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Thermodynamic Study of Sensitivity of Polyaniline based Nanocomposite Membrane towards Hazardous Dithiocarbamate

Leena Paquiza[*1], Asif Ali Khan[2] and W. A. Siddiqui[1]

[1]Department of Applied Science and Humanities, Jamia Millia Islamia, New Delhi, INDIA

[2]Analytical and Polymer Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, INDIA

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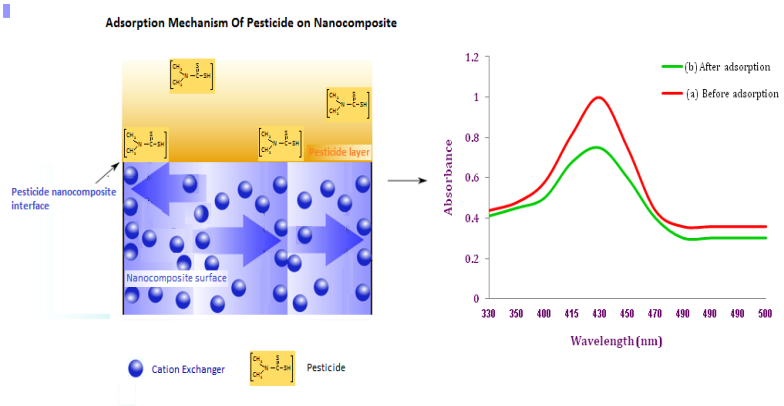
Abstract: *Adsorption behavior of Thiram, a dithiocarbamate pesticide, was studied on the surface of nanocomposite polyaniline zirconium titanium phosphate (PANI-ZTP) cation-exchanger. Adsorption experiments were carried out as a function of time, initial pesticide concentration and temperature. Thermodynamic parameters ($\Delta H°$, $\Delta G°$, $\Delta S°$) were determined and the adsorption process was found to be exothermic. Spectrophotometric method was applied to determine dithiocarbamate compound at λ_{max} 420 nm. A pesticide-sensitive membrane electrode was fabricated using PANI-ZTP nanocomposite as an electroactive material. Its sensitivity towards this hazardous dithiocarbamate was monitored using potentiometry. The proposed method was applied to determine pesticide in synthetic mixture with good recovery.*

Keywords: Dithiocarbamate, Thiram, Adsorption thermodynamics, Potentiometry, Spectrophotometric method.

Graphical Abstract



Introduction

Pesticides stand out as one of the major developments of the twentieth century. During the past twenty years, however, concern has arisen as to the extent their presence in the environment poses a threat to wildlife and mankind. The use of pesticides also constitutes an important aspect of modern agriculture, for without chemicals to control various pests like insects, weeds, plant diseases, worms and rodents, our food supply would decrease and prices would increase. Unfortunately, pesticides are poisons and have exposed the human life to many potential hazards. A current environmental concern is the contamination of aquatic systems due to pesticide discharges from manufacturing plants, surface runoff, leaching accidental spills and other sources. They degrade in the

environment due to physical, chemical or biological factors, giving rise to several residues, which may include the parent compound that forms the pesticide[1-4]. Some degradation products are reported to be even more hazardous than the pesticide that is degraded[5]. Hence, the investigation of the fate of pesticides, and pesticide residue analysis are important steps in monitoring their pollution in the environment. Pesticides of the carbamate family have been progressively replacing more persistent species (mainly organophosphates) due to their low persistence in the environment, biological activity and large spectrum of utilization. Dithiocarbamates are widely used in agriculture as fungicide and in rubber industry as vulcanization accelerators and antioxidants. Among the numerous agrochemicals in use today, the fungicide Thiram is a general pesticide which belongs to the ethylene bisdithiocarbamate (EBDC) chemical class. It is used as a fungicide to protect seed and fruit, vegetable, ornamental and turf crops from a variety of fungal diseases, prevent crop damage in the field and protect harvested crops from deterioration in storage or transport. Detection of thiram and similar sulphur containing compounds has been advanced significantly in the recent past because of their usage in agriculture and industry[6-8]. Two well known pesticides Ferbam and Ziram give thiram as its degradation product in the environment[9]. Chronic exposure to thiram in humans includes drowsiness, confusion and loss of sex drive, slurred speech and weakness. In the human body, its degradation gives rise to carbon disulfide which contributes to the toxicity of thiram to the liver[10-11].

