

VARIATION IN THE OPTICAL SENSING PROPERTIES OF DITHIOCARBAMATE POLYMER MICROSPHERES AS FUNCTION OF SURFACE MORPHOLOGY

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ABSTRACT

Three polymers with N-ethanolamino-, N-benzylamino-, and N-t-butylamino-dithiocarbamate groups were synthesized from polyvinylbenzylchloride. Each of the three polymers was incorporated in a hydrogel membrane (PVA) cross-linked with glutaraldehyde to form a sensing element. The latter was, then, evaluated for its optical sensing behavior by subjecting it to varying concentrations (1.0×10^{-5} up to 0.1 M) of metal ions (Zn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cr^{3+} , Ni^{2+} , Cu^{2+}). Significant response was observed for the Hg^{2+} ions while the others showed negligible or no response. The turbidity absorbance increased consecutively from the dithiocarbamate polymer derived from N-t-butylamine towards that from ethanolamine as the concentration of the Hg^{2+} solution increased. The response time measured for the three polymer microspheres ranged between 2 and 30 minutes. The aminodithiocarbamate polymers were stable at normal temperatures (25° - 40° C) and as pH was changed between 2 and 7. In addition, the polymers demonstrated excellent stability with time and a capacity of 3.967, 3.787, 3.355 mmol Hg^{2+} ions per gram of polymer for the N-ethanolamino-, N-benzylamino-, and N-t-butylamino-dithiocarbamate respectively. SEM and Eds analyses showed an increase in size of about 25% in the case of complexation with N-ethanolamino-, no size change with N-benzylamino-, and a 16.6% decrease in size with N-t-butylamino-dithiocarbamate.

Key words: *Dithiocarbamate polymer microspheres, optical sensing, heavy metals, SEM, Eds.*

1. INTRODUCTION

The increasing concern about the rising levels of heavy metal ions in waste and drinking water instigated research activity in two related areas. The first activity is concentrating on developing efficient, low cost and practical methods to remove heavy metal ions from water [1-6]. The second is targeting the production of a variety of sensors that are capable of detecting and monitoring the heavy metal ions [7-20]. Optical chemical sensors represent an important class of sensors that demonstrated good response to varying concentrations of analyte. Some of these sensors underwent swelling and shrinking as a function of heavy metal ion concentrations [7,8,18-20]. These sensors exhibited superior properties over others primarily due to their resistance to photo degradation and to their excellent mechanical stability associated with the swelling and shrinking processes. The sensing elements were produced by dispersing suitably functionalized polymer microspheres in a hydrogel membrane constructed from polyvinyl alcohol cross-linked with glutaraldehyde [8].

In previous studies, lightly cross-linked dithiocarbamate polymer microspheres underwent shrinking upon subjecting them to increasing concentrations of Hg^{2+} ions. This was due to the neutralization of the negatively charged dithio group by the mercuric ions. This led to a lower percentage of water in the polymer and thus to an increase in its refractive index relative to that of the hydrogel. An increase in the absorbance was observed along the UV-Visible region 300-800nm as the concentration of the Hg^{2+} ions was changed from 1.0×10^{-5} to 0.1 M [18,20].

In this work, three dithiocarbamate polymer microspheres containing amines of different steric and/or electronic composition (N-ethanolaminodithiocarbamate, N-benzylaminodithiocarbamate, and N-t-butylaminodithiocarbamate) were synthesized starting with polyvinyl benzyl chloride and then their optical sensing properties were studied. In order to understand the nature of the interactions between the polymer microspheres and the mercuric ions and also to monitor the morphological changes on the surface of the microspheres, SEM and Eds analyses were performed.

2. EXPERIMENTAL

2.1. Materials

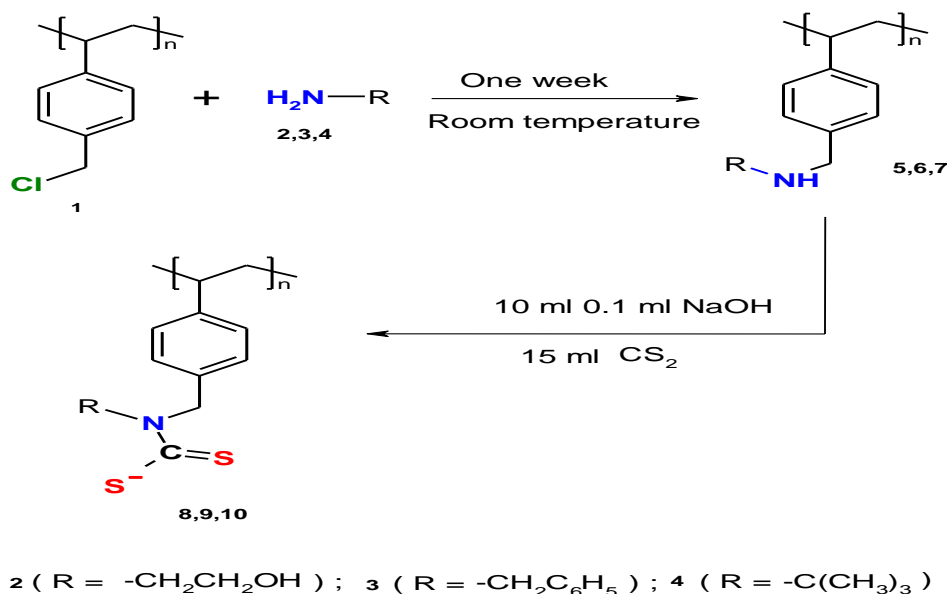
All chemicals were of analytical grade and were purchased from Sigma-Aldrich and used as such unless indicated otherwise. All solutions were prepared in deionized distilled water. Polyvinylbenzyl chloride lightly cross-linked with divinylbenzene (2 % mole) was donated by W.R. Seitz of the University of New Hampshire (USA).

