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The Potential of Ferrocenium as a Sensing Reagent for Determination of 2,4,6-Trichlorophenol in Water Samples

Potensi Ferosenium sebagai Reagen Penderia bagi Penentuan 2,4,6-Triklorofenol dan Sampel Air

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Abstract

A ferrocenium namely bisferrocenium bis(tetrachloroantimonate) trichloroantimony ($(Fe(C_2H_5)_2)[SbCl_4]_2[SbCl_3]$) was proposed as a sensing reagent to detect the presence of 2,4,6-trichlorophenol (2,4,6-TCP) in domestic tap water and river water by using a UV-Visible spectrophotometric. The absorbance intensity of ferrocenium was found to decrease at wavelength 617 nm and cause the reagent solution to change its colour from blue to yellowish green which indicates the conversion of ferrocenium to ferrocene. This sensing reagent (2000 mg/L) showed optimum respon in acidic medium (pH 5) within 3 minutes. A good linear concentration was obtained in the range of 20 to 190 mg/L with limit of detection to be 1.56 mg/L. The proposed reagent was recommended as a potential reagent for 2,4,6-TCP detection in aqueous solution.

Keywords ferrocenium, optical sensor, pesticides, phenolic compound, 2,4,6-trichlorophenol

Abstrak

Sebatian ferosenium iaitu bisferosenium bis(tetrakloroantimonat) trikloroantimoni ($(Fe(C_2H_5)_2)[SbCl_4]_2[SbCl_3]$) telah dicadangkan sebagai reagen penderia untuk mengesan kehadiran 2,4,6-Triklorofenol (2,4,6-TCP) di dalam air paip domestik dan air sungai dengan menggunakan spektrofotometri UV-nampak. Keamatan keserapan ferosium didapati menurun pada panjang gelombang 617 nm dan warna larutan reagen bertukar dari biru ke hijau kekuningan yang menunjukkan penukaran ferosenium kepada ferosena. Reagen penderia ini (2000 mg/L) menunjukkan tindak balas optimum dalam medium berasid (pH 5) dalam jangka masa 3 minit. Kepekatan linear yang baik telah diperolehi dalam julat 20-190 mg/L dengan had pengesanan 1.56 mg/L. Reagen penderia yang dicadangkan ini berpotensi digunakan sebagai reagen penderia untuk pengesanan 2,4,6-TCP dalam larutan akueus.

Kata kunci ferosenium, penderia optik, racun perosak, sebatian fenolik, 2,4,6-triklorofenol

INTRODUCTION

Pesticides are a powerful tool to reduce the agricultural problems in order to control the number of pests and continuous application of pesticides can cause severe environmental problems and food contaminations (Pinto et al., 2010). As a result of their wide usage, pasticides find their way to rivers water, groundwater, wastewater, sediments and soils (Fakhr Eldin et al., 2006) which were finally become sources of contamination in drinking water (van Leeuwen, 2000). Due to the demand of drinking water supplies by human being, therefore it is necessary to ensure that treated water is safe and free from harmful substance. Phenolic compounds is one of the harmful substances release into our natural water resources which give bad impact to aquatic life and human being if the water is not treated in a right way. Some phenolic compound, mainly chlorophenols and nitrophenols have been clarified as priority pollutant by US Environmental Protection Agency (EPA) and European Union (EU) (Galve et al., 2002; Santana et al., 2009). Since the early 1930s, chlorophenol namely 2,4,6-trichlorophenol (2,4,6-TCP) has been applied as formulation in insecticides, bactericides and antiseptic as well as becoming an intermediate in the production of chlorophenoxy acid herbicides and other important organic substance. Concentration of phenol which is higher than 2 mg L^{-1} with four days exposure is considered toxic to the fish while concentrations between 10 mg L^{-1} and 100 mg L^{-1} are lethal to most aquatic life (Andrade et al., 2006). Prolonged oral exposure leads to damages to the lungs, liver, kidneys and genitor-urinary tract. Therefore, US Environmental Protection Agency (EPA) recommends a maximum of 1.0 mg L^{-1} of total phenolic compounds in domestic water and 5 mg L^{-1} of other water resources (El-Kosasy et al., 2001).

