

Adsorption and Electroanalytical Studies of a Poly-*o*-toluidine Zr(IV) Phosphate Nanocomposite for Zinc(II) Dimethyldithiocarbamate

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ABSTRACT: The adsorption behavior of zinc(II) dimethyldithiocarbamate (Ziram) was studied on the surface of a poly-*o*-toluidine Zr(IV) phosphate nanocomposite cation exchanger. A spectrophotometric method based on the conversion of Ziram into a copper dimethyldithiocarbamate complex was applied for the study of Ziram at the maximum absorption wavelength of 437 nm. A Ziram-sensitive membrane electrode was fabricated with poly-*o*-

toluidine Zr(IV) phosphate (an electroactive composite material). The sensitivity of Ziram for the composite cation-exchange material was monitored with potentiometric methods. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1393–1397, 2011

Key words: adsorption; composites; electrochemistry; ion exchangers; nanocomposites

INTRODUCTION

Pesticides of the carbamate family have been progressively replacing more persistent species (mainly organophosphates) because of their low persistence in the environment, biological activity, and large spectrum of utilization. They are used as insecticides, fungicides, nematocides, miticides, and molluscicides. Dithiocarbamates are widely used in agriculture as fungicides and in the rubber industry as vulcanization accelerators and antioxidants. Metal salts of dithiocarbamates are more effective as fungicides because the toxicity of the dithiocarbamates is increased by the metal. Dithiocarbamates have also been studied in vegetable foodstuffs with high-performance liquid chromatography,¹ extraction voltammetry,² and titrimetry.³ Capillary electrophoresis was used by Rossi and Rotilio⁴ for the qualitative and quantitative analysis of different carbamates, thiocarbamates, and dithiocarbamates. However, all these methods suffer from the following disadvantages: (1) methods other than gas chromatography are indirect and time-consuming and have low sensitivity, and (2) gas chromatography methods are sensitive but suffer from a lack of selectivity because all dithiocarbamate pesticides evolve carbon disulfide during acid hydrolysis.

Zinc(II) dimethyldithiocarbamate (Ziram) is an agricultural fungicide. It can be applied to the foliage of plants, but it is also used as a soil and/or seed treatment. Ziram is used primarily on almonds and stone fruits. It is also used as an accelerator in manufacturing rubber, packaging materials, adhesives, and textiles and as a bird and rodent repellent. Ziram can cause skin and mucous membrane irritation. Humans with prolonged inhalation exposure to Ziram have developed nerve and visual disturbances.⁵ Ziram is corrosive to eyes and may cause irreversible eye damage.⁶

Ziram has also been converted into molybdenum⁷ and copper complexes.^{8,9} The extraction of the molybdenum complex is slow, and complexation occurs in an acid medium. A simple, rapid, and sensitive spectrophotometric method based on the conversion of Ziram into a copper dimethyldithiocarbamate complex was applied in this work to study Ziram. However, the main objective of this research was to develop an electroanalytical method for making a Ziram-sensitive membrane electrode to find trace amounts of Ziram in water.

EXPERIMENTAL

Equipment and reagents

A digital pH meter (Elico, Hyderabad, India), a potentiometer (Elico), and an SL 164 double-beam ultraviolet–visible spectrophotometer (Elico) were used. Solutions (0.1M) of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and phosphoric acid (H_3PO_4) of

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different molarities were prepared in 4M HCl and demineralized water (DMW), respectively. Solutions of 20% (v/v) *o*-toluidine (C₇H₉N) and 0.4M ammonium persulfate [(NH₄)₂S₂O₈] were prepared in 2M HCl.

Preparation of the Ziram solutions

A stock solution of Ziram (1 g/L) was prepared by the dissolution of 100 mg of Ziram in NaOH (0.1N) and by dilution to 100 mL in a volumetric flask; further dilutions were performed with 0.1N NaOH as desired. Copper sulfate (1.0 g/L) was prepared by the dissolution of 0.1 g in 100 mL of distilled water, which was then acidified with 0.1 mL of concentrated sulfuric acid. An acetate buffer was prepared in distilled water by the dissolution of sodium acetate trihydrate (68 g; analytical-reagent grade; Merck, Mumbai, India) in water (400 mL) and by the adjustment of the pH to 4.5 through the addition of glacial acetic acid (25–30 mL; analytical-reagent grade; Merck); the total volume was 500 mL.

In a blank solution, a copper sulfate solution (1.0 mL) was added with an aqueous acetate buffer solution (1.0 mL) and Triton X-100 (2 mL), and the volume was increased to 10 mL with distilled water without the Ziram solution.