2.2. Instruments

Absorption measurements were performed using a Perkin-Elmer Lambda 5 UV-visible spectrophotometer, equipped with a thermostated cell compartment. The temperature inside the cell was monitored to within (± 0.2 °C) by means of a calibrated thermometer. The temperature was controlled using a circulating thermostat (Julabo U 3). The pH measurements were recorded on a Jenway pH meter (3310) with a combination glass electrode and a tolerance of ± 0.01 pH units. A Varian Vista charged-coupled device axial simultaneous inductively coupled plasma - atomic - emission spectrometer (ICP-AES) was used to determine the capacity of each of the dithiocarbamate polymers. A Fourier transform infrared spectrophotometer (Testscan Shimadzu FT-IR 8000 series), was used to obtain IR-Spectra.

2.3. Synthesis of the dithiocarbamate polymers

One gram of polyvinyl benzyl chloride (**1**) was soaked in few milliliter of DMF for several days, the soaked polymer was then filtered and washed several times with deionized distilled water and then immersed in 7 ml of the appropriate amine (**2,3,4**) at room temperature and stirred for one week. The corresponding product (**5,6,7**) was washed several times with deionized distilled water and then the excess aminating agent was removed under reduced pressure. Then, to one gram of the amine polymer (**5,6,7**), 10 ml of 0.1M NaOH solution was added. And then 15 ml of 0.1M carbon disulfide solution in THF were added dropwise to the reaction mixture and allowed to stir for 24 hr at room temperature. The resulting dithiocarbamate polymer (**8,9,10**) was then washed several times with deionized distilled water, methanol, and finally with 0.1M sodium acetate solution (pH = 8). The product was then air dried (Scheme 1).



Scheme 1. Preparation of the Dithiocarbamate polymers.

2.4. Optical measurements

The sensing elements were prepared and used as described earlier [8]. The change in optical properties of the microspheres was monitored using a Perkin Elmer conventional spectrophotometer. The solution in the cuvette was changed using a disposable pipette, starting with the analyte of lower concentration (1.0×10^{-5} – 1.0×10^{-1} M). The change in turbidity of the sensing element as a function of analyte concentration was measured as absorbance.

The performance of the sensing elements under different pH conditions (pH 2.0-7.0) was examined for a solution of 0.1M Hg^{2+} ions at 700nm. The response time of the sensing element towards Hg^{2+} ions was obtained by measuring the absorbance at 700 nm of 0.1 M Hg^{2+} ions until steady state is reached. The stability of the sensing element was also examined. Readings towards different concentration of Hg^{2+} ions were taken once a week for several weeks. The response was recorded as absorbance in the visible region (350-800nm). The reproducibility of the sensor was tested by cycling between blank and 1×10^{-1} M Hg^{2+} aqueous solution for several times. Readings as turbidity absorbance at 700nm were taken. Between each reading, Hg^{2+} ions were eluted by washing the cuvette while in the chamber of the instrument, with a saturated solution of EDTA and then with deionized distilled water until obtaining the blank reading. The effect of temperature was determined by measuring the absorbance of 0.1M Hg^{2+} solution at 700 nm starting from 25 °C and moving up to 60 °C, with a 7 °C increment in every temperature interval. The

absorbance was measured after one hour of each controlled temperature.

2.5. Polymer capacity of the sensor

A specific mass of the dithiocarbamate polymer (**8,9,10**) (0.05 grams) was soaked in 50 ml of aqueous 0.1 M HgCl_2 and stirred over 48 hr. The polymer was filtered, The un adsorbed metal ions in the filtrate were determined by inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

2.6. SEM and EDS analysis

Samples were mounted on metal stubs and coated with gold (Polaron Spatter coater). The microphotographs were recorded using scanning electron microscope JEOL model, JSM-5410 LV available at the microscopy lab at the faculty of agriculture, food and environmental quality Sciences, The Hebrew University. The images were taken with an accelerating voltage of 25 kV, at high vacuum (HV mode) and secondary electron image (SEI). The analysis was done using Oxford systems –Liquid Nitrogen cooled solid state Energy Dispersive Spectrometer detector and link ISIS software.

