Development of dithizone based fibre optic evanescent wave sensor for heavy metal ion detection in aqueous environments.

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Abstract. Detection of highly toxic heavy metal ions requires rapid, simple, sensitive and selective detection methods in the environment. Optical fibre based sensing facilitates the remote, continuous and in-situ detection approaches in the environment. Herein, we report the development of a dithizone based fibre optic sensor with a simple procedure to detect heavy metal ions in the aqueous environment using an evanescent wave sensing approach. The chromogenic ligand dithizone and its spectral specificity with metal ions has been elaborated in this work.

1. Introduction

Heavy metal ions are highly toxic and are released into the aqueous environment due to the result of industrial activities. These pollutants accumulate in living organisms and create long-term adverse effects on humans, animals and plants [1,2].

Compared to the bulky, expensive, time consuming laboratory based analytical techniques optical fibre based sensing techniques have great potential for remote field sensing applications. Optical fibres are chemically inert, smaller in size, suitable for most of the surface modifications and enable in-situ, real time, distributed, rapid and remote detection with an environment friendly simple setup. One of the optical fibre based sensing approaches is evanescent wave sensing, where light propagating along the fibre generates the evanescent waves at the near surface region of the fibre core. These waves are highly susceptible to changes in the surrounding medium and hence can be used for sensing. This method is sensitive and reliable.

Recent developments on fibre optic sensors to detect metal ions include calixarene molecule based [3], DNA based [4], poly(4-vinylpyridine) based [5] and Al_2O_3 nanoparticles based [6] sensors. Most of these sensors have been reported to detect submicromolar concentrations with fast response times, but lack in procedural simplicity, with complicated design and operation. Among these sensors, use of a single wavelength for detecting multiple metal ions especially based on absorption are known to be highly susceptible to interference and lack selectivity [3].

Dithizone is a well-known ligand used in the spectrophotometric determination of metal ions [7]. Dithizone produces distinct absorption spectra in the presence of metal ions in aqueous solution [8]. Herein, we report a novel dithizone based fibre optic evanescent wave sensor for metal ion detection in aqueous solutions. A simple set up with an evanescent wave spectroscopy based detection approach using dithizone offers increased specificity from other contaminants in the environment compared to

the single wavelength based detection approaches reported earlier. In this current research, interaction of chromium, cadmium, copper and mercury ions with dithizone has been elaborated and the detection principle has been demonstrated using mercury ion as model metal ion.

2. Experimental

2.1. Chemicals/Materials
Analytical grade dithizone, 2-propanol and mercury (II) standard solution in nitric acid were purchased from Sigma Aldrich, UK and used without any further purification. All glassware was cleaned in de-ionized water prior to the experiment.

2.2. Principle of metal ions detection and selectivity
Metal ions were adsorbed on the binding site formed by apex S and N atoms, as shown in Figure 1(a), which results in the formation of metal dithizonates by the removal hydrogen atom [7] as shown in Figure 1 (b). Chelation of dithizone with metal ion, results in a change in the absorption
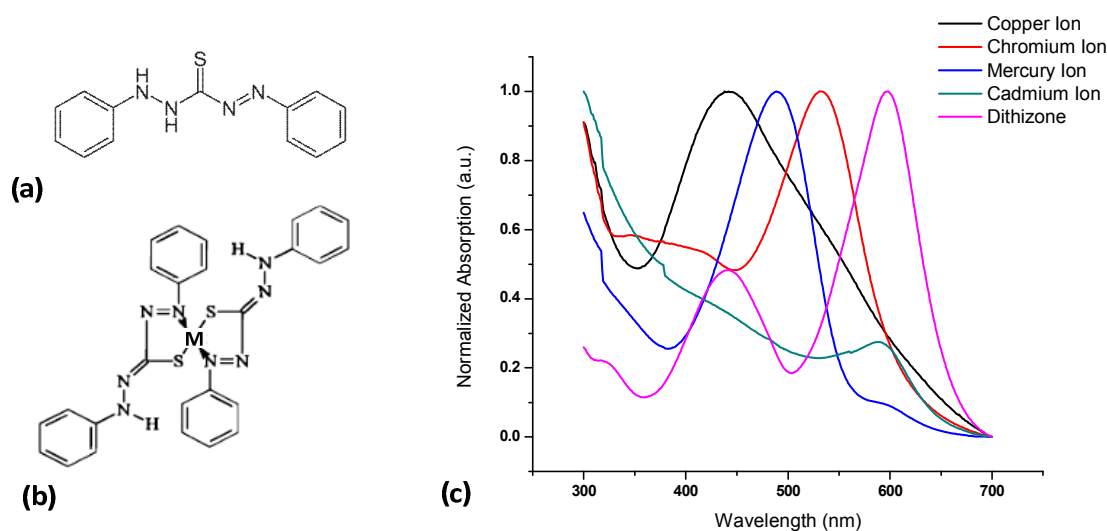

Figure 1(a) Chemical structure of dithizone, (b) metal dithizonate [9] and (c) absorption spectrum of 1ppm Hg, Cu, Cr and Cd ions with dithizone in aqueous solution.

spectra. Spectral response of the metal ions such as copper, chromium, cadmium and mercury with dithizone was evaluated with 1ppm concentration of each with 78μM dithizone and the corresponding absorption spectra are shown in the Figure 1(c). The absorption peak observed for chromium, copper, cadmium and mercury ions were at 532nm, 438nm, 588nm and 490nm respectively. The absorption peak of Hg^{2+} was 43nm, 51nm and 99nm away from the absorption peak of chromium, copper and cadmium respectively. Also, due to the higher toxicity of Hg^{2+} compared to other metal ions, further results are evaluated below using Hg^{2+} as model metal ion.

2.3. Experimental set-up
A simple experimental set up is shown in the

Figure-2. A white light LED (400-700nm) from Electrospell Ltd has been used as light source and the light was coupled to the fibre through an LED-Fibre coupler. For easier light coupling and detection, a multimode polymer fibre of 1mm core diameter has been used. The effect of dithizone to metal ion interaction has been characterised using a Perkin Elmer (Lambda 900) UV/VIS absorption spectrometer. The optical signal has been detected using a Stellarnet (EPP2000C) spectrometer in transmission mode.
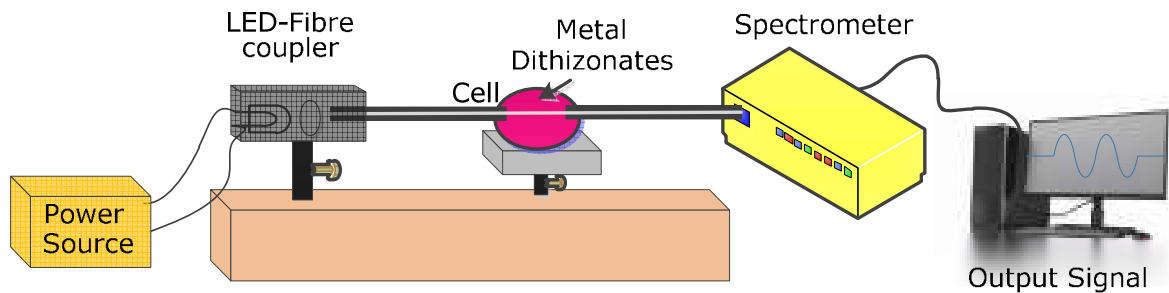
Figure-2 A pictorial view of experimental setup.

2.4. Theory

Light propagating through the fibre generates an evanescent field in the cladding. This exponentially decaying evanescent field in the cladding region will be exploited for the development of the evanescent wave absorption sensor. The phenomenon is achieved by removing the cladding of the fibre. The uncladded fibre acts as an evanescent wave sensor.

The penetration depth (dp) of the evanescent wave is defined as the distance at which the strength of electric field decays to its "1/e" value and is given by [10],

$$dp = \frac{\lambda}{2\pi n_1 \sqrt{sin^2\theta - \frac{n_2^2}{n_1^2}}} \qquad (1)$$

where, n_1 and n_2 are the refractive indices of the core and cladding, θ is the internal incidence angle normal to the core-cladding interface and λ is the wavelength of light.

Optical power transmitted in the uncladded fibre of length L, is given by [10],

$$P(L) = P(0)e^{-\gamma L} \qquad (2)$$

where, P(0) is the initial optical power launched into the fibre, L is the length of uncladded fibre and γ is the evanescent absorption coefficient.

The evanescent absorption coefficient is governed by Beer-Lambert's Law [11] :

$$\gamma = \alpha L \eta \qquad (3)$$

where, α is the absorption coefficient, L is the interaction length and η is the fraction of light in the evanescent field.

Therefore, in the case of evanescent wave based sensors, sensitivity depends on the fibre geometry such as diameter, interaction length and other parameters such as incidence angle, critical angle, wavelength of light, refractive index of core and cladding and absorption coefficient of analyte.

3. Results and discussions

Absorption spectra of mercury dithizonates for 78μM dithizone and various Hg^{2+} concentrations were studied using a UV-VIS absorption spectrometer and used as reference data as shown in Figure-3 (a).

A similar experiment was carried out with the fibre optic sensor and the output signal is shown in Figure-3(b). For optimizing the linear working range, the trend of mercury dithizonates absorption peak for 5ppb-20ppm Hg^{2+} concentrations was plotted for both reference data and sensor data as shown Figure-4(a). Results of the sensor follow the same trend as in the case of the reference data. The trend indicates that above 5ppm Hg^{2+} absorption saturates while below 1ppm it drops drastically. It also shows a linear response range within 1-5ppm Hg^{2+} which has been explored further.

To explore the nonlinear trend observed in the mercury dithizonates absorption spectra (>5ppm and <1ppm), the concentration ratio of Hg^{2+}:dithizone was evaluated for a fixed value of Hg^{2+}. 500ppb

Hg^{2+} was used to optimize the Hg^{2+}:dithizone ratio for detection and the corresponding UV-Vis spectra were recorded for 1:1, 1:2, 1:5 and 1:10 Hg^{2+}:dithizone as shown in Figure-4(b). Results
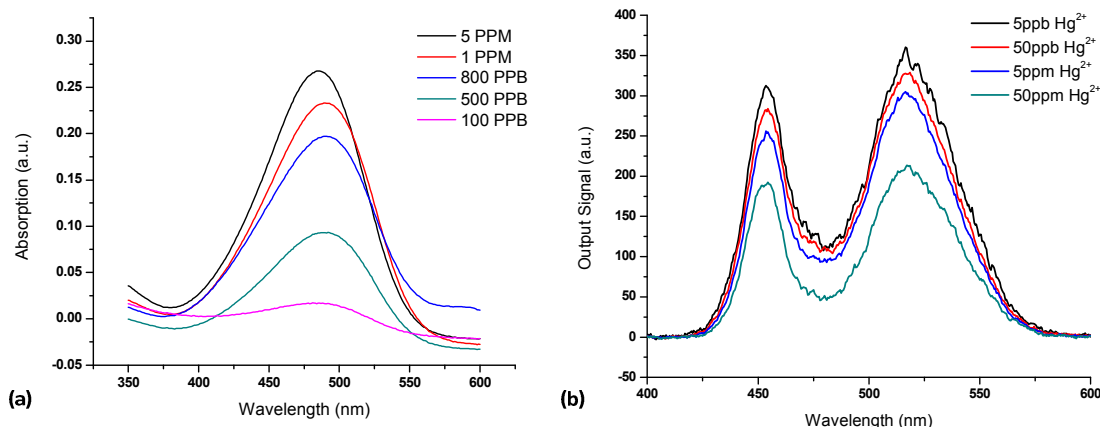

Figure-3 (a) UV-Vis absorption spectra of mercury dithizonates and, (b) output signal from fibre optic sensor at various Hg^{2+} concentrations.

indicate that 2-5 times the dithizone concentration provides optimum value of mercury detection. As discussed, in the Hg^{2+} detection principle with dithizone, each Hg^{2+} requires two dithizone molecules to form the chelate. Therefore, for the concentration ratio <=1 the chelation was poor and lower absorption was observed. The absorption value increases by increasing the Hg^{2+}:dithizone ratio up to a certain extent, thereafter, the dithizone molecules saturates and remains unbound with Hg^{2+}. These unbound dithizone molecules give rise to their absorption peak at 598nm along with the Hg^{2+} peak which can be observed for 1:10 ratio spectrum in the Figure-4(b).
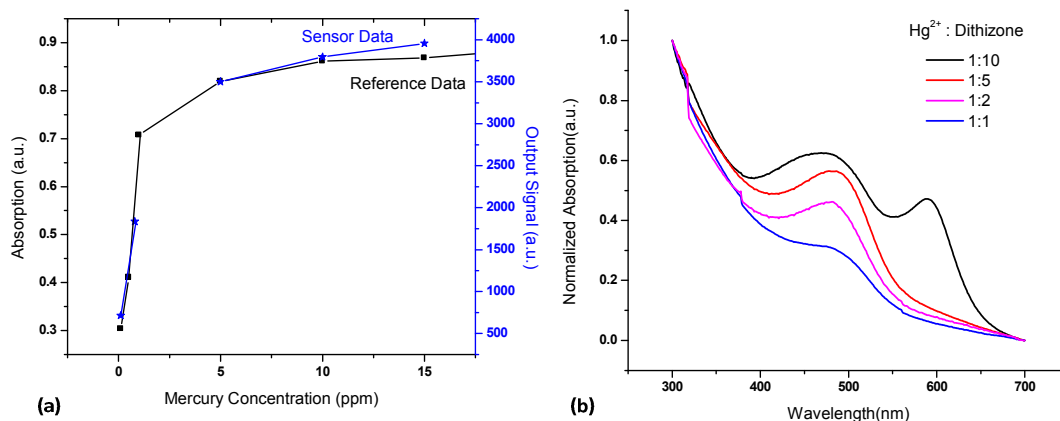

Figure-4 (a) Absorption readings of mercury dithizonates at 490nm with varying concentration of Hg^{2+} and (b) UV-Vis absorption spectra of 500ppb Hg^{2+} with different dithizone concentrations.

As discussed earlier, results in the linear range between 1-5ppm Hg^{2+} obtained from UV/Vis absorption data and the fibre optic sensor are shown in the Figure-5(a) and (b) respectively.
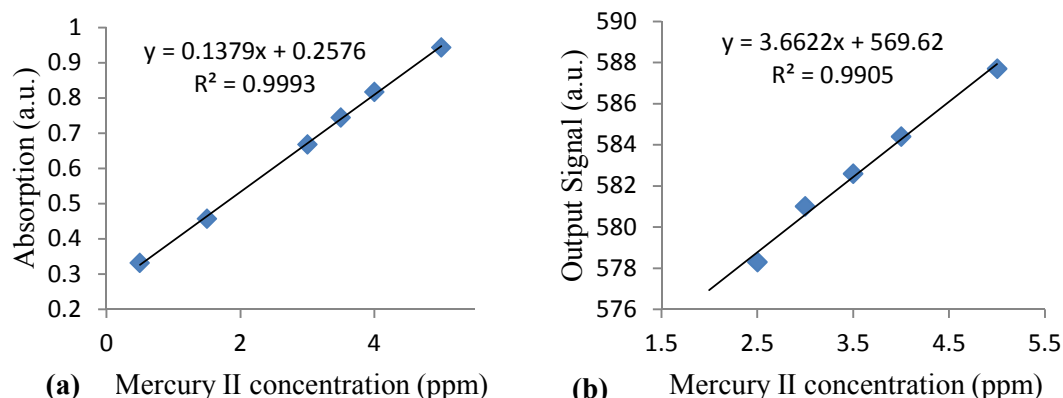
Figure-5 (a) Mercury dithizonate absorption trend measured at 490nm (b) Calibration curve of the fibre optic mercury sensor

4. Summary

Development of a novel dithizone based fibre optic sensor for heavy metal ion detection was demonstrated. Also, the spectral specificity to detect individual ions such as mercury, copper, chromium and cadmium in aqueous solutions using dithizone has been evaluated. The developed sensor demonstrated using Hg^{2+} , features an environment friendly simple procedure and instrumental setup for Hg^{2+} detection with high sensitivity (LOD-5ppb) and adequate specificity. These features demonstrate that the developed sensor can be extended to detect other metal ions from the environment. Further work is being carried out to develop an integrated sensor for real time field applications in onsite monitoring in the agricultural, environmental and marine industries.

5. References

[1]   Zahir F, Rizwi SJ, Haq SK and Khan RH. 2005 *Environ.Toxicol.Pharmacol.* **20** 351-60
[2]   Tchounwou PB, Ayensu WK, Ninashvili N and Sutton D. 2003 *Environ.Toxicol.* **18** 149-75
[3]   Benounis M, Jaffrezic-Renault N, Halouani H, Lamartine R and Dumazet-Bonnamour I. *Mater. Sci. Eng. C*2006 **26**
[4]   Long F, Gao C, Shi HC, He M, Zhu AN, Klibanov AM, et al. 2011 *Biosens Bioelectron* **26** 4018-23
[5]   Gu B, Yin M, Zhang AP, Qian J and He S. 2011 *Sensor Actuat B. Chem* **160** 1174-9
[6]   Perez-Hernandez J, Albero J, Llobet E, Correig X, Matias IR, Arregui FJ, et al. 2009 *Sensor Actuat. B-Chem.* **143** 103-10
[7]   White WE. 1936 *J.Chem.Educ.* **13** 369
[8]   Litman R, Williams ET and Finston HL. 1977 *Anal.Chem.* **49** 983-7
[9]   Yang XQ, Qi SW, Zhang CP, Chen K, Liang X, Yang G, et al. 2005 *Opt.Commun.* **256** 414-21
[10] Sai VVR, Kundu T, Deshmukh C, Titus S, Kumar P and Mukherji S. 2010 *Sensor Actuat B* **143** 724-30
[11] Burke C, StrÃ¡nik O, McEvoy H, MacCraith B. Planar Optical Sensors and Evanescent Wave Effects. In: Baldini F, Chester AN, Homola J, Martellucci S, editors. : Springer Netherlands; 2006 193-215