPCE of electrochemical sensor.

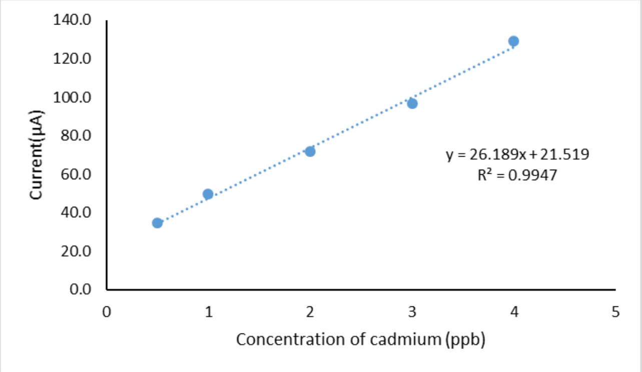

Fig. 10: Standard calibration graph for series of standard Cadmium solution in acetate buffer pH 6.4, scan rate 0.1V/s tested on ionic liquid cellulose based thin film SPCE electrochemical sensor.

Based on Fig. 5, 7 and 9, there were differences between the result of bare SPCE and modified SPCE with cellulose and modified SPCE with ionic liquid cellulose. The differences showed that higher current produced and better coefficient determination, R^2 by using modified SPCE electrochemical sensor with ionic liquid cellulose based thin film compared to bare SPCE. Theoretically, as the concentration increases, the higher the current produced. Firstly, the current produced for modified SPCE with ionic liquid cellulose based thin film is higher than the current produced with bare SPCE. This was shown in Fig. 5 and 9, for example at 4 ppb, modified SPCE has higher current produced, 1.30E-05A as compared to bare SPCE, low current produced, 2.58E-05A. As cellulose has a little bit low conductivity, it produced current that was slightly lower than modified SPCE with ionic liquid cellulose. It means that pure cellulose is not considerably good as compared to cellulose with ionic liquid. It showed that ionic liquid cellulose based thin film as sensing layer of electrochemical sensor has good conductivity in determining the amount of cadmium presented in the standard solution than bare SPCE.

Secondly, the coefficient determination, R^2 of bare SPCE is 0.9658 in Fig. 6 and modified SPCE with ionic liquid cellulose based thin film, 0.9947 in Fig. 10. This showed that modified SPCE had better R^2. The coefficient of determination (denoted by R^2) is a regression analysis output. The closer the value of R^2 is to 1, means the regression analysis is better fits the data in comparison to the simple average. From this, it indicated modified electrochemical sensor with ionic liquid cellulose based thin film had better data fit to the simple average in compared to bare SPCE electrochemical sensor.

3.3. Interference study

Interference study was done by using cyclic voltammetry and anodic square wave voltammetry for 0.5 ppb of Mercury (Hg), Cadmium (Cd) and lead (Pb) standard solutions. Cadmium, lead and mercury metals are having almost the same maximum limit of contaminants in wastewater, as shown in Appendix A. For cadmium, 0.003 ppm; lead, 0.01 ppm and mercury, 0.006 ppm. This interference study was done to investigate the ability of the electrochemical sensor to separate and distinguish cadmium peak with other metal and to evaluate the selectivity of modified SPCE by testing common interferences, that is the effect of Cd (II), Pb (II) and Hg(II) under optimized conditions.

A 0.5 ppb individual standard solutions and a mixed of cadmium, lead and mercury standard solution were prepared and tested with the modified electrochemical sensor. The comparison of potential applied or standard potential for each metal in both method, cyclic voltammetry (CV) and anodic square wave voltammetry (ASWV) were tabulated in Table 1.

Table 1: Standard Potential of 5 ppb three heavy metals in standard cadmium, standard lead and standard mercury solution.