3. RESULTS AND DISCUSSION

The dithiocarbamate polymers were synthesized from polyvinyl benzyl chloride by a previously published protocol [18] as shown in Scheme 1 and were characterized by FT-IR spectroscopy. The polymers showed characteristic absorption bands in three to four regions. The bands in the 1550 to 1480 cm^{-1} region are attributed to the C-N vibration of the CS_2-NR_2 bond. While the bands in the 1030-960 cm^{-1} region are associated with the CSS vibrations.²¹ The dithiocarbamate derived from ethanolamine showed an O-H band at 3400 cm^{-1} (table 1).

The three polymers responded to varying concentrations of Hg^{2+} ions as the turbidity absorbance was recorded along the visible region (300-800nm) (Plot 1). The increase in absorbance as the concentrations of the mercuric ions were changed from 1.0×10^{-5} to 1.0×10^{-1} M was highest with the dithiocarbamate derived from ethanolamine and lowest with that derived from t-butylamine (table 2). The stability of the sensing element was determined by measuring the response of different concentrations of Hg^{2+} solutions once a week for several weeks(Fig. 1). The sensing element did not undergo any change over the tested period. The reproducibility was also determined by cycling between blank and 1×10^{-1} M Hg^{2+} four times at 700nm. The absorbance stayed constant during the four runs with a SD value of 5×10^{-4} (table 3). Furthermore, the response time measured for the three polymer microspheres (ethanolamino-, benzylamino- and t-butylamino-) was 2, 10, and 30 minutes, respectively(Fig. 2). Thus the sensing element prepared from the dithiocarbamate polymer microspheres demonstrated practicability due to its high stability and excellent reproducibility and fast response time. It is also worth noting that the response of our sensor to other heavy, alkali and alkali earth metal ions was negligible. This behavior was similar to a previous study with copolymer microspheres [20].

Table 1. FT-IR characteristic absorption bands (in cm^{-1}) of the dithiocarbamate polymers

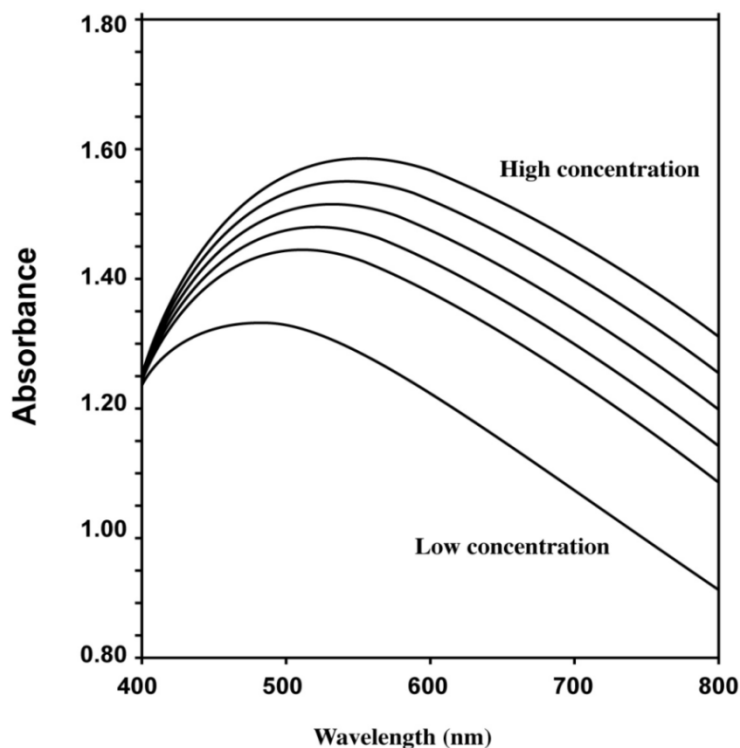
Polymer	Functional Groups			
	C-N	C-S	C-H	O-H
Ethanol amine	1490	1030, 980	3040, 2910	3400
t-Butylamine	1550	1000	3020, 2960	
Benzyl amine	1480	1020, 960	3040, 2900	

Table 2. Turbidity absorbance vs. concentration of Hg^{2+} ions of the dithiocarbamate polymers

Concentration HgCl_2 aq(M)	Turbidity Absorbance (nm)		
	Ethanol amine dithiocarbamate	t-Butylamine dithiocarbamate	Benzyl amine dithiocarbamate
0.0000	1.070	1.275	1.715
0.00001	1.250	1.300	1.720
0.0001	1.310	1.325	1.735
0.001	1.375	1.350	1.765
0.01	1.430	1.380	1.848
0.1	1.485	1.405	1.920

Table 3. The reproducibility of the sensing element of the dithiocarbamate polymers at 700nm.

