

## Assessment of $\text{Hg}^{2+}$ in hazardous wastes using chemosensor neutral red dye

Mohamed S. Attia<sup>1\*</sup>, Mohamed E. Saad<sup>2</sup>, Taha F. Hassanein<sup>2</sup>, Eid Metwally<sup>2</sup> Khalil, Sheta M. Sheta<sup>3</sup> and Said M. El-Sheikh<sup>4</sup>

1-Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

2- Chemistry Department, Faculty of Science, Helwan University, Cairo, 11795, Egypt

3- Inorganic Chemistry Department, National Research Centre, 33 El-Behouth St., Dokki, Giza, 12622, Egypt

4- Nanomaterials and Nanotechnology Department, Central Metallurgical R & D Institute, Cairo, 11421, Egypt

\*Correspondence: [Mohamed\\_sam@yahoo.com](mailto:Mohamed_sam@yahoo.com)

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### ABSTRACT

A new, simple, sensitive and selective spectrofluorimetric method for the determination of trace amounts of  $\text{Hg}^{2+}$  in hazardous wastes of fluorescent lamps using chemosensor neutral red dye is developed in acetonitrile at pH 6.6. The  $\text{Hg}^{2+}$  can remarkably quench the fluorescence intensity of neutral red dye in acetonitrile at  $\lambda_{\text{ex}} = 380$  nm. The lowering of fluorescence intensity of neutral red dye is proportional to the concentration of  $\text{Hg}^{2+}$  and it is used as optical sensor for its assessment. The dynamic range found for the determination of  $\text{Hg}^{2+}$  concentration is  $2.3 \times 10^{-9} - 8.0 \times 10^{-6} \text{ mol l}^{-1}$  with a detection limit of  $1.0 \times 10^{-11} \text{ mol l}^{-1}$ .

**Keywords:**  $\text{Hg}^{2+}$ , Neutral red dye, Optical Sensor, Quenching, Fluorescence Intensity.

### INTRODUCTION

A fluorescent lamp is a gas-discharge lamp that uses electricity to excite mercury vapor. The inner surface of the bulb is coated with a fluorescent coating made of varying blends of rare-earth phosphor salts. A typical "cool white" fluorescent lamp utilizing  $\text{Tb}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{LaPO}_4$  for green and blue emission and  $\text{Eu}$  and  $\text{Y}_2\text{O}_3$  for red emission. Mercury is slowly absorbed into glass phosphor substance and tube electrodes throughout the lamp life. The loss of mercury initially causes an extended run-up time to full light output and finally causes the lamp to glow a dim pink when the mercury runs out. If a fluorescent lamp is broken, a very small amount of mercury can contaminate the surrounding environment, where about 99% of the mercury is typically contained in the phosphor substance, especially on lamps that are near their end of life<sup>(1)</sup>. The broken glass is usually considered as a hazard waste.

During the past decade, the development of optical chemosensors for the determination of  $\text{Hg}^{2+}$  ion has become a rapidly expanding area of analytical chemistry because it offers certain advantages over electrochemical sensors<sup>(2-4)</sup>. The optical sensors possess the advantages of simple preparation, reasonable selectivity, improved sensitivity and no need for reference devices. Thus, in recent years, a number of optodes with different optical principles have been reported for the determination of mercury<sup>(5-11)</sup>. The main problem associated with some of these optodes is the lack of enough selectivity to  $\text{Hg}(\text{II})$  over other soft heavy metal ions. Basic principles and techniques of bulk optodes have been described and theoretical description of

them has been elucidated<sup>(12-15)</sup>. Previous work was performed to determine the mercury in the food samples<sup>(16,17)</sup>.