A number of methods such as spectrophotometric[12], chromatography[13], voltammetric[14], polarographic[15], capillary electrophoretic[16], FTIR spectrometry[17] etc., has been reported for the detection and analysis of thiram. However, all these methods suffer from the following disadvantages (i) methods other than gas chromatography are indirect, time-consuming and sensitivity is low, (ii) they involve expensive instrumentation and toxic solvents and (iii) gas chromatographic methods are sensitive, but suffers from a lack of selectivity since all dithiocarbamate pesticides evolve carbon disulfide on acid but the method lacks sensitivity. Comprehensive reviews on thiram pesticide in environmental and pharmaceutical samples have also been reported[18-19.] Here, we present a relatively simple, rapid, sensitive and selective spectrophotometric and electroanalytical method for determination of Thiram using a nanocomposite cation exchanger, polyaniline zirconium titanium phosphate (*PANI-ZTP*).

Material and Methods

Equipment and Reagents

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, Merck and Qualigens (India Ltd.) of analytical grade. Carlo-Erba, model 1108, a digital potentiometer (Equiptronics EQ 609, India, accuracy ±0.1mV with a saturated calomel electrode as reference electrode, an electronic balance (digital, Sartorius-21OS, Japan), and an automatic temperature controlled water bath incubator shaker-Elcon (India), Elico SL 164 Double Beam UV visible spectrophotometer and Transmission electron microscope – TEM Philips EM 400 were used.

Preparation of Thiram solutions

A stock solution of thiram (1g/L) was prepared by dissolving 100 mg of this in acetone and diluting to 100 ml in a standard flask and then further dilutions were done as desired. A rapid, simple and direct method was developed by Malik et al. for spectrophotometric determination of Thiram in commercial samples using sodium selenite as a reagent[20]. Reagent was prepared by adding 0.01g of sodium selenite in solution of acetone and acetate buffer, prepared in distilled water by dissolving sodium acetate trihydrate in water (200 ml) adjusting the pH to 3.75 by adding glacial acetic acid (25–30 ml), making up the total volume to 500 ml.

Synthesis of nanocomposite cation exchanger polyaniline zirconium titanium phosphate (*PANI-ZTP*)

The composite cation-exchanger was prepared via the sol–gel interaction of polyaniline (an organic polymer) into the inorganic precipitate of zirconium titanium phosphate (ZTP). The preparation method for inorganic precipitate of zirconium titanium phosphate (ZTP) was very similar to that of Alberti and Constantino[21], with slight modification[22]. Dark green color polyaniline gel was prepared by oxidative coupling using ammonium persulphate in acidic aqueous medium. The precipitate of polyaniline was added into the white inorganic gel of ZTP with a constant stirring. Black colored precipitate obtained was allowed to settle overnight and then filtered off and washed thoroughly with DMW to remove excess acid and any adhering ions (chloride and sulphate).The washed gel was dried over P_4O_{10} at 30^0C in an oven. The dried product was immersed in 1M HNO_3 solution for complete replacement of counter ions by H^+ form. The excess acid was removed after several washing with DMW then dried at 40^0C and sieved to obtain shiny black granules of *PANI-ZTP*. The resulting composite was chosen for adsorption studies on the basis of its extraordinary high Na^+ ion-exchange capacity (4.5meq/g) as reported earlier[23].

TEM (Transmission electron microscopy) studies

TEM studies were carried out to know the particle size of the *PANI-ZTP*composite cation-exchange material.