Replicate #	ethanolamine		benzylamine		N-t- butylamine	
	0 M	0.1 M	0 M	0.1 M	0 M	0.1 M
1	1.516	1.931	1.205	1.410	0.222	0.352
2	1.516	1.931	1.205	1.411	0.223	0.353
3	1.516	1.931	1.206	1.411	0.223	0.353
4	1.516	1.932	1.206	1.411	0.223	0.353
Average		1.931		1.411		0.353
SD		5×10^{-4}		5×10^{-4}		5×10^{-4}
RSD		0.03%		0.04%		0.14%

Plot 1. Absorbance spectra of different concentrations of Hg^{2+} along the visible region with the sensing element containing N-ethanolaminodithiocarbamate polymer microspheres.

The effect of pH on the chelation of the mercuric ions to the dithiocarbamate functionality on the sensing element was examined by measuring the absorbance at 700nm for 0.01M Hg^{2+} buffered solutions in the pH range 2-7. Higher and lower pH values were avoided because of precipitation problems above pH 8 and acid hydrolysis reactions below pH 2 [22]. There was no significant change in absorbance observed for the three dithiocarbamate microspheres apparently due to protonation of the dithiocarbamate functional group over the pH range studied. Although a slight increase in absorbance at $\text{pH} \geq 7$ indicated some insignificant deprotonation of the S-H of the dithiocarbamate occurred (Fig. 3). The effect of the temperature on the behavior of the sensing element was examined by taking the absorbance of a 0.1 M Hg^{2+} solution at 700nm and at different temperatures starting from 25 °C and up to 60 °C with an increment of 7 °C. The absorbance was recorded after an equilibration time of one hour at each controlled temperature in order to reach steady state. An insignificant increase in absorbance is observed probably related to a slight increase in the difference of the refractive index between the hydrogel and the polymer microspheres (Fig. 4).

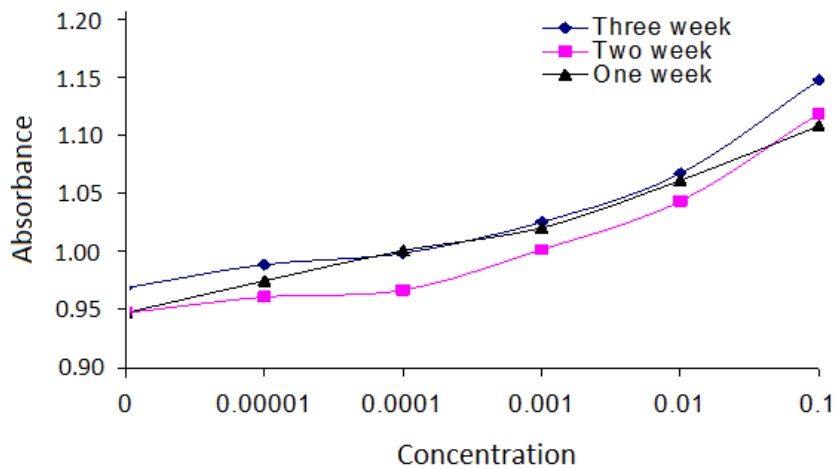


Figure 1. Representative turbidity absorbance vs. concentration of Hg^{2+} ions as function of time.

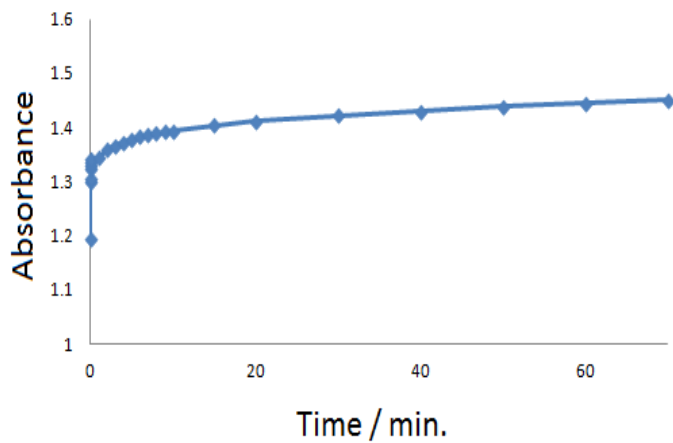


Figure 2. Representative turbidity absorbance vs. time of 0.1M Hg^{2+} at 700nm.