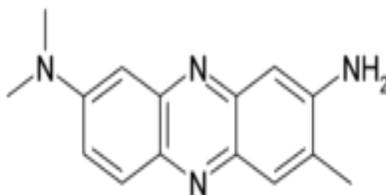
The previous studies were performed either in sol-gel matrix such as; pyrrolizinato dye entrapped into sol-gel<sup>(18)</sup> and porphyrin derivatives into sol-gel films<sup>(19)</sup> or pyridylazo)-2-naphthol in PVC membrane<sup>(11)</sup>; 4-(*p*-nitrophenyl azo)-pyrocatechol as ionophore<sup>(20)</sup>, bis (diisobutylthiocarbamate) with a proton-selective chromoionophore<sup>(7)</sup>, valinomycin ionophore together with ETH5294 chromoionophore<sup>(21)</sup>, oxacarbocyanine dye and borate<sup>(22)</sup>, porphyrin derivatives<sup>(23,24)</sup>, tetraarylborate and a porphyrin protonselective fluoroionophore<sup>(25)</sup>. Some of the above mentioned sensors suffer from lack of sensitivity and selectivity that is required for the determination of low concentration levels of mercury ions and/or have relatively long response time.

In this work a highly selective, sensitive and rapid response optical sensor neutral red dye in acetonitrile at pH 6.6 was used to assessment the mercury in fluorescent lamps of different shapes.

## EXPERIMENTAL

### 1. Materials and Reagents

Pure standard neutral red dye is purchased from Sigma Company, its structure is shown in Figure (1). Mercuric Chloride, Europium Chloride, Terbium Chloride, Lanthanum Chloride, Cadmium Chloride, Cupric Chloride, Zinc Chloride, Cobalt Chloride, Manganes Chloride, Lead chloride, Nickel Chloride, Ferrous chloride, Chromium chloride, and Potassium Chromate are purchased from Sigma Company.



**Fig. 1. Structure of neutral red dye**

All chemicals used are analytical-reagents of higher grade. Distilled water and pure grade solvents from (Aldrich) are used for the preparation of all solutions and during the determinations. A stock solution of metal salts ( $1 \times 10^{-4}$  mol  $l^{-1}$ ) is directly prepared and dissolved in distilled water. The working standard solutions of metal salts ( $1 \times 10^{-5}$  mol  $l^{-1}$ ) are freshly prepared by appropriate dilution with acetonitrile. A stock solution of neutral red dye ( $1 \times 10^{-4}$  mol  $l^{-1}$ ) is directly prepared and dissolved in ethanol. The working standard solution of neutral red ( $2 \times 10^{-5}$  mol  $l^{-1}$ ) is freshly prepared by appropriate dilution with acetonitrile.

### 2. Apparatus

All fluorescence measurements are carried out on Shimadzu RF5301 Spectrofluorophotometer in the range (290–750 nm). The absorption spectra are recorded with a Unicam UV-Visible double-beam spectrophotometer from Helios Company. It employs a Tungsten filament light source and a Deuterium lamp, which have a continuous spectrum in the ultraviolet region. The spectrophotometer is equipped with a temperature-controller cell holder. Mercuric ion was determined by atomic absorption spectrometry (AAS), using Perkin Elmer AAS 3100.

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(All measurements are measured at Photoenergy Center and Central Lab., Faculty of Science, Ain Shams Univ.).

### 3. General procedure

To 10 ml measuring flasks, solutions are added in the following order: 0.2 ml ( $2 \times 10^{-5} \text{ mol l}^{-1}$ ) of the neutral red dye solution and different additions of ( $1 \times 10^{-4} \text{ mol l}^{-1}$ )  $\text{HgCl}_2$  solution. The pH of solutions was adjusted by using appropriate volume of  $\text{HCl}$  /  $\text{NH}_4\text{OH}$ , then the mixture is diluted to the mark with acetonitrile at room temperature. The above method is used for the subsequent measurements of absorption, emission spectra as well as the effect of time. The fluorescence intensity is measured at  $\lambda_{\text{ex}} = 380 \text{ nm}$ .