Adsorption thermodynamics

Adsorption studies were carried out by batch process. 100mg of adsorbent (*PANI-ZTP*) was placed in different 100ml conical flasks in which 10ml of varying concentration of Thiram solution (10-100 ppm) was added and then the mixture was shaken in temperature controlled shaker incubator for 1hr. The resulting supernatant liquid was filtered. 2ml of filtrate was added into the solution of acetate buffer (1ml) and sodium selenite prepared in acetone (5ml) making up the volume to 10ml with distilled water. A light pink color solution obtained. The absorbance of the solution was measured by UV-visible spectrophotometer at 420nm against a reagent blank.

The adsorption percentage (Ads %) from standard solution was calculated as:

$$\text{Ads \%} = [(C_o - C_e)/C_o] \times 100 \quad \text{..... (1)}$$

Where C_o and C_e are absorbance before and after adsorbed on cation exchanger respectively.

Fabrication of pesticide-sensitive *PANI-ZTP* membrane electrode

The membrane electrode was fabricated employing the method reported in the literature[24-25]. EMF measurements were carried out using the following cell assembly:

I.R.E. (SCE) | 0.1MThiram || Membrane || Test solution| E.R.E. (SCE)

Where I.R.E. and E.R.E. correspond to the internal and external reference electrodes respectively. Potentiometric measurements were observed for a series of standard solutions of Thiram (10^{-10}–10^{-1} mol/dm^3), prepared by gradual dilution of the stock solution, as described by IUPAC Commission for Analytical Nomenclature[26]. The calibration graphs were plotted three times to check the reproducibility of the system.

Characteristics of the electrode

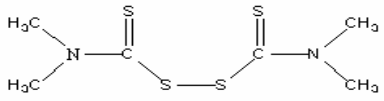
In order to study the characteristics sensitivity of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time.

Determination of Thiram concentrations in synthetic samples

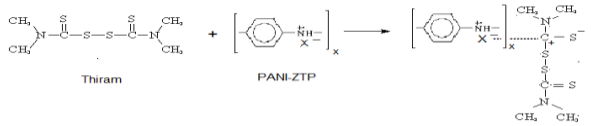
The practical utility of the proposed membrane sensor assembly was tested by using it in the potentiometric determination of the Thiram concentration in synthetic samples. For this, synthetic mixtures of pesticide like Ziram, Zineb and Thiram were prepared ranging from 1×10^{-3} to 1×10^{-7} mol/dm^3 solution and the potential of each sample was measured by the pesticide-sensitive membrane electrode. By comparing this potential with the calibration curve, it was possible to calculate the percentage recovery of Thiram.

Results and Discussion

A number of samples of 'organic–inorganic' nanocomposite cation exchanger polyaniline-zirconium titanium phosphate (*PANI-ZTP*) were prepared by the sol–gel mixing of conducting polymer polyaniline with tetravalent bimetallic inorganic ion-exchanger zirconium titanium phosphate (ZTP). The extraordinary ion-exchange capacity of *PANI-ZTP* (4.52 meq /g) makes it an excellent adsorbent for pesticide. Thiram (tetramethyldithiocarbamate) is a well-known dithiocarbamate fungicide used as a seed protectant having structural formula:



The mechanism of adsorption can be represented by the following equation.



Where X is zirconium titanium phosphate (ZTP).

Absorption Spectra

Figure 1 shows the absorption spectra of sodium tetramethyldithiocarbamate complex of Thiram before and after adsorption on the nanocomposite cation exchanger at λ_{max} 420 nm.