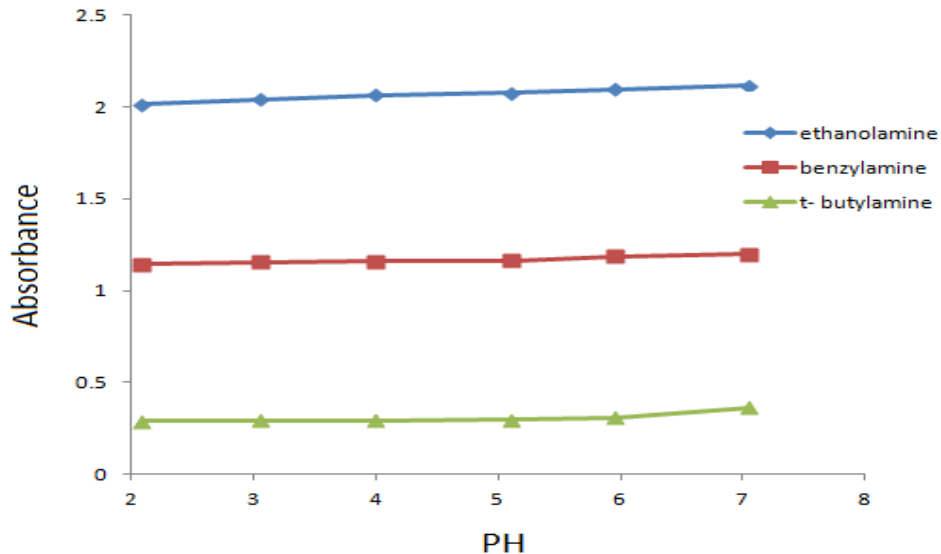


Figure 3. Turbidity absorbance of the sensing elements as a function of pH for a 0.01 M Hg^{2+} buffered solutions.

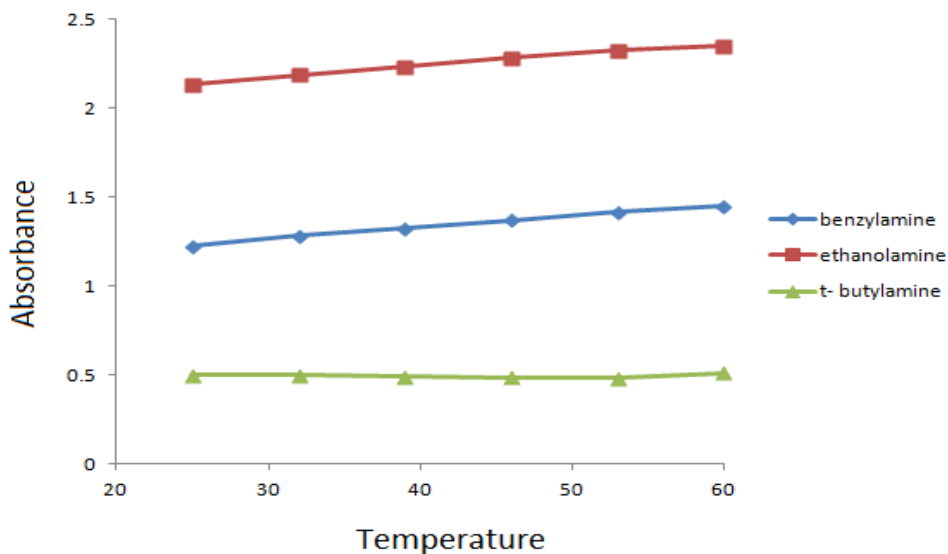


Figure 4. Turbidity absorbance vs. temperature

Microspheres morphology was studied by SEM analysis. This was performed by first mounting a sample of the polymer on a metal stubs and then coating it with gold by sputtering. The results showed a uniform distribution, of singly separated microspheres. The SEM image of the Ethanolamino- dithiocarbamate polymer microspheres with an average size of 6 μm is shown in Figure 5. Upon complexation with Hg^{2+} ions, the size of the microspheres increased by a factor of 25%, to reach approximately 8 μm . In order to further characterize the type of interactions between Hg^{2+} ions and the polymeric microspheres, Eds analysis was performed (Fig. 6). It is clear and beyond doubt that the Hg^{2+} ions are chelating with the sulfur of the dithiocarbamate functionality situated on the polymer backbone. It is also apparent that significant adsorption has occurred on the polymer surface possibly assisted by the electron-donating nature of the OH group of the aminoethanol moiety [1]. As the adsorption of the Hg^{2+} ions is

more pronounced than their chelation with the dithiocarbamate functionality, an increase in the size of the polymer microspheres is observed.