Over the past decades, many researchers preferred to use high performance liquid chromatography (HPLC) for the separation and determination of chlorophenols. Various detectors that are frequently use are ultraviolet-visible (UV), fluorescence, electrochemical and mass spectroscopy (Jin-Feng et al., 2006). El Kosasy et al. (2001) has succesfully determine phenolic pollutants in waste water by using poly (vinyl chloride) matrix membrane electrodes sensor. Their suggested sensor exhibit fast response time (1 minute), low detection limit, good stability and reasonable selectivity to phenolic compounds in the presence of other water pollutants. This sensor was successfully used for direct potentiometric determination of traces of these phenolic compounds in waste water sample. Ribeiro et al., (2002) developed and validated a new methodology regarding solid-phase microextraction (SPME) with gas chromatography and mass spectrometry (GC-MS). Throughout this study, they proved that SPME was a suitable methodology to extract 13 chlorophenols and phenol from leachate sample. Even though this SPE method use small amounts of organic solvents but it can be expensive as the cartridge used need to be dispose after one to four extraction.

Analysis of chlorophenols in environmental samples has been proposed by various methods but the prior method is based on chromatographic separation. In most cases, this method often required a previous pre-concentration or cleaning step. Unfortunately, even with the use of pre-concentration step, some of the methods exhibit relatively high limits of detection (LODs) and therefore only restricted to a very contaminated samples (de Morais et al., 2011). Therefore a usage of reagent for determination of phenolic compound will overcome the problems such as time consumed, expensive and lots of solvent usage.

A new proposed reagent namely ferrocenium can be synthesized by oxidation of ferrocene by using organic or inorganic solvents. This oxidation will yield a blue and relatively stable ferrocenium ion (Manzi-Nshutti & Wilkie, 2007). It has been found that ferrocene yields highly reversible heterogenous redox processes in most organic solvents, including ionic liquids. As a result, its heterogenous electron transfer kinetics has been widely studied and redox potential has been established in many different solvents. Due to its electron-transferring abilities, ferrocene act as “redox mediator” in amperometric biosensors and has been introduced for the first time to detect glucose (Sanchis et al., 2008). Based on redox mediator properties of ferrocenium, it was believed that this reagent has a potential to become a sensing reagent for the determination of 2,4,6-TCP in aqueous solution.

Regarding to the dangerous effects of phenolic componud especially of 2,4,6-TCP to the community, time consumed and expensive cost of method to detect phenolic compound, it is vital to develop an accurate and simple detection method to give early warning to the public and continuous contamination monitoring by enforcement officers. Therefore, a new reagent bisferrocenium bis(tetrachloroantimonate) trichloroantimony ($(Fe(C_2H_5)_2)[SbCl_4]_2[SbCl_3]$) is proposed to ensure the detection of phenolic compound (2,4,6-TCP) in our environment especially in water sample to be more efficient, fast result and aplicable to on-site detection.

EXPERIMENTAL

Materials and reagents

Antimony (III) trichloride was purchased from Sigma-Aldrich. Ferrocene and 2,4,6-TCP was supplied by Across Organic. Hexane, acetic acid glacial and sodium acetate was obtained from R & M Chemicals. All chemicals were used without any further purification.

The preparation of sensing reagent ferrocenium was carried out based on method by Razak et al. (2000). About 1.86 g of ferrocene and 2.28 g of antimony trichloride was dissolved in acetonitrile separately. Both solutions were mixed and stirred for 2 hours. The mixture was allowed to dry for 4 to 5 days in a fume hood. The mixture turned slowly to blue green solution and finally formed dark blue precipitate. The precipitate was filtered and washed with hexane until the filtrate formed clear solution. Finally, the ferrocenium yielded was allowed to dry and kept in desiccators for further experiment.

Stock solution of ferrocenium (5000 mg/L) was prepared by dissolving dark blue solid ferrocenium in 50 mL of acetonitrile. The stock solution of ferrocenium was freshly prepared before used in a further experiment. All 2,4,6-TCP solution were daily fresh prepared in deionized water before used.

pH studies, optimize reagent and steady state response time

The pH study was carried out by varying the pH of reaction solution with buffer. A ferrocenium solution (2000 mg/L) was mix with 1 mL of 100 mg/L 2,4,6-TCP in 25 mL volumetric flask. Then the buffer solution was added in the flask and the pH value was measured with pH meter and recorded. This procedure was repeated by using different buffer solution to obtain different pH. The absorbance spectrum of ferrocenium before and after react with 2,4,6-TCP in different pH was recorded using UV-Visible specthrophotemeter. The relative absorbance was calculated at wavelength 617 nm for each pH effect using Equation (1).

$$\text{Relative Absorbance} = I_F - I_i \qquad (1)$$

where,

I_F =Absorbance intensity of ferrocenium after react with 2,4,6-TCP
I_i =Absorbance intensity before react with 2,4,6-TCP

Optimum concentration of ferrocenium reagent was studied by using various concentration of ferrocenium solution (1000 – 5000 mg/L). 1 mL of stock solution of 2,4,6-TCP, buffer solution pH 5 was added into ferrocenium solution. The absorbance spectrum of ferrocenium was recorded as same as in pH effect.