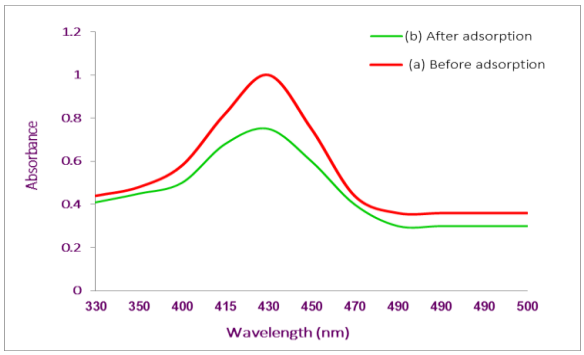


Figure 1: Absorption Absorption spectra of (a) Thiram complex before adsorption (b) After adsorption on *PANI-ZTP* nanocomposite cation-exchanger

Adsorption isotherm

Adsorption studies were carried out to determine the uptake rates of Thiram on the adsorbent as function of time. Figure 2 shows equilibrium studies for three different concentrations which indicated that 50 min was sufficient for the attainment of equilibrium in the system.

Table 1 summarizes the data that Thiram was adsorbed completely up to 20 ppm of the concentration and retain about 75% of its adsorption up to 100 ppm on the surface of *PANI-ZTP* composite cation exchange material**.** This may be due to the marked localization of attractive forces associated with the thio group (C=S) of the carbamate leading to interaction with exchanger cations (H^+).

TEM micrograph shows composite's particle size are in the range of 30nm-53nm (Figure 3) which proved that the prepared cation exchanger *PANI-ZTP* is a nanocomposite.

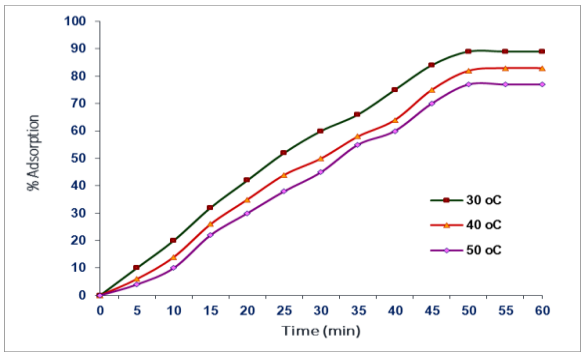


Figure 2: Percentage adsorption of Thiram on *PANI-ZTP* surface with time at different temperature

Table 1: The adsorption percentage (Ads %) of Thiram before and after adsorption on *PANI-ZTP*

S. No.	Concentration (ppm)	Absorbance		% Adsorbance
		Before Adsorption	After Adsorption	
1.	10	0.20	Completely adsorbed	100
2	20	0.181	Completely adsorbed	100
3.	30	0.254	0.004	98.43
4.	40	0.282	0.010	96.45
5.	50	0.427	0.022	94.85
6.	60	0.606	0.038	93.73
7.	70	0.781	0.071	90.90
8.	80	0.932	0.116	87.55
9.	90	1.212	0.209	82.76
10.	100	1.505	0.366	75.68

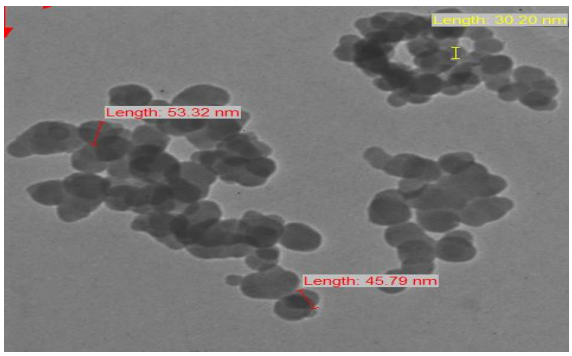


Figure 3: Transmission electron microphotographs (TEM) of *PANI-ZTP* nanocomposite cation exchanger.showing different particle size

PANI-ZTP is formed by ionic interaction between the radical cation of polyaniline and anionic group of zirconium titanium phosphate(ZTP). A phosphate group of ZTP behaves as co-ions for cation exchange material and has an electrostatic potential for thio group (C=S) present in the carbamate fungicide. Moreover, the nanosize of the material increases the surface area of adsorbent, resulting maximum adsorption of pesticide.