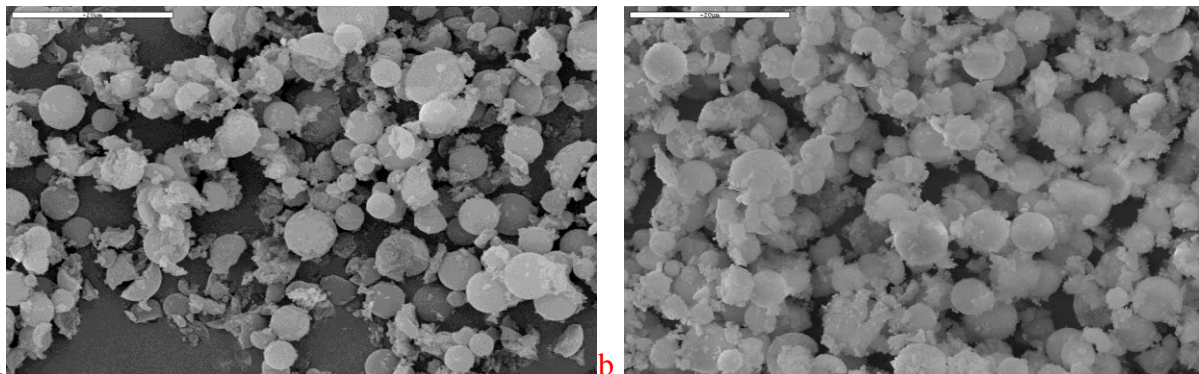


Figure 5. SEM image of ethanolamino-dithiocarbamate polymer microspheres before(a) and after complexation(b) with Hg^{2+} ions.

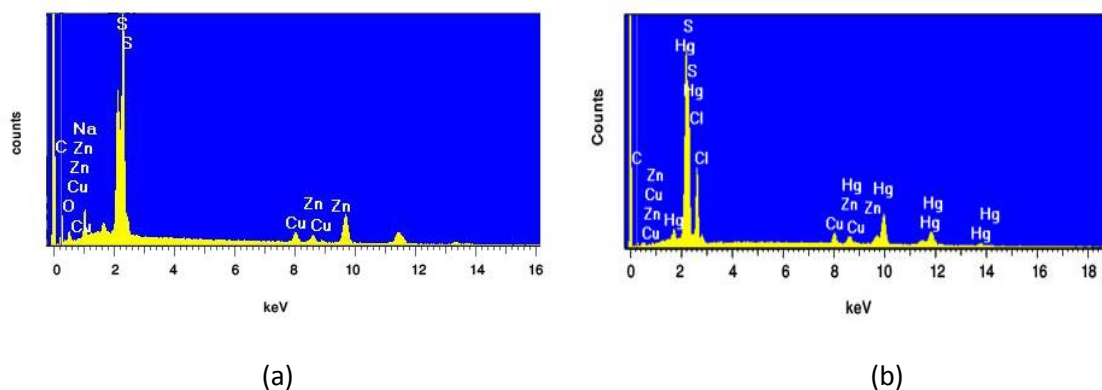


Figure 6. EDS spectrum of ethanolamino-dithiocarbamate polymer microspheres before(a) and after(b) complexation with Hg^{2+} ions. (Full scale = 7.09 k counts).

Furthermore, upon SEM analysis of the benzylamino-dithiocarbamate polymer, the microspheres sizes did not change after complexation with Hg^{2+} ions. Thus the average size stayed at $6\mu\text{m}$ (Fig. 7). EDS analysis indicated a good concentration of the mercury confirming the complexation of the Hg^{2+} ions with the benzylamino-dithiocarbamate polymer and possibly π -complexation between Hg^{2+} ions and the aromatic ring [23] .

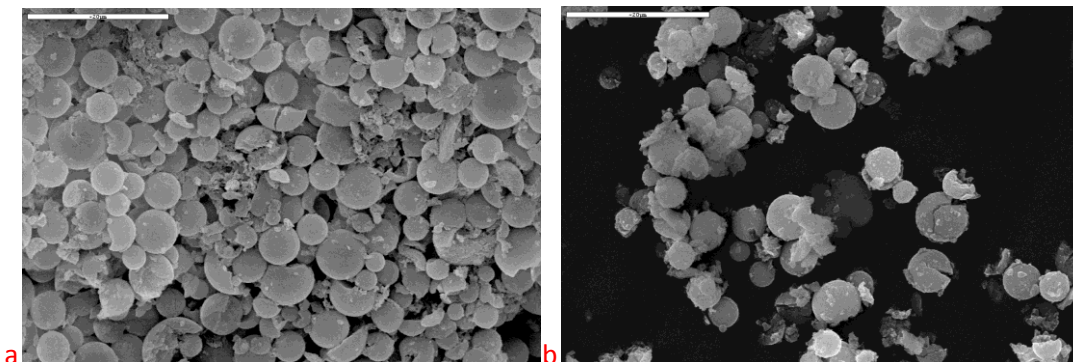


Figure 7. SEM images of benzylamino-dithiocarbamate polymer microspheres before(a) and after (b) complexation with Hg^{2+} ions.