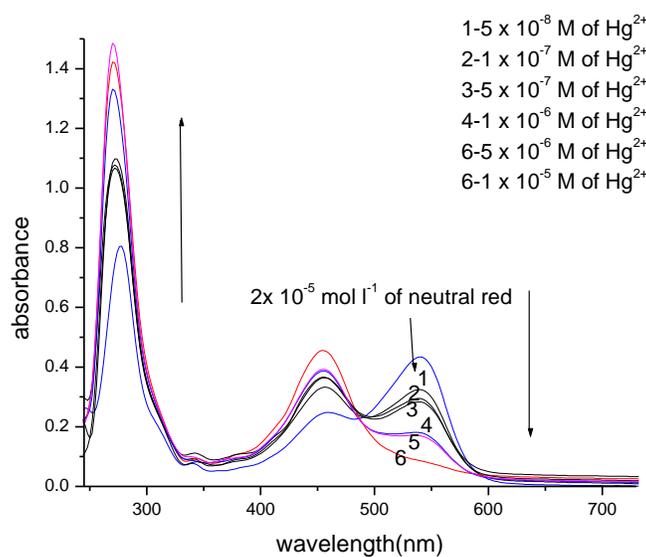
### 4. Determination of $\text{Hg}^{2+}$ in hazardous waste samples

0.2 gm of the real fluorescent lamp samples were digested with 1 ml aqua regia reagent plus 6 ml HF in microwave oven (CEM innovators, microwave technology MDS 2000) then diluted to 250 ml measuring flask by distilled water (The solution of coated surface of the fluorescent lamp is considered as hazardous waste). Then an appropriate volume from each sample was analyzed by atomic absorption spectroscopy.

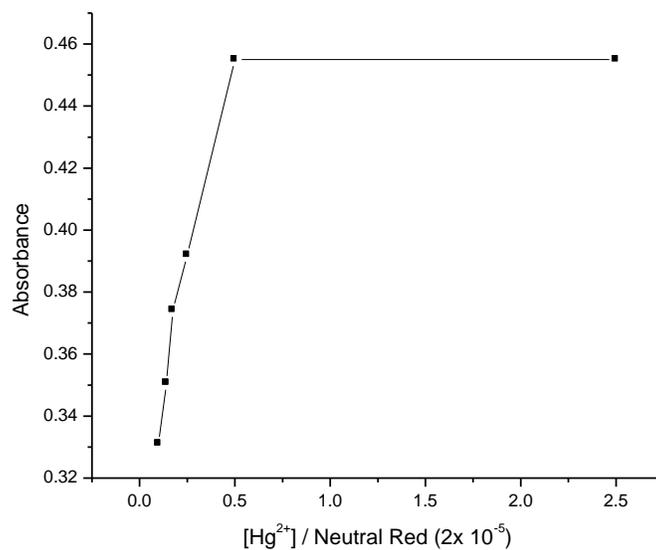
## RESULTS AND DISCUSSION

### 1. Spectral characteristics

The absorption spectrum of  $2 \times 10^{-5} \text{ mol l}^{-1}$  of neutral red dye in acetonitrile shows three bands in UV/VIS spectra at 278, 460 and 542 nm with a molar absorptivity coefficient ( $\epsilon = 832300, 231000$  and  $436000 \text{ M}^{-1}\text{cm}^{-1}$ ), respectively. The protonated (NRH) and neutral (NR) forms of monomeric neutral red (NR) exhibit distinct absorption maxima at 542 and 460 nm, respectively). Upon complexation of  $\text{Hg}^{2+}$  ions, a blue shift is observed in the three bands by 6, 6 and 10 nm respectively, as shown in Figure (2). The ion titration revealed that the complex formed is of M: L ratio (1: 2), which indicates that the ligand may coordinate to the metal from one coordination site (Fig. 3). The emission spectrum of neutral red dye in the presence of different concentrations of  $\text{Hg}^{2+}$  ions in acetonitrile at  $\lambda_{\text{ex}}=380 \text{ nm}$  is shown in Figure (4).