The capacity of any adsorbent for the removal of substances is generally calculated from Langmuir and Freundlich isotherms. The equilibrium data obtained from batch experiments were used to calculate the value of the isotherms constants.

Freundlich isotherm

The Freundlich isotherm[27] is an empirical equation employed to describe heterogeneous systems. The adsorption isotherms at 30°C, 40°C and 50°C follow Freundlich behaviour which can be represented by the equation:

$$C_s = K_f C_e^{1/n} \quad \text{.....} \quad (2)$$

The linear form of Freundlich equation is given as:

$$\ln Cs = \ln Kf + 1/n \ln Ce \quad \text{.....} \quad (3)$$

where, Ce is the equilibrium concentration of the adsorbate (mg/L), C_s is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants, the value of *K* shows the adsorption capacity of the sorbent and *n* indicates whether the process is favorable or not. K_f and 1/n determined from the intercepts and slopes of the straight lines fitted to the experimental data points via the least-squares method. The slope of 1/n ranging

between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero[28].

It can be seen from Figure 4 that the plot of log Cs versus log Ce was linear, thereby indicating the applicability of the classical adsorption isotherm to the adsorbate–adsorbent system. The values obtained for the Freundlich constants, K_f and 1/n, are listed in Table 2. While 1/n above one is indicative of cooperative adsorption[29]. As the 1/n value found from slope is less than 1, thus adsorption of thiram on composite *PANI-ZTP* is favourable. The higher value of K_f at 30°C is an indication of the higher affinity of the adsorbent for Thiram at this temperature.

Table 2: Freundlich constant for the adsorption of Thiram

Freundlich constant	Temperature (°C)		
	30	**40**	**50**
K_f	1.052	1.045	1.006
1/ n	0.7512	0.6185	0.8214
R^2	0.9999	0.9996	0.9998

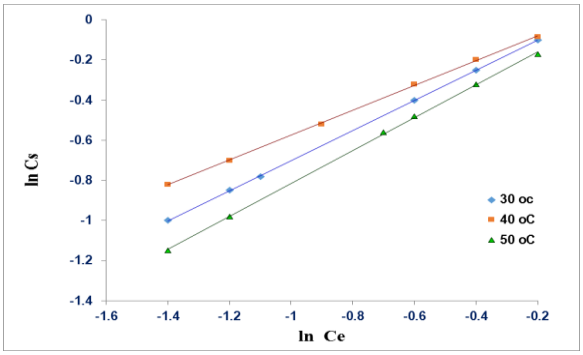


Figure 4: Freundlich plot for the adsorption of Thiram on *PANI-ZTP*

Thermodynamic parameters

The thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) were calculated by using the following equations:

$$\ln Kd = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{..... (4)}$$

where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution Temperature and K_d is the distribution coefficient which can be calculated as:

$$K_d = C_{Ae}/C_e \quad \text{..... (5)}$$

where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is equilibrium concentration. From Van't Hoff plot i.e. Figure 5, the corresponding values of (ΔH°), and (ΔS°) were calculated and (ΔG°) can be calculated using the relation below:

$$\Delta G^\circ = -RT\ln k_d \quad \text{..... (6)}$$

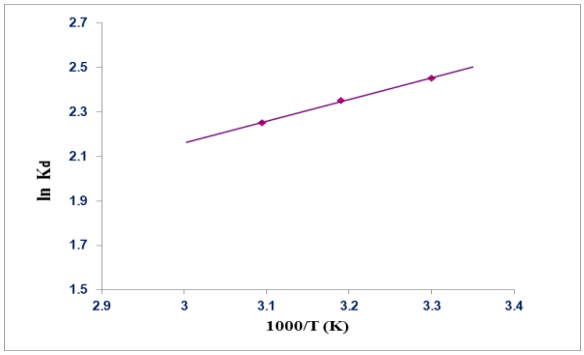


Figure 5: Van't Hoff plot for the determination of thermodynamic parameters

The calculated values of (ΔH°), (ΔS°) and (ΔG°) are listed in Table 3. The positive value of ΔS° indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process; In addition, the negative value of (ΔH°) indicates that the adsorption is exothermic. The negative values of (ΔG°) indicate both the feasibility and the spontaneous nature of the adsorption process, having high preference towards the adsorption of Thiram. The various thermodynamic quantities evaluated indicate that the adsorption process is physical in nature.