N- t-Butylamino- dithiocarbamate polymer microspheres underwent shrinking by a factor of 16.6% when complexed with Hg^{2+} ions. Thus the average size changed from $7.2\mu m$ to $6\mu m$ (Fig. 8). This is consistent with our hypothesis in which we propose a shrinking process when the heavy metal ions are chelated to the negatively charged sulfur atoms on the dithiocarbamate group. The fact that the ethanolamino- and the benzylamino-dithiocarbamate polymer microspheres did not undergo similar reduction in size is most probably associated with the role played by the adsorbed Hg^{2+} ions. The adsorbed Hg^{2+} ions on the surface of the polymer were responsible for the increase in size as well as in the refractive index of the polymer microspheres and hence an increase in their turbidity absorbance. Apparently two effects are counter acting; chelation causes shrinking while adsorption causes swelling. When the adsorption of the mercuric ions was the predominant effect, as in the case of the ethanolamino-dithiocarbamate polymer microspheres, we observed a net increase in size of about 25%. While when the adsorption was a minor determinant, as in the case of the t-butylamino-dithiocarbamate microspheres, a decrease in size of about 16.6% is observed.

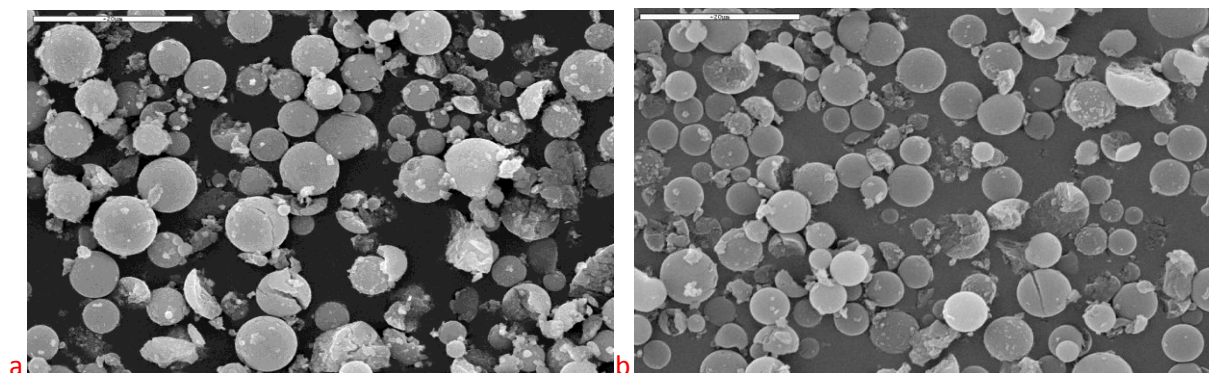


Figure 8. SEM image of t-Butylamine dithiocarbamate polymer microspheres before(a) and after(b) complexation with Hg^{2+} ions.

4. CONCLUSIONS

Three dithiocarbamate polymer microspheres were synthesized in this work. All showed response to Hg^{2+} ions. The Ethanolamine based dithiocarbamate exhibited the largest change in absorbance upon changing the concentration of Hg^{2+} ions from 0.0 to 0.1 M. In addition, the response time measured for the three polymer microspheres (ethanolamino-, benzyl amino- and t-butyl amino-; 2, 10, 30 minutes respectively) was fastest with the ethanolamino- based dithiocarbamate. This is probably associated with a significant electronic effect from the OH group.

The three sensing elements derived from the three dithiocarbamate polymer microspheres demonstrated good stability after three weeks of storage. SEM and Eds analyses showed beyond doubt that both complexation of Hg^{2+} ions with the dithiocarbamate groups on the polymer microspheres and adsorption of Hg^{2+} ions on the surface of the sensing element are occurring.

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6. REFERENCES

- [1]. A. McClain, Y-L. Hsieh, Synthesis of Polystyrene-Supported Dithiocarbamates and Their Complexation with Metal Ions *J. Appl. Polym. Sci.* **92**,218-225(2004)
- [2]. A. Denizli, K. Kesenci, Y. Arica, E. Piskin, Dithiocarbamate-incorporated monosize polystyrene microspheres for selective removal of mercury ions *Reactive & Functional Polymers* **44**,235-243(2000)
- [3]. B.L. Rivas, I. M. Peric, S. Villegas, Synthesis and metal ion uptake properties of water-insoluble functional copolymers: removal of metal ions with environmental impact *Polym. Bull.* **65**,917-928(2010)
- [4]. T. Hirotsu, S. Katoh, K. Sugasaka, M. Sakuragi, K. Ichimura, Y. Suda, M. Fujishima, Y. Abe, T. Misonoo, Synthesis of Dihydroxamic Acid Chelating Polymers and the Adsorptive Property for Uranium in Sea Water *J. Polym. Sci., part A; Polym. Chem.* **24**, 1953-1966(1986)
- [5]. D. Afzali, A. Mostavavi, F. Etemadi, and A. Ghazizadeh, Application of modified multiwalled carbon