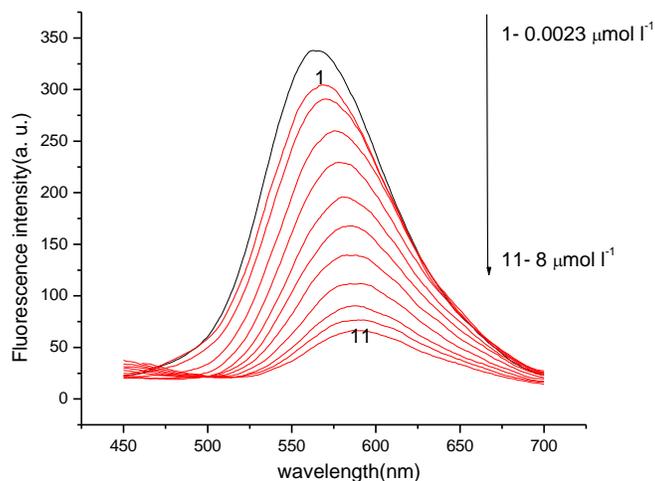


**Fig. 2.** Absorption spectra of  $2 \times 10^{-5} \text{ mol l}^{-1}$  of neutral red dye in the presence of different concentrations of  $Hg^{2+}$  in acetonitrile



**Fig. 3.** Relationship between different molar concentration ratios of  $Hg^{2+}$  / neutral red and the absorbance (molar ratio method)

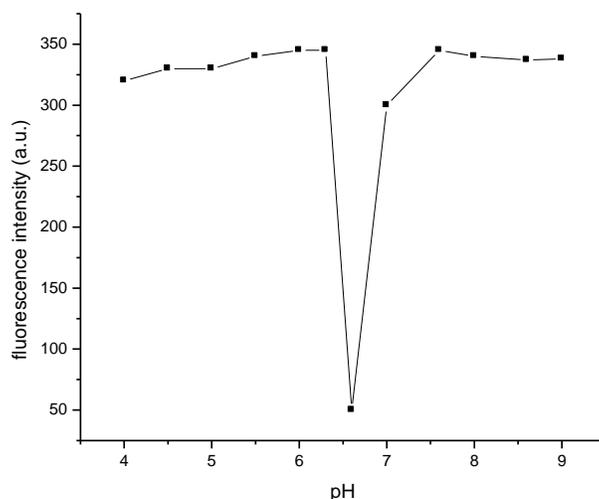
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**Fig. 4. Fluorescence emission spectra of  $2 \times 10^{-5} \text{ mol l}^{-1}$  of neutral red dye in the presence of different concentrations of  $\text{Hg}^{2+}$  in acetonitrile at  $\lambda_{\text{ex}} = 380 \text{ nm}$  and  $\text{pH} = 6.6$**

### 2. Effect of pH

The pH of the medium has a great effect on the fluorescence intensity of the neutral red dye. Where the more preferred pH at which the complex formation between the neutral red dye (the reaction between neutral red and  $\text{Hg}^{2+}$  is oriented to the formation of the protonated form of the neutral red which is the predominant form of the neutral red below pH 7) and  $\text{Hg}^{2+}$  ions and a perfect quenching process was occurred at  $\text{pH} = 6.6$  (Fig. 5).



**Fig.5. Fluorescence emission spectra of  $2 \times 10^{-5} \text{ mol l}^{-1}$  of neutral red dye with  $1 \times 10^{-5} \text{ mol l}^{-1}$  of  $\text{Hg}^{2+}$  at different pH.**

### 3. Effect of time

The effect of time on the chelating reaction of the  $\text{Hg}^{2+}$ - (neutral red dye) system at room temperature is studied, it has been found that the reaction occurs in situ and reaches to maximum intensity. The fluorescence intensity then remained constant for at least 4 hrs. Therefore all

measurements are made within 4 hrs. during the study.