Preparation of the poly-*o*-toluidine Zr(IV) phosphate composite cation-exchange material (adsorbent)

The nanocomposite cation exchanger was prepared by the sol-gel mixing of poly-*o*-toluidine, an organic polymer, into the inorganic precipitate of zirconium(IV) phosphate. In this process, when the poly(*o*-toluidine) gels were added to the white inorganic precipitate of zirconium(IV) phosphate with constant stirring, the resultant mixture was turned slowly into a greenish-black slurry. The resultant greenish-black slurry was kept for 24 h at room temperature.

Then, the poly-*o*-toluidine-based composite gels were filtered off and washed thoroughly with DMW for the removal of excess acid and any adhering trace of (NH₄)₂S₂O₈. The washed gel was dried over P₂O₅ at 40°C in an oven. The dried product was washed again with acetone to remove oligomers present in the material and was dried at 40°C in an oven. The dried product was cracked into small granules and converted into the H⁺ form via treatment with 1M HNO₃ for 24 h with occasional shaking; the supernatant liquid was intermittently replaced with fresh acid two to three times. The excess acid was removed after several washings with DMW and finally dried at 50°C. A particle size of approximately 125 μm for the composite cation exchanger was obtained via sieving, and the material was stored in desiccators.¹⁰

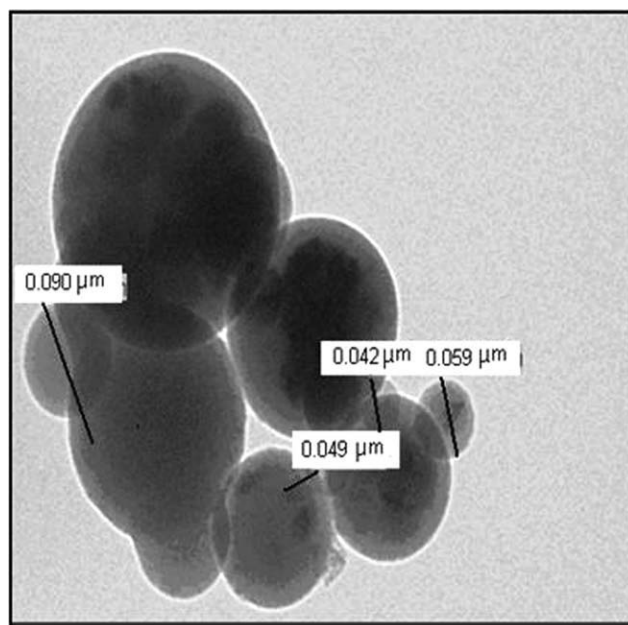


Figure 1 TEM image showing the particle size of the poly-*o*-toluidine Zr(IV) phosphate cation-exchange material.

Transmission electron microscopy (TEM) studies

TEM studies were carried out to determine the particle size of the poly-*o*-toluidine Zr(IV) phosphate composite cation-exchange material, as shown in Figure 1. From the TEM studies, it is clear that the poly-*o*-toluidine Zr(IV) phosphate cation-exchange material had a particle size range of 42.0–100.0 nm; that is, the material particle size was in the nanorange.

Adsorption of Ziram onto the poly-*o*-toluidine Zr(IV) phosphate cation exchanger

To different 100-mL conical flasks, 25-mL Ziram solutions of different concentrations (0.5–10 ppm) were added; 0.5 g of the adsorbent (poly-*o*-toluidine Zr(IV) phosphate) was also added. The flasks were closed and allowed to stand for 1 h with intermittent shaking. Then, the contents were filtered, and 1 mL of the filtrate of each concentration was placed into another conical flask. To each flask, a copper sulfate solution (1.0 mL), an aqueous acetate buffer solution (1.0 mL, pH = 4.5), and Triton X-100 (2 mL) were added, and the volume was increased to 10 mL with distilled water. The mixture was shaken vigorously for 2–3 min. The absorbance of the solution was measured at 437 nm against a reagent blank.¹¹

The adsorption percentage from a standard solution was calculated as follows:

$$\text{Adsorption}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

TABLE I
Adsorption Percentage of Ziram Before and After Adsorption onto the poly-*o*-toluidine Zr(IV) Phosphate Cation Exchanger

Sample	Concentration (ppm)	Initial absorbance before adsorption	Absorbance after adsorption	Adsorbent (g)	Adsorption (%)
1	0.5	0.012	Completely adsorbed	0.5	100
2	0.6	0.016	Completely adsorbed	0.5	100
3	0.8	0.018	Completely adsorbed	0.5	100
4	1.0	0.0229	0.001	0.5	95.6
5	2.0	0.0592	0.019	0.5	84.7
6	3.0	0.0732	0.015	0.5	79.5
7	4.0	0.0976	0.022	0.5	77.5
8	6.0	0.1472	0.036	0.5	75.5
9	8.0	0.1995	0.055	0.5	72.4
10	10	0.253	0.095	0.5	62.5

where C_0 and C_e are the absorbances before and after adsorption on the cation exchanger, respectively. The adsorption percentages of Ziram before and after adsorption onto the poly-*o*-toluidine Zr(IV) phosphate cation exchanger are listed in Table I.