Table 3: Thermodynamic parameters for adsorption

Temperature (°C)	ΔG° (KJ mol^{-1})	ΔH° (KJ mol^{-1})	ΔS° (KJ $mol^{-1}K^{-1}$)
30	-6.178	-8.085	6.29×10^{-3}
40	-6.115	-8.085	6.29×10^{-3}
50	-6.042	-8.085	6.29×10^{-3}

Study of Thiram-sensitive membrane electrode

On the basis of the adsorption behaviour of Thiram on the surface of *PANI-ZTP*, the Thiram sensitive heterogeneous precipitate membrane electrode was prepared using *PANI-ZTP* electroactive cation exchange material which gave linear response in the range 1×10^{-2} -1×10^{-8}mol/dm^3 with a Nernstian slope of 57.91mV per decade change in Thiram concentration as observed from Figure 6. Experiments were conducted a number of times to check the reproducibility of the results. The limit of detection determined from the intersection of the extrapolated segments of the calibration graph[30] was found to be 7 $\times 10^{-8}$mol/dm^3.

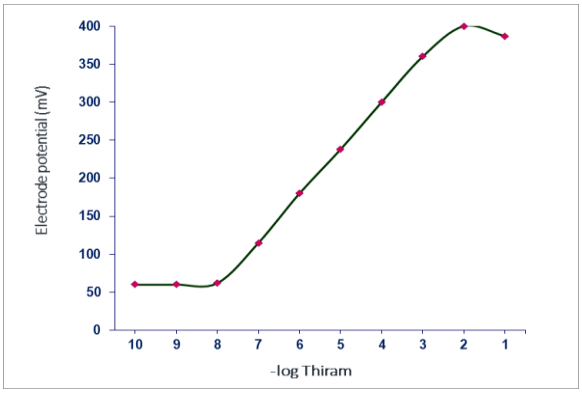


Figure 6: Calibration curve for Thiram sensitive membrane electrode

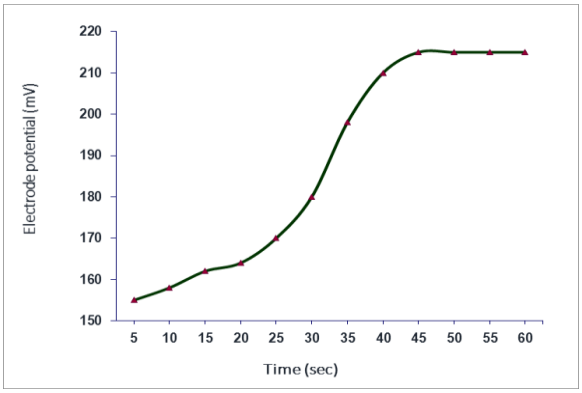


Figure 7: Time response curve of Thiram sensitive membrane electrode

Table 4: Determination of Thiram in synthetic solution by potentiometric titration using Thiram sensitive electrode

Sample	Amount of Thiram (mol/dm^3)		% Recovery
	Added	Found	
Thiram	1×10^{-5}	0.96×10^{-5}	96%
Thiram	5×10^{-4}	4.5×10^{-4}	90%
Synthetic mixture of Thiram +Ziram (1:1)	1×10^{-3}	0.92×10^{-4}	92%
Synthetic mixture of Thiram + Zineb (1:2)	6×10^{-6}	5.7×10^{-6}	95%

Promptness of the response of the pesticide sensitive electrode was also determined. It is clear from the Figure 7 that the response time of the membrane sensor is found to be ~45s. The long-term stability was worked out by performing calibrations periodically with standard solutions and calculating the slopes over the concentration ranges of 10^{-10}mol/dm^3 to 10^{-1}mol/dm^3 of Thiram solutions over a period of 70 days and the results shown that the membrane could be successfully used upto 2 months without any notable change in potential during which the potential slope is reproducible within ±1 mV per concentration decade.