Steady state response time was studied by adding 100 mg/L of 2,4,6-TCP, buffer solution pH 5 into ferrocenium solution. The absorbance intensity of ferrocenium at 617 nm was recorded in different time interval (0.5 – 3 minutes) using UV-Visible spectrophotometer.

Effect of 2,4,6-TCP concentration

The effect of 2,4,6-TCP concentration on the relative absorbance of ferrocenium was done with optimum concentration of 2000 mg/L, buffer solution pH 5 and steady-state response time of 2 minutes. The analyte concentration was varied in the range of 20 – 190 mg/L. A ferrocenium was added with different concentration of 2,4,6-TCP separately. The absorption spectrum of ferrocenium solution was recorded with Agilent Cary 60 UV-Visible spectrophotometer. The relative absorbance of ferrocenium response to the presence of 2,4,6-TCP which was calculated using Equation (1).

RESULTS AND DISCUSSION

pH studies, optimize reagent and seady state reponse time

Figure 1 showed the absorbance spectrum of ferrocenium before and after react with 2,4,6-TCP. The absorbance intensity of ferrocenium at 617 nm decrease in the presence of 2,4,6-TCP. The decreased in absorbance intensity showed colour change from blue colour ferrocenium solution to yellowish green. The colour changes were considered to the conversion of ferrocenium ion to ferrocene (Hurvois & Moinet 2005). This occurrence was believed due to a redox reaction between ferrocenium and 2,4,6-TCP. The ferrocenium ion, [$FeCp_2^+$], is a mild one-electron oxidant, usually regarded as an outer-sphere reagent. The stability of the couple ferrocenium ion/ferrocene, [$FeCp_2^+$]/[$FeCp_2$] suggest the ferrocenium ion act as a potential redox catalyst (Conelly & Geiger 1996). Ferrocenium which act as oxidizing agent will oxidized 2,4,6-TCP to 2,4,6-trichlorocyclohexanone (Figure 2). The oxidation will disrupt the aromatic ring (Smith 2002) leading to the formation of 2,4,6-trichlorocyclohexanone.

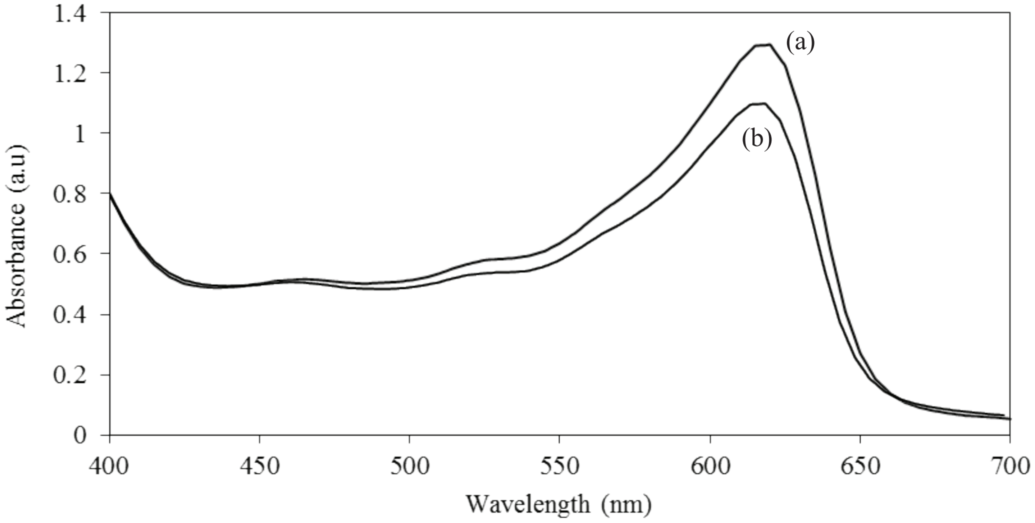

Figure 1 The absorbance spectrum of ferrocenium (a) before and (b) after react with 2,4,6-TCP in aqueous solution