#### 4. Effect of the addition order of reagents

Addition of the reagents in different orders has great influence on the fluorescence intensity. The experimental results indicate that the optimum fluorescence intensity is obtained when solutions are added in the following order: (neutral red dye) and  $\text{Hg}^{2+}$  then adding of the acetonitrile and adjusting the pH. So this order is chosen in the all experiments.

#### 5. Effect of the concentration of neutral red dye

The influence of the concentration of (neutral red dye) on the fluorescence intensities of the solutions is studied. It has been observed that fluorescent intensity increases as the concentration of neutral red dye increases and reaches a maximum and remained constant when neutral red dye concentration is  $2 \times 10^{-5} \text{ mol l}^{-1}$ .

#### 6. Effect of the concentration of $\text{Hg}^{2+}$

The influence of the concentration of  $\text{Hg}^{2+}$  ions on the fluorescence intensities of the solutions containing  $2.0 \times 10^{-5} \text{ mol l}^{-1}$  of neutral red dye is studied under the same experimental conditions shown above. The quenching of the fluorescence intensity increased with the increasing amount of  $\text{Hg}^{2+}$  ions up to  $1 \times 10^{-5} \text{ mol l}^{-1}$ . The mechanism of the quenching is determined from the  $R_0$  value calculated by Stern-Völmar equation ( $R_0$  is distance between  $\text{Hg}^{2+}$  and neutral red dye) =  $1.77 \text{ \AA}$  (electron transfer mechanism). This means that the  $\text{Hg}^{2+}$  ion makes a very strong complex with neutral red dye.

#### 7. Effect of solvent

The influence of the solvent on the fluorescence intensities of the solutions containing  $2.0 \times 10^{-5} \text{ mol l}^{-1}$  of neutral red dye is studied under the conditions established above. The high intensity of the fluorescence of neutral red dye was observed in aprotic solvents like acetonitrile and DMF. This can be attributed to the formation of anhydrous solvates of neutral red dye introducing solvent molecules into sphere of the studied dye leading to the enhancement of fluorescence intensity<sup>(26)</sup>. Also, the fluorescence intensities for the neutral red dye in aprotic solvents likes acetonitrile and DMF are stronger than in protic solvent likes water and ethanol. This may be due to the excited state of the dye is efficiently quenched by interactions with high-energy vibration oscillators like O-H groups<sup>(27)</sup>.

#### 8. Effect of interfering ions

The interfering ions have no effect on the method of the determination except for  $\text{CrO}_4^{--}$  which make interference at concentration up to  $3 \times 10^{-6} \text{ M}$  and below this concentration no interfering effect on the method of determination.

### Analytical application

#### 1. Linear range and limit of detection

Under the experimental conditions, there is a linear relationship between fluorescence intensity of the neutral red dye and the 1/concentration of  $\text{Hg}^{2+}$  in the range of  $2.3 \times 10^{-9}$  to  $8.0 \times 10^{-6} \text{ mol l}^{-1}$  with a correlation coefficient of 0.9949. The deduced regression equation is fluorescence intensity =  $9395057580 \times 1/\text{Concentration (mol l}^{-1}) + 64.5$ . The limits of detection (LOD) and quantitation (LOQ) are defined as  $3 \text{ SD}$  and  $10 \text{ SD}$ , respectively, [28] where  $\text{SD}$  is its

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standard deviation =  $1 / 3$  slope. LOD and quantitation (LOQ) are calculated to be  $1 \times 10^{-11}$  and  $3 \times 10^{-11}$  mol  $\Gamma^{-1}$ , respectively.