Absorption spectra

Figure 2 shows the absorption spectrum of Ziram as a copper(II) dimethyldithiocarbamate complex dissolved in Triton X-100 against a reagent blank and the spectrum after adsorption onto the cation exchanger.

Preparation of the Ziram pesticide-sensitive membrane electrode

The ion-exchange membrane was prepared according to the procedure of Coetzee and Benson.¹² The poly-*o*-toluidine Zr(IV) phosphate cation exchanger (100 mg), an electroactive material, was ground into

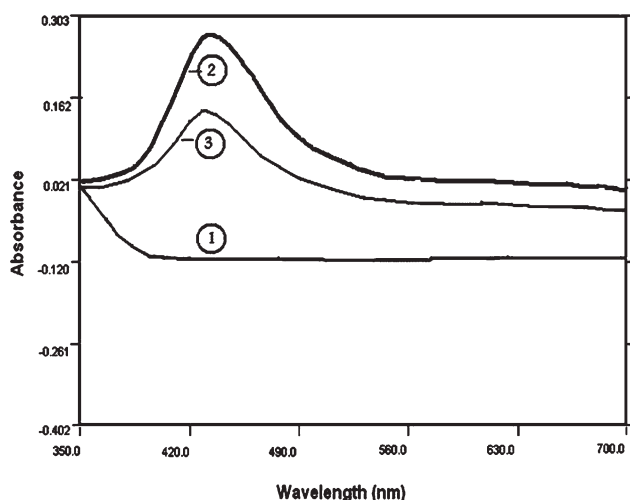


Figure 2 Absorption spectra of (1) a blank solution, (2) the Ziram/copper (II) dimethyldithiocarbamate complex in Triton X-100 against a reagent blank before adsorption, and (3) the Ziram/copper (II) dimethyldithiocarbamate complex after adsorption onto the poly-*o*-toluidine Zr(IV) phosphate cation-exchanger.

a fine powder and was mixed thoroughly with Araldite (Hindustan, Ciba-Geigy, Ltd., Mumbai, India; 100 mg) in a 1 : 1 (w/w) ratio to make a homogeneous paste, which was then spread between the folds of Whatman no. 42 filter paper (D Haridas & Co., Pune, India). The phase of the exchanger and Araldite was kept under a pressure of 2 kg cm² for 24 h and allowed to dry. One sheet of the master membrane with a thickness of 0.16 mm was prepared. This sheet was dipped into distilled water to remove the filter paper. After it dried, the membrane sheet was cut into the shape of a disc with a sharp-edge blade.

Fabrication of the pesticide-sensitive membrane electrode of the poly-*o*-toluidine Zr(IV) phosphate cation exchanger

The membrane electrode was fabricated as reported in a previous study.¹³

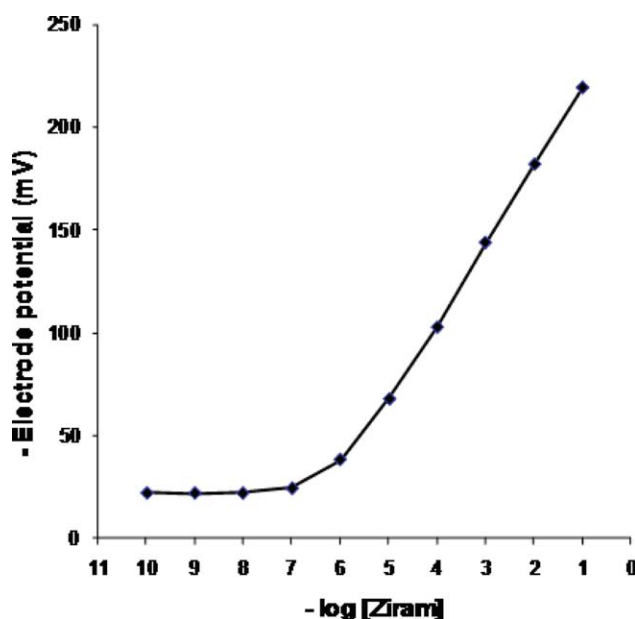


Figure 3 Calibration curve for the Ziram-sensitive membrane electrode. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