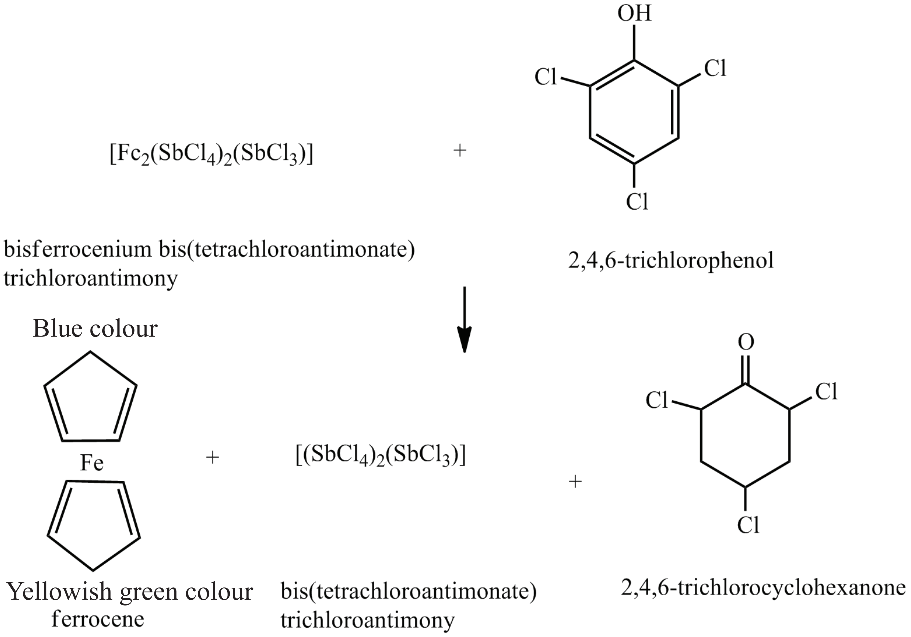

Figure 2 The reaction equation of Ferrocenium and 2,4,6-TCP in aqueous solution.

The effect of solution pH against the reaction of ferrocenium and 2,4,6 – TCP was conducted in range of pH 2 – 8. The absorbance intensity of ferrocenium increased from pH 2 to pH 5 and start decreasing sharply when approaching pH 7 (Figure 3). This situation occurred due to the instability of phenolic compound at neutral pH (Sirajuddin et al., 2007). The optimum absorbance intensity was obtained at pH 5. Consequently, this pH was selected as working pH.

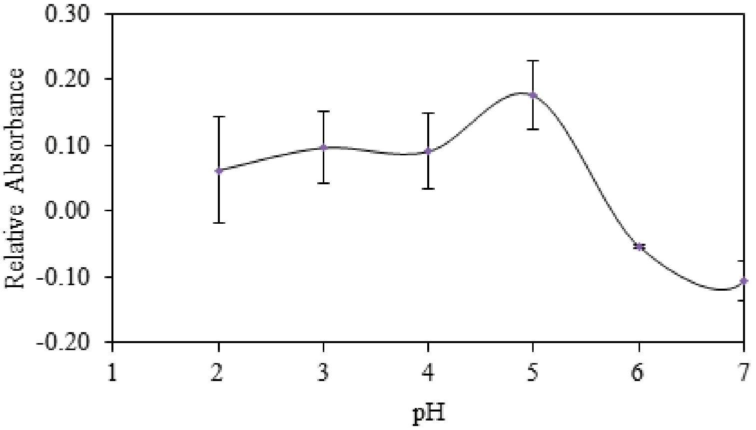

Figure 3 Effect of solution pH against the reaction of Ferrocenium and 2,4,6-TCP in aqueous solution

The optimum concentration of ferrocenium concentration react with 2,4,6-TCP was 2000 mg/L (Figure 4). An increase in ferrocenium concentration will give more reaction to 2,4,6-TCP. After 2000 mg/L, the absorbance intensity decreased due to limiting 2,4,6-TCP presence in solution. After all the limiting reactant was reacted, therefore the absorbance intensity will decrease (Robinson & Schwartz 1956).

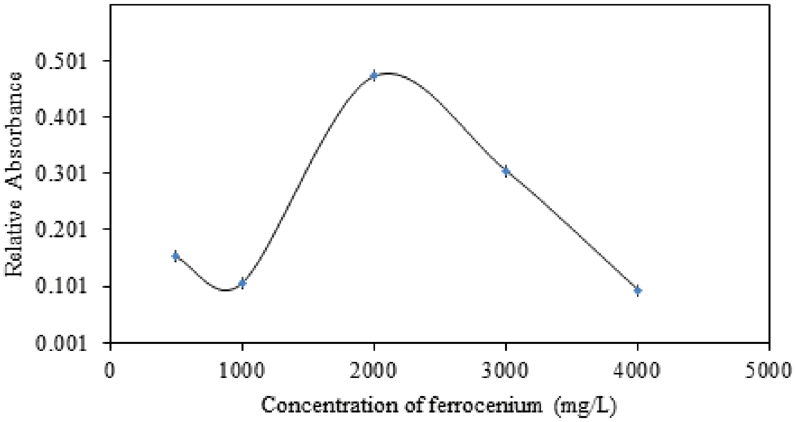

Figure 4 Optimum concentration of ferrocenium against 2,4,6-TCP in aqueous solution.