### 2. Determination of ( $\text{Hg}^{2+}$ ) in Hazardous wastes

The developed method is applied to the determination of ( $\text{Hg}^{2+}$ ) in Hazardous waste preparations. For the assay of ( $\text{Hg}^{2+}$ ), the samples must be diluted appropriately within the linear range of determination of ( $\text{Hg}^{2+}$ ) and the sample solution is analyzed by the method developed above, using the standard calibration method. The average recovery and relative standard deviation (R.S.D) are (98.5 % and 0.012 %) respectively. Data obtained by standard method (average recovery 99.0 % and S.D 0.01 %) are also presented for comparison and show a good correlation with that obtained by the proposed method. The developed method can be easily performed and afforded good precision and accuracy when applied to determination of ( $\text{Hg}^{2+}$ ) in Hazardous wastes as shown in Table (1).

**Table 1: Determination of ( $\text{Hg}^{2+}$ ) in hazardous wastes using the neutral red dye.**

Sample	Standard method (mg/ml) (AAS)	(Average) Optical sensor method (mg/ml)	Average recovery $\pm$ R.S.D. (%)
Regular lamp 60 cm	0.549	0.5471	99 $\pm$ 0.001
Regular lamp 120 cm	0.250	0.2471	98 $\pm$ 0.017
U-shaped lamp	0.001	0.0010	100 $\pm$ 0.000
Compact fluorescent lamp	0.010	0.0097	97 $\pm$ 0.019

By comparison with some existing methods, as shown in Table (2), the present method has the advantages in terms of high sensitivity, good selectivity, rapid response and a wide linear range of applications. It avoids potential background fluorescent emission interferences from hazardous solution background. So this method may provide a new kind of optical sensor for the determination of  $\text{Hg}^{2+}$  in hazardous wastes.

**Table 2: Comparison of different methods for the determination of ( $\text{Hg}^{2+}$ )**

Method	Linear range	Detection limit (mol $\Gamma^{-1}$ )	References
( $\text{H}_2\text{NCHMeCH}_2\text{NH}_2$ )( $\text{H}_2\text{O}$ ) $_2$ $\text{HgCl}_2$ ( <b>I</b> ) was used for the fabrication of a potentiometric sensor	$1.25 \times 10^{-5}$ to $1.0 \times 10^{-1}$	$8.9 \times 10^{-6}$	[29]
A cationic 5,15-(p-(9,9-bis(6-trimethylammoniumhexyl)uorenylethynyl)phenyl)porphyrin tetrabromide was used for the fabrication of a chemosensor	$1 \times 10^{-1}$ - $10^{-7}$	$2 \times 10^{-6}$	[30]
4-phenyl-2,6-bis(2,3,5,6-tetrahydrobenzo[b][1,4,7] trioxonin-9-yl)pyrylium perchlorate as an ionic carrier in a plasticized poly(vinyl chloride) membrane as a chemosensor	$3.2 \times 10^{-3}$ - $2.95 \times 10^{-10}$	$1 \times 10^{-10}$	[31]
Mono-disperse CdSe nanoclusters have been prepared facilely and functionalized with l-cysteine as optical sensor	$0.2 \times 10^{-6}$	$6 \times 10^{-9}$	[32]
Optode membrane based on a dansylamidopropyl pendant arm derivative of 1-aza-4,10-dithia-7-oxacyclododecane([12]aneNS $_2$ O)	$1 \times 10^{-4}$ - $5 \times 10^{-12}$	$5 \times 10^{-12}$	[33]
Chemosensor based on a neutral red dye	$8 \times 10^{-6}$ - $2.3 \times 10^{-9}$	$1.0 \times 10^{-11}$	Present work

## Validation

### 1. Selectivity

The selectivity was performed on four different products of fluorescent lamps for the assessment of potential interfering ions in the hazardous wastes in the linear range of the determination of  $\text{Hg}^{2+}$ .