Heavy Metals	Standard potential (V)	
	Cyclic Voltammetry (CV)	**Anodic Square Wave Voltammetry (ASWV)**
Cd	0.159	0.450
Pb	0.125	-0.860
Hg	0.115	0.180

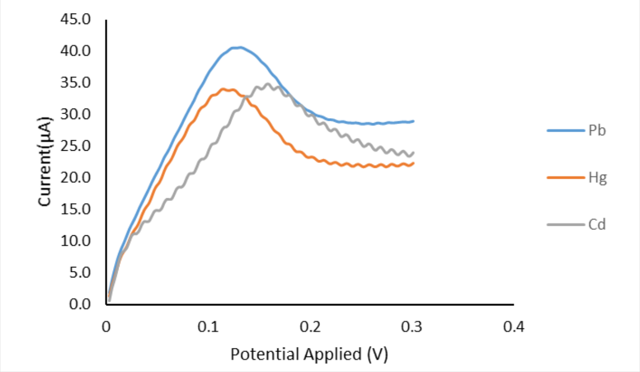

Fig. 11: Voltammogram of 5 ppb Cd, Pb and Hg standard solutions in 0.1M acetate buffer pH 6.5, scan rate 0.1V/s tested on ionic liquid cellulose based thin film SPCE of electrochemical sensor.

From Fig. 11 and Table 1, it showed that the voltammogram produced for each metal, Cd, Pb and Hg were at 0.159V, 0.125V and 0.115V. This shows the potential applied for each metal were almost in the same range, thus, cyclic voltammetry cannot be used to analyse mixed standard solutions because it cannot separate the voltammogram of cadmium, lead and mercury. Thus, cyclic voltammetry cannot be used to differentiate all three metals in a mixed solution. It can only produce one peak for each metal, so it is an unreliable method [20]. Thus, anodic square wave method was used to see the ability of the sensor to distinguish between the metals.

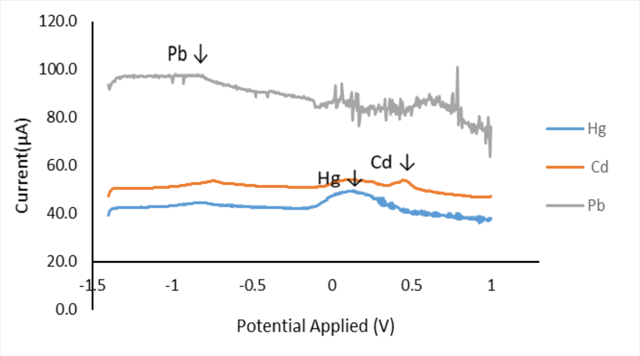

Fig. 12: Voltammogram of Cd, Pb and Hg standard solutions in 0.1M acetate buffer pH 6.5, -1.4V deposition potential and 120 second deposition time tested on modified SPCE with Ionic Liquid Cellulose based thin film of electrochemical sensor.

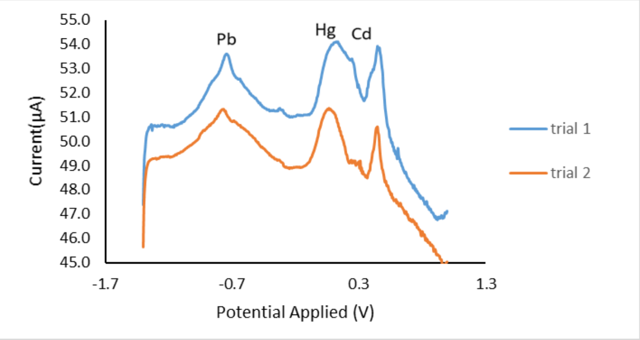

Fig. 13: Voltammogram of mixed Cd, Pb and Hg standard solutions in 0.1M acetate buffer pH 6.5, -1.4V deposition potential and 120 second deposition time tested on modified SPCE with Ionic Liquid Cellulose based thin film of electrochemical sensor.

Fig. 12 showed the individual cadmium, lead and mercury standard solution analysed by using anodic square wave voltammetry. Based on the graph in Fig. 13, mixed standard solutions of cadmium, lead and mercury analysis were distinguished by the peaks produced. The voltammograms produced were sharp and reproducible peak at different standard potential for each metal. The results shown in Table 1. There were two trial made in this analysis as to confirm the peak for each metal. No peaks overlap of other element. This proved that the modified electrochemical sensor with ionic liquid cellulose based thin film are able to separate and differentiate cadmium peak with other metals peak regardless of other interference in which lead and mercury in one mixed standard solution.

3.4. Sample analysis using ICP-OES

ICP-OES or inductively coupled plasma optical emission spectroscopy is an analytical instrument that has highest productivity with great performance, delivers excellent selectivity in which the detection limit of elements from low ppb to % level concentration and high matrix capability. ICP-OES is one of the effective techniques and commonly used in the analysis of major, minor and trace elements including cadmium. According to United State Environment Protection Agency (US EPA), the analysis of elements in environmental samples such as industrial wastewater, groundwater’s, sludge and sediments by ICP-OES was significantly important.