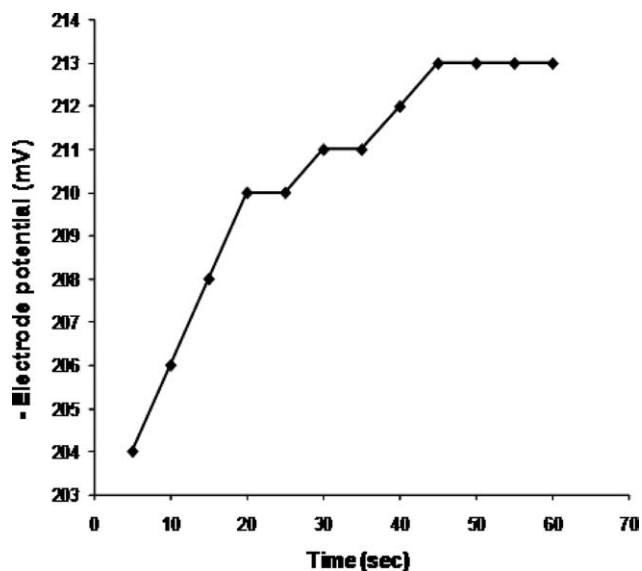


Figure 4 Time-response curve for the Ziram-sensitive membrane electrode.

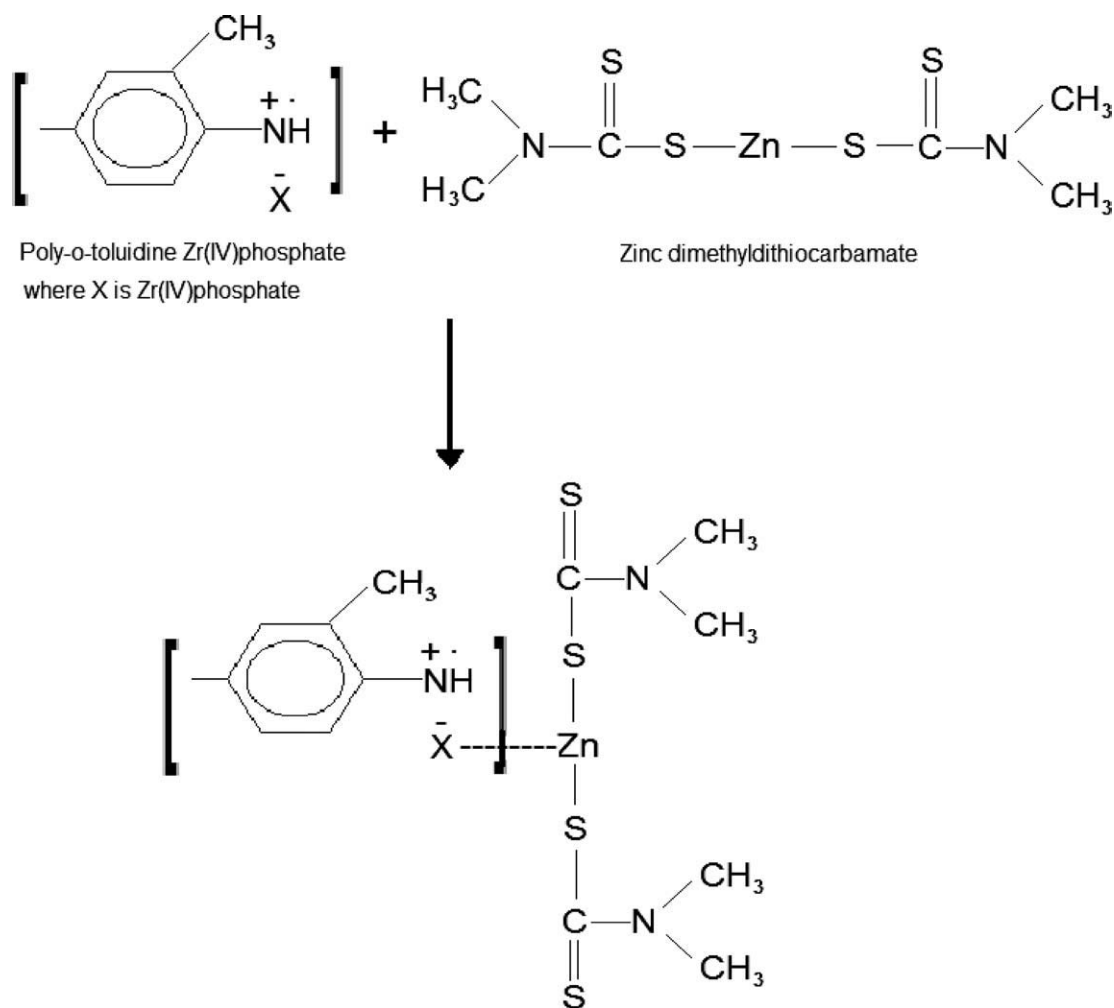
The following parameters were evaluated to study the sensitivity of the electrode to Ziram: the lower detection limit, electrode-response curve, and response time.