### 2. Linearity

The four hazardous wastes of the fluorescent lamps were processed according to the procedure described above for the construction of calibration curves. The ten-points ( $8 \times 10^3$ ,  $4 \times 10^3$ ,  $1 \times 10^3$ ,  $5 \times 10^2$ ,  $1 \times 10^2$ , 50, 10, 5 and  $2.3 \text{ nmol l}^{-1}$ ) calibration curve was obtained by plotting the intensity at  $\lambda = 585 \text{ nm}$  of neutral red dye on x-axis vs.  $1/\text{concentration}$  of  $\text{Hg}^{2+}$  on y-axis. The concentrations of calibrated standards were analyzed and the linearity was evaluated by comparing the correlation coefficient ( $r$ ) between theoretical and back-calculated concentrations of calibrated standard samples.

### 3. Precision

The intraday precision of optical sensor was evaluated by replicate ( $n = 3$ ) analysis of hazardous waste samples containing  $\text{Hg}^{2+}$  for three different concentrations, Table 1 of (25, 30, and  $35 \text{ nmol l}^{-1}$ ). The intraday precision was evaluated at the above concentrations levels for 3 days. The precision was estimated by the relative standard deviation (R.S.D. %).

### 4. Recovery

The average recoveries of  $\text{Hg}^{2+}$  were evaluated for three concentration levels of 25, 30, and  $35 \text{ nmol l}^{-1}$ , each one was repeated three times and from peak intensity of assayed samples comparison to the one of reference standards prepared in acetonitrile. The recoveries were calculated using the formula:

$$\% \text{ Recovery} = \text{peak intensity in hazardous waste} / \text{peak intensity of standard solution} \times 100$$

### 5. Sensitivity

The optical sensor neutral red dye in acetonitrile at pH 6.6 is very sensitive to the  $\text{Hg}^{2+}$  in the presence of different interfering ions except  $\text{CrO}_4^{2-}$  ions up to  $3 \times 10^{-6} \text{ mol l}^{-1}$ , where the  $\text{CrO}_4^{2-}$  ions has no interfering effect for concentration below  $3 \times 10^{-6} \text{ mol l}^{-1}$ .

## Conclusion

The intensity of the emission peak at 585 nm of neutral red dye is quenched by increasing the concentration of  $\text{Hg}^{2+}$ . The neutral red dye in acetonitrile at pH 6.6 was found to have higher sensitivity, selectivity and rapid response time to  $\text{Hg}^{2+}$  in hazardous waste of the fluorescent lamps with less interference from different ions used in this work.

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## Assessment of $Hg^{2+}$ in hazardous wastes using chemosensor neutral red dye

### تقدير الزئبق الايوني في النفايات الخطرة باستخدام مجس كيميائي صبغة الحمراء المتعادلة

- محمد سعيد عطيه<sup>1</sup>، محمد امام سعد<sup>2</sup>، طه فرج فرغلى حسنين<sup>2</sup>، عيد متولي خليل<sup>2</sup>، شتا محمد شتا<sup>3</sup>، سعيد محمد الشيخ<sup>4</sup>
- 1- قسم الكيمياء ، كلية العلوم ، جامعة عين شمس ، القاهرة ، مصر  
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### المستخلص

تم تطوير طريقة طيفية جديدة وبسيطة وحساسة وانتقائية لتحديد الكميات القليلة جدا من  $Hg^{2+}$  في النفايات الخطرة لمصابيح الفلورسنت باستخدام صبغة حمراء محايدة كيميائياً في الأستونيتريزل عند الرقم الهيدروجيني 6.6. يمكن لـ  $Hg^{2+}$  إخماد كثافة التآلق للصبغة الحمراء المحايدة في الأستونيتريزل عند  $\lambda_{ex} = 380$  نانومتر. يتناسب خفض شدة التآلق للصبغة الحمراء المحايدة مع تركيز  $Hg^{2+}$  ويستخدم كمستشعر ضوئي لتقييمه. النطاق الديناميكي الذي تم العثور عليه لتقدير تركيز  $Hg^{2+}$  هو  $2.3 \times 10^{-9}$  -  $8.0 \times 10^{-6}$  مول لتر مع حد اكتشاف  $1.0 \times 10^{-11}$  مول لتر.