In this analysis, the cadmium ion was quantitated by ICP-OES at 228.02nm. ICP-OES has characterization of the detection limit of each heavy metal, as for cadmium, was less than 10 ppb (<10 ng/ml). Wastewater sample was obtained from lake of section 7, Shah Alam. The samples were analysed after acidified with nitric acid to pH 2 prior to prevent the metal cation to be oxidized and form precipitate or be absorbed by the wall or surface of the container. If not, the cadmium ion would not be detected in the chemical analysis of water. Then, the cadmium standard solutions were prepared from single element standards by diluting with 1% nitric acid as well as the sample. A standard calibration curve was plotted from a series of cadmium standard solutions in Table 2, in which used to detect the concentration of cadmium in wastewater samples.

Table 2: Data for calibration curve of cadmium standard solutions ranging from 0.0 ppb to 4 ppb by using ICP-OES.

Concentration of cadmium standard solution (ppb)	**Mean intensity**
0	50
0.5	77.7
1	110.2
2	169.6
3	229.1
4	271.1

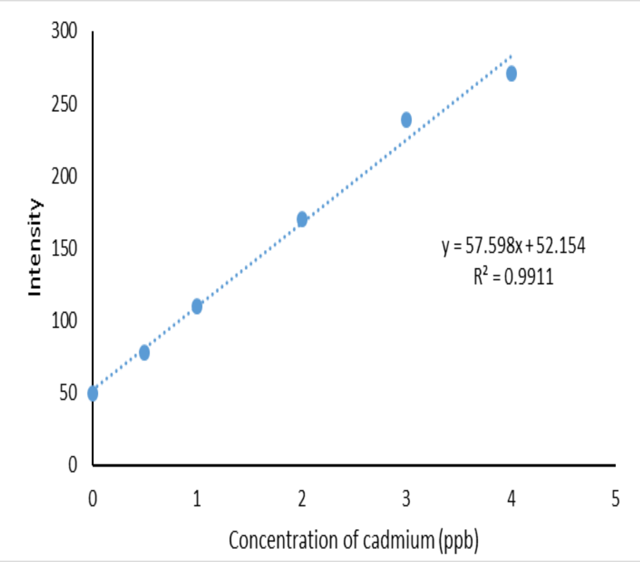

Fig. 14: Standard calibration curve for series of cadmium standard solutions under optimized conditions using ICP-OES.

Based on Table 2, sample A1 was the sample without being spiked and sample A2 was spiked with 0.5 ppb cadmium solutions. Sample A1 was made to see the exact amount of cadmium concentration in the wastewater sample. As the result shown in the Table 3, the amount of cadmium concentration in the wastewater was 0.00 ppm. It means that the concentration of cadmium in the sample was undetectable or below detection limit.

According to Water Quality Standard in Malaysia and World Health Organization, WHO, the maximum limit of cadmium concentration is 0.001 ppm or 1 ppb and 0.003 ppm or 3 ppb. It showed that the sample was not contaminated with cadmium. It is safe for the aquatic life to live in lake of Section 7, Shah Alam. Next, it does not require any further and complicated water treatment for drinking water to remove all the contaminants in the wastewater. Then, the result of this ICP-OES, was used as a reference for electrochemical sensor in detection of cadmium concentration.

Table 3: Determination of cadmium concentration in wastewater sample by using ICP-OES.

Sample	Mean intensity	Mean concentration of cadmium (ppb)
A1 (non-spiked)	-33.5	0.00
A2 (spiked with 0.5 ppb of Cd)	69.7	0.50

3.5. Sample analysis using optimized electrochemical sensor

There were two wastewater samples that was used tested for ICP-OES. All standards and samples solutions were tested by using sensor under optimized conditions as represented in Table 4.

Table 4: Optimized condition of electrochemical sensor used in determining cadmium ion in standard cadmium solution and wastewater sample.

Buffer	Acetate buffer
pH	6.4
Scan rate	0.1V/s

Table 5: Determination of cadmium concentration in wastewater sample under optimized conditions of modified electrochemical sensor with ionic liquid cellulose based thin film.