The absorbance intensity increase with time and reach steady state within 2 minutes (Figure 5). This is an optimum time for the formation of stable colour which may be assigned as the stability of ferrocenium solution to detect the presence of 2,4,6-TCP in aqueous solution.

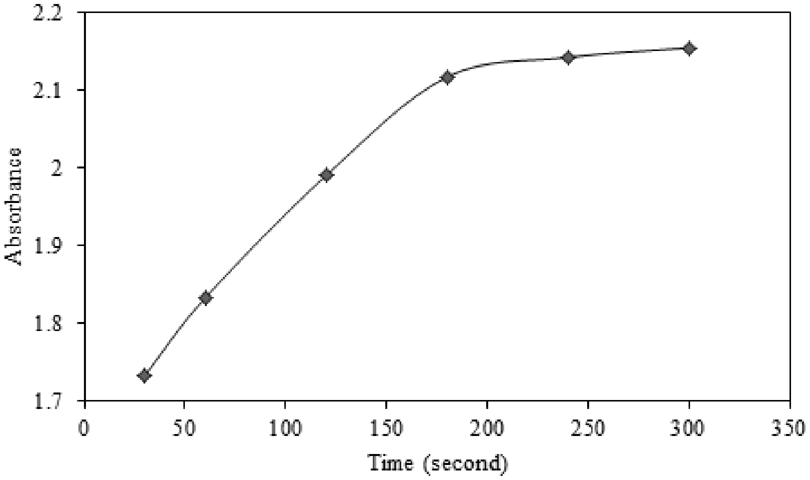

Figure 5 The steady state response time of ferrocenium against 2,4,6-TCP in aqueous solution

Effect of analytes concentration to the absorbance of ferrocenium

The effect of 2,4,6-TCP concentration against ferrocenium has been studied in the range of 20 to 190 mg/L (Figure 6). The absorbance intensity of ferrocenium increases with the 2,4,6-TCP concentration and this was expected due to more reaction occurred when more 2,4,6-TCP available in the solution. An increase in absorbance intensity due to the added analyte will exhibit a linear relationship (Robinson et al., 2005).

The plot of relative absorbance against concentration of 2,4,6-TCP which was arranged in logarithme form give linear correlation in the range of 20 to 190 mg/L (Figure 5). The limit of detection was calculated and found to be 1.56 mg/L which apparently indicates that ferrocenium can detect the presence of 2,4,6-TCP in low concentration as compared to the

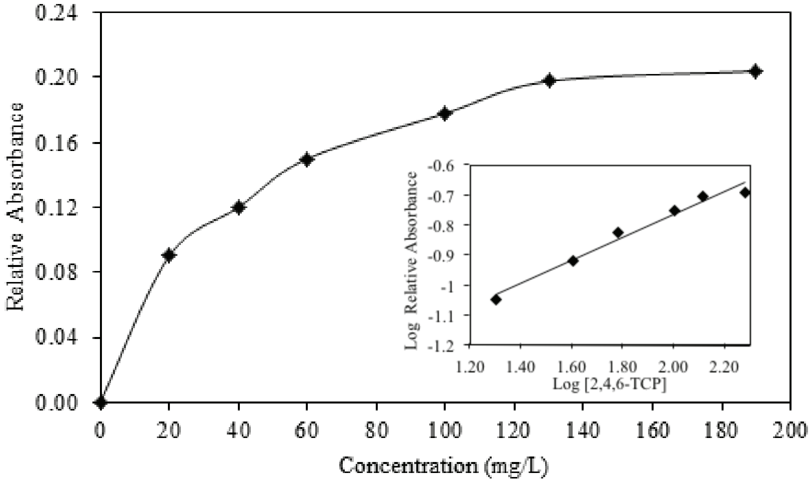

Figure 6 Effect of 2,4,6-TCP concentration against Ferrocenium

conventional method using HPLC which can only detect the presence of 2,4,6-TCP in 2.85 mg/L (Opeolu et al., 2010).

CONCLUSION

The ferrocenium showed a good sensitivity against 2,4,6-TCP, fast steady state response time with lower detection limit (1.56 mg/L). This proposed reagent was recommend as a potential reagent for determination of 2,4,6-TCP in aqueous solution.

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