Determination of Thiram in synthetic mixtures

Aliquots of the samples were prepared by mixing solutions of thiram with other dithiocarbamate solutions, which were then analyzed using calibration plot. The results of the determinations are given in Table 4, shows the recovery was satisfactory.

Conclusion

The present study shows that nanocomposite *PANI-ZTP* can be used as an efficient adsorbent for the rapid removal of Thiram from effluents. TEM photograph showed that cation exchanger can be considered as nanocomposite. The equilibrium data was fitted to the Freundlich model for adsorption mechanism of the pesticide, Thiram, onto the surface of *PANI-ZTP* nano-composite. The negative value of ΔG° and ΔH° indicates the spontaneity and exothermic nature of the process. The sensitivity of the *PANI-ZTP* membrane electrode towards Thiram was demonstrated by the change in potential observed with changes in concentration. The limit of detection demonstrates the practical utility of electrode for the determination of pesticide concentration in drain and agriculture field pond water. The present method is more selective than the earlier methods as it permits safe and cost effective determination of Thiram in the presence of other pesticide without any significant interference.

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References

1. Klaus U.W.E., Pfeifer T. and Spiteller M., A Powerful Tool for the Analysis of Bound Residues Resulting from the Interaction of Pesticides with DOM and Humic Substances, *Environ. Sci. Tech.*, **34:** 3514 **(2000)**

2. Meijer S.N., Halsall C.J., Harner T., Perters A.J., Okenden W.A., Johnston A.E. and Jones K.C., Organochlorine Pesticide Residues in Archived UK Soil, *Environ. Sci. Tech.*, **35:** 835 **(2001)**

3. Zheng H. and Ye C., Identification of UV Photoproducts and Hydrolysis Products of Butachlor by Mass Spectrometry, *Environ. Sci. Tech.*, **35:** 2889 **(2001)**

4. Crespin M.A., Gallego M., Valcarcel M. and Gonzales J.M., Study of the Degradation of the Herbicides 2,4-D and MCPA at Different Depths

in Contaminated Agricultural Soil, *Environ. Sci. Tech.*, **35:** 4259 **(2001)**

5. British Crop Protection Council and Royal Society of Chemistry, In: Clieve Tomlin (Ed.), A World Compendium Pesticide Manual, Bath Press, UK, (**1994)**

6. Tanase G., David I.G., Cercasov C., Iorgulescu E.E., Louciana G. and Radu G.L., Electrochemical behaviour and electroanalysis of Thioamides, *Roman. Biotech. Lett.*, **6:** 81 **(2001)**

7. Priyantha N. and Weliwegamage S., Amperometric Method for Trace Level Determination of the Fungicide, Thiram, *J. Nat. Sci. Found. of Sri Lanka*, **33:** 17 **(2005)**

8. Aulakh J.S., Malik A.K. and Mahajan R.K., Solid phase microextraction-high pressure liquid chromatographic determination of nabam, thiram and azamethiphos in water samples with UV detection, *Talanta*, **66:** 266 **(2005)**

9. Walia S., Sharma R.K. and Parmar B.S., Isolation and simultaneous LC analysis of Thiram and its less toxic transformation product in DS formulation, *Bull. Environ. Contam. Toxicol*., **83,** 363 **(2009)**

10. Edwards I.R., Ferry, D.G. and Temple W.A., *Handbook of Pesticide Toxicology*, Academic Press: New York, **(1991)**

11. Kidd H. and James D.R., The Agrochemicals Handbook, 3rd ed., *Royal Society of Chemistry*, Cambridge, UK, **(1991)**

12. Kesari R. and Gupta V.K., A sensitive spectrophotometric method for the determination of dithiocarbamate fungicide and its application in environmental samples, *Talanta,* **45:** 1087 **(1988)**