Sample	Mean current (A)	Mean concentration of cadmium (ppb)
A1 (non-spiked)	0.00	0.0 ppb
A2 (spiked with 0.5 ppb of Cd)	4.1925E-5	0.5 ppb

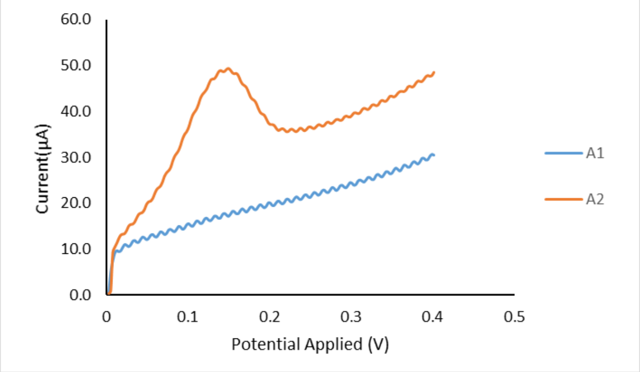

Fig. 15: Voltammograms of wastewater sample that is spiked with 0.5ppb cadmium standard solution and sample without being spiked.

Since the results of ICP-OES showed the amount of cadmium in wastewater samples was undetectable or below detection limit. The samples were then tested by using modified electrochemical sensor of ionic liquid cellulose based thin film to see the ability of the sensor to detect the cadmium below detection limit. Based on Fig. 12, the modified electrochemical sensor cannot detect any cadmium concentration in wastewater samples as well as ICP-OES. This was shown, in the sample A1, no peak was produced. It means the electrochemical sensor cannot detect the below detection limit of cadmium concentration in the wastewater sample.

However, when the sample A2 was spiked with 1ppb of cadmium standard solution, the modified electrochemical sensor was still able to detect the cadmium concentration regardless any solution. The current produced also in the same range as Fig. 9 whereby the modified electrochemical sensor tested with 0.5 ppb cadmium standard solution. This means the detection limit of this modified electrochemical sensor is as applicable as ICP-OES, because it can detect heavy metals in concentration as low as ppb concentration.

3.6. Sample's detection difference between electrochemical sensor and ICP-OES

Based on Table 6, both ICP-OES and the modified electrochemical sensor cannot detect any cadmium concentration in the wastewater sample. However, the electrochemical sensor can still trace 0.5 ppb spiked cadmium concentration in the wastewater sample solutions. This verified that ionic liquid cellulose based thin film has the ability and high conductivity to detect cadmium concentration in the wastewater sample and act as a good sensing layer for the electrochemical sensor. It can be concluded, that the optimized and modified electrochemical sensor is as applicable as ICP-OES.

Table 6: Determination of mean concentration of cadmium in wastewater using both ICP-OES and modified electrochemical sensor with ionic liquid cellulose based thin film.

Sample	Mean concentration of Cadmium in wastewater sample (ppb)	
	Electrochemical sensor	**ICP-OES**
A1 (non-spiked)	0.00 ppb	0.00 ppb
A2 (spiked with 0.5 ppb Cd)	0.5 ppb	0.5 ppb

4. Conclusion

The ionic liquid cellulose based thin film electrochemical sensor was very useful in detection of cadmium regardless of any solutions under optimized conditions. There were three optimized conditions for the electrochemical sensor, that are, the used of acetate buffer as supporting electrolyte, the pH is 6.5 and the scan rate is 0.1 V/s. The result showed the wastewater sample contain undetectable amount of cadmium, therefore internal standard method was used whereby another sample was spiked with 0.5 ppb cadmium standard solutions. It showed the modified electrochemical sensor was still able to detect the amount of cadmium in the wastewater sample. The amount of cadmium in the wastewater sample was below maximum limit, 0.003 ppm that is based on World Health Organization, WHO. This modified electrochemical sensor has a minimum detection limit, as it can detect the amount of cadmium in a very low concentration (ppb) via cyclic voltammetry (CV) method. Is a rapid process to determine the amount of cadmium in standard and sample solutions. Then, the used of ionic liquid cellulose based thin film as sensing layer of screen printed carbon electrode, SPCE is a significantly good alternative as to modify the electrochemical sensor prior to increase the conductivity of the sensor to detect cadmium in standard and sample solutions. It also used less cost as compared to other trace analysis method. Hence, this can be said the ionic liquid cellulose based thin film electrochemical sensor has higher sensitivity and applicable as ICP-OES.

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