Electrode response or membrane potential

A series of Ziram solutions of various concentrations ranging from 10^{-1} to $10^{-10}M$ were prepared. The external electrode and the pesticide-selective membrane electrode were plugged into a digital potentiometer, and the potentials were recorded. First, the electrode was soaked in a $1 \times 10^{-1}M$ solution of Ziram for 2–3 days and for 1 h before use. When the electrode was not in use, it was kept in a $1 \times 10^{-1}M$ solution. The measured potential is plotted against selected concentrations of the pesticide in solution in Figure 3.

Response time

The electrode was first dipped into a $1 \times 10^{-2}M$ solution of Ziram and then into a $1 \times 10^{-1}M$ solution. The potential of the solution was read at 0 s; just



Scheme 1

after the electrode was dipped into the second solution, the potential was recorded subsequently at the interval of 5 s. The potentials versus the time are plotted in Figure 4.

RESULTS AND DISCUSSION

Poly-*o*-toluidine Zr(IV) phosphate is an established nanocomposite cation exchanger.¹⁰ Its excellent ion-exchange behavior is due to the presence of strong phosphate groups (co-ions) present in the matrix of the composite, which have electrostatic attraction for positive cations (counterions). Ziram, a zinc-based dimethyldithiocarbamate, was adsorbed completely up to a concentration of 0.8 ppm and retained 60% of its adsorption up to 10 ppm (Table I). The mechanism of adsorption is presented in Scheme 1.

Poly-*o*-toluidine Zr(IV) phosphate is formed by ionic interactions between the radical cations of poly-*o*-toluidine and anionic groups of zirconium(IV) phosphate.¹⁰ Phosphate groups of zirconium(IV) phosphate behave as co-ions for the cation-exchange material and have an electrostatic potential for metal present in the carbamate fungicide. However, the nanoparticle size of the material (24.0–100 nm) increases the surface area of the adsorbent, and this results in the maximum adsorption of the pesticide.

On the basis of the adsorption behavior of Ziram on the surface of poly-*o*-toluidine Zr(IV) phosphate, a Ziram-sensitive, heterogeneous-precipitate membrane electrode was prepared from the poly-*o*-toluidine Zr(IV) phosphate cation-exchange material, and it yielded a linear response in the range of 1×10^{-1} to $1 \times 10^{-7}M$. The working concentration range was 1×10^{-1} to $1 \times 10^{-10}M$ (Fig. 3) for Ziram with a lower Nernstian slope of 28.1 mV per decade change in the Ziram concentration. The limit of detection, determined from the intersection of the extrapolated segments of the calibration graph,¹⁴ was found to be $1 \times 10^{-7}M$.

The promptness of the response of the pesticide-sensitive electrode was also determined. The average response time was defined as the time required for the electrode to reach a stable potential. The response time of the membrane sensor was approximately 45 s (Fig. 4). The membrane could be successfully used up to 1 month without any notable change in the potential; during this time, the potential slope was reproducible within ± 1 mV per concentration decade. When a drift in the potential was

observed, the membrane was re-equilibrated with a $1 \times 10^{-1}M$ solution for 1 week.

CONCLUSIONS

In this research, a nanocomposite cation exchanger, poly-*o*-toluidine Zr(IV) phosphate, showed excellent adsorption of Ziram in the range of 0.8–10 ppm. A TEM photograph showed that the particle size of the composite material was between 42.0 and 100.0 nm, so the material could be considered a nanocomposite. The sensitivity of Ziram toward the membrane electrode of the poly-*o*-toluidine Zr(IV) phosphate nanocomposite cation exchanger was indicated by a change in the potential with a change in the concentration. The membrane electrode possessed a quick response time of only 45 s with a slope of 28.1 mV per decade change in the concentration range of 1×10^{-1} to $1 \times 10^{-7}M$. The membrane electrode showed a detection limit of good reproducibility and could be used successfully up to 1 month.

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