- nanotubes as solid sorbent for separation and preconcentration of trace amounts of manganese ions *Arabian Journal of Chemistry* **5**,155-161(2012)
- [6]. O. Genc, K. Kesenc, E. Piskin, N. Satiroglu, Dithiocarbamate incorporated Monodispersed Polystyrene Microspheres as Specific Sorbents *J. Appl. Polym. Sci.* **59**, 109-117(1996)
- [7]. I. Oehme, O. S. Wolfbeis, Optical Sensors for Determination of Heavy Metal Ions *Mikrochim. Acta* **126**, 177-192(1997)
- [8]. Z.M. Shakasher, I. odeh, S. Jabr, W. R. Seitz, An Optical Chemical Sensor Based on Swellable Dicarboxylate Functionalized Polymer Microspheres for pH , Copper and Calcium Determination *Mikrochim Acta* **144**, 147-153(2004)
- [9]. M. T. V. Rooney, W. R. Seitz, An optically sensitive membrane for pH based on swellable polymer microspheres in a hydrogel *Anal. Comm.* **36**, No. 7, 267- 270(1999)
- [10]. W. R. Seitz, M. T. V. Rooney, E. W. Miele, H. Wang, N. Kaval, L. Zhang, Derivatized, swellable polymer microspheres for chemical transduction *Anal. Chem. Acta.* **400**, No. 1-3, 55-64(1999)
- [11]. M. F. McCurley, W. R. Seitz, Fiber optic sensor for salt concentration based on polymer swelling *Anal. Chem. Acta* **249**, 373-380(1991)
- [12]. Z. Zhang, Z. Shaksher, W. R. Seitz, Aminated polystyrene membranes for a fiber optic pH sensor based on reflectance changes accompanying polymer swelling *Mikrochim. Acta* **121**, No. 1 4, 41-50(1995)
- [13]. Z. Shaksher, W. R. Seitz, K. D. Legg, Single fiber-optic pH sensor based on changes accompanying polymer swelling *Anal. Chem.* **66**, 1731-1735(1994)
- [14]. Z. Zhujun, Y. Zhang, M. Wangbai, R. Russell, Z. M. Shakhsher, C. L. Grant, W. R. Seitz, D. C. Sundberg, Poly(vinyl alcohol) as a substrate for indicator immobilization for fiber optic chemical sensors *Anal. Chem.* **61**, 202-205(1989)
- [15]. H-C. Lin, Y-H. Chou, J. Yang, Development of an aminocarboxylic acid-modified infrared chemical sensor for selective determination of copper ions in aqueous solutions *Anal. Chim. Acta* **611**,89-96(2008)
- [16]. M. Bai, M.E. Langmuir, Z. Li, W. R. Seitz, A sensor for pH based on an Aminated polystyrene Membrane *Talanta* **44**, 1691-1698(1997)
- [17]. B. Adhikari, S. Majumdar, Polymer in sensor application *Prog. Polym. Sci.* **29**, 699-766(2004)
- [18]. I. Odeh, S. Siam, M. Khatib, and Z. Shakhsher, An Optical Chemical Sensor Based on Polymer Swelling and Shrinking using Dithiocarbamate-Polymer Microspheres *Jordan Journal of Chemistry* **4**, 55- 64(2009)
- [19]. I. Odeh, Z. Shakhsher, S. Jaber, M. Khatib, F. Al-Rimawi, An Optical Sensor Based on Polyvinyl Benzyl Malonate Cross-Linked with Divinyl Benzene Dispersed in a Hydrogel Membrane for Detection of Some Heavy Metals *Am.J.Anal.Chem.* **3**, 283-287(2012)
- [20]. Z. Shakhsher, I. Odeh, I. Rajabi, and M. Khatib, Optical Sensing Properties of Dithiocarbamate-Functionalized Microspheres, Using a Polyvinylpyridine- Polyvinylbenzyl Chloride Copolymer *Sensors* **10**,8953-8962(2010)
- [21]. A.D. Brown, W.K. Glass, M.A. Burke, The general use of i.r. spectra criteria in discussions of the bonding and structure of metal dithiocarbamates *Spectrochimica Acta* **32A**,137-143(1976)
- [22]. S.P. Huang, K.J. Franz, E. H. Arnold, J. Devenyi, R. H. Fish, Polymer pendant ligand chemistry-The selective and competitive removal of Ag⁺, Hg²⁺, Cu²⁺, Pb²⁺ and Cd²⁺ ions from aqueous solution utilizing a N-sulfonyl ethylene bis (dithiocarbamate) ligand anchored on macroporous polystyrene-divinylbenzene Beads *Polyhedron* **15**,4241-4254(1996)
- [23]. W. Lau, J. C. Huffman, and J. K. Kochi, Molecular Structure and Charge Transfer Excitation of Electron Donor-Acceptor Complexes. Ion Pairs from Arenes and Mercury(II) *J. Am. Chem. Soc.* **104**,No.20,5515-5517(1982)