13. Ubeda M.R., Sevilla Escribano M.T. and Hernandez Hernández L., Determination of Thiram by high-performance liquid chromatography with amperometric detection in river water and fungicide formulations, *J. Microchem.*, **41:** 22 **(1990)**

14. Ziawiony I., Polarographic investigations and determination of thiuram, *Chemia Analitcyzna*, **41:** 1043 **(1996**)

15. Sharma D.K., Verma N., Singh J., Prasher K. and Verma B.C., Pulse polarographic-determination of tetramethylthiuram disulfide in commercial fungicides and rubber accelerators, *Proc. Cont. & quant.*, **9:** 11 **(1998)**

16. Rossi M. and Rotilio D., Analysis of carbamate pesticides by micellar electrokinetic chromatography, *J. High Res. Chromatog.*, **20:** 265 **(1997)**

17. Cassella A.R., Garrigues S., de Campos R.C. and de la Guardia M., *Talanta,* **54:** 1087 **(2001)**

18. Sharma V.K., Aulakh J.S. and Malik A.K., Fourier transform infrared spectrometric determination of Ziram, *J. Environ. Monit*., **5:** 717 **(2003)**

19. Szolar O.H.J., Environmental and pharmaceutical analysis of dithiocarbamates, *Anal. Chim. Act,* **582,** 191 **(2007)**

20. Malik A.K. and Rao A.L.J., Spectrophotometric determination of some dithiocarbamates, *Talanta* **37:** 1205 **(1990)**

21. Alberti G. and Constantino U., Crystalline insoluble acid salts of tetravalent metals: X. Fibrous thorium phophate, a new inorganic ion-exchange material suitable for making (support-free)inorganic sheets, *J. Chromatogr*., **50,** 482 **(1970)**

22. De A.K. and Chowdhury K., Studies on thorium phosphate ion exchanger: Synthesis, properties and ion-exchange behaviour of thorium phosphate, *J. Chromatogr*., **101:** 63 **(1974)**

23. Khan A.A., Paquiza L., Characterization and ion-exchange behavior of thermally stable nano-composite polyaniline zirconium titanium phosphate: Its analytical application in separation of toxic metals, *Desalination*, **265:** 242 **(2011)**

24. Khan A.A and Paquiza L., Analysis of mercury ions in effluents using potentiometric sensor based on nanocomposite cation exchanger Polyaniline–zirconium titanium phosphate, *Desalination*, **272:** 278 **(2012)**

25. Khan A.A, Paquiza L. and Khan A., An advanced nano-composite cation-exchanger polypyrrole zirconium titanium phosphate as a Th(IV)-selective potentiometric sensor: preparation, characterization and its analytical application, *J. Mat. Sc.*, **45:** 3610 **(2010)**

26. Recommendation for publishing manuscripts on ion-selective electrodes (prepared for publication by G.G. Guilbault), Commission on Analytical

Nomenclature, Analytical chemistry Division, IUPAC, *Ion-Sel. El. Rev*. **1 (1969)**

27. Freundlich H.M.F., Uber die adsorption in lösungen, *Z. Phys. Chem*., **57:** 385 **(1906)**

28. Haghseresht F., Lu G., Adsorption characteristics of phenolic compounds onto Coal reject- derived adsorbents, *Energy Fuels*, **12, 1100 (1998)**

29. Fytianos K., Voudrias E. and Kokkalis E., Sorption-desorption behavior of 2,4-dichlorophenol by marine sediments, *Chemosphere*, **40:** 3 **(2000)**

30. Amini M.K., Mazloum M. and Ensaf A.A., Lead-selective membrane electrode using cryptand [2 2 2] neutral carrier, *Fres. J. Anal. Chem*., **364:** 690 **(1999)**.