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Fibre Optic Sensor to Detect Heavy Metal Pollutants in Water Environments

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Abstract— **Heavy metal ion pollution emerges as a potential threat to humankind and the ecosystem due to their increased spreading into the environment. Detection of highly toxic heavy metal ions requires rapid, simple, sensitive and selective detection methods in water environments. Optical fibre sensors facilitate the remote, continuous and in-situ detection due to their inherent properties. Herein, we report a fibre optic sensor based on evanescent wave absorption to detect heavy metal ions in water environments. Fibre optic sensor has been developed by coating dithizone on the surface of an optical fibre. Selectivity of the mercury, copper and chromium ions using dithizone has been illustrated using spectroscopy based detection approach. Effect of pH on the sensor has been investigated. The possibility of simultaneous multi-ion detection has been investigated. Copper ions concentrations in water has been detected using the developed fibre optic sensor.**

Keywords — Heavy metal ions, evanescent wave, dithizone, spectroscopy, environmental sensors

INTRODUCTION

Heavy metals ions form an important group of pollutants which can be found in air, water and soil. Some heavy metals such as mercury, copper, cadmium, lead, chromium, nickel, arsenic have severe harmful effects on humans and the ecosystem because of their toxicity [1]. These toxic heavy metal ions are primary elements and hence cannot be destroyed. Heavy metal ions are not biodegradable, have very low water solubility and tendency to accumulate in living organisms [2]. Direct or indirect discharge of industrial and consumer waste, mining operations, fossil fuels combustion and volcanoes led to contamination of rivers, groundwaters, land fields and oceans with these pollutants [3,4]. Therefore, heavy metal ion pollution emerges as a serious environmental problem today due to their toxicity, volatility and mobility [5].

Current analytical instrumental techniques used to detect the heavy metal ions are laboratory based, expensive, time-consuming and require sophisticated instruments and trained personnel [6-9]. Therefore, there is a constant need for the development of in-situ, rapid, highly sensitive and selective sensors to monitor the very low concentration levels of these toxic heavy metal ions.

An optical fibre based sensor will allow real-time, remote and in-situ monitoring of heavy metal ions. This paper reports the fibre optic sensor to detect heavy metal ions in water such as mercury, chromium and copper. Heavy metal ions have been detected using a chromogenic ligand dithizone [10]. Furthermore, the effect of pH on the sensor have been investigated and discussed. Detection of multi-ions was carried out and the possibility of simultaneous multi-ion detection exploited for copper, chromium and mercury ions.

EXPERIMENTAL

A. Materials

Analytical grade dithizone, isopropanol, mercury, copper and chromium ion standard solutions in nitric acid, anisole and copper sulphate were purchased from Sigma-Aldrich, UK and used without any further purification. All glassware was cleaned in deionized water prior to the experiment.

B. Principle of metal ions detection

Chemical structure of dithizone is shown in Fig.1(a). The metal ion chelates with dithizone by the removal of hydrogen atom [11] and forms the metal dithizonate [12] as shown in Fig.1(b). When the metal ions chelate with dithizone, due to the electrostatic interaction among them, electrons in the S-C-N-N group of dithizone move towards the metal ion [13]. This movement causes the deformation in the highest occupied molecular orbital (HOMO) of the dithizone [14]. The deformation in HOMO causes the alteration in the electron energy levels and consequently, is responsible for the change in an absorption spectrum of dithizone.
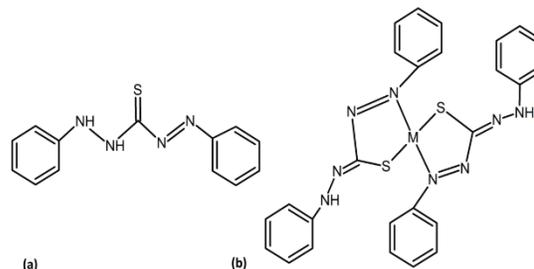
Fig.1. (a) Chemical structure of dithizone and (b) metal dithizonate.

Light propagating through the core of the optical fibre generates an evanescent field in the cladding near the core-cladding interface which propagates along with the light. Removal of the cladding exposes this propagating evanescent field, referred as evanescent waves, to its surroundings. These

evanescent waves are highly susceptible to minute changes in the surroundings. This phenomenon has been exploited to detect changes in the dithizone optical absorption spectrum due to metal ion binding, surrounding the core of the optical fibre.

C. Experimental setup

A simple experimental setup of the fibre optic sensor is shown in Fig. 2(a). A white light LED from Electrospell Ltd was used as light source and the light was coupled to the fibre through a LED-Fibre coupler. For easier light coupling and detection, a multimode polyclad fibre of 200 μm core diameter was used. Commercial optical fibre stripper was used to remove the cladding (6 cm in length) followed by acetone treatment. The uncladded fibre was fixed inside the custom-made sample cell and exposed to aqueous solution of metal ions throughout the experiment. Concentrations of the metal ions were made from the metal ion standards and added to the dithizone solution to form the metal dithizonates. The optical signal transmitted through the fibre was detected using a Stellarnet (EPP2000C) spectrometer. For each sample, three spectra (each averaged over three) were collected to avoid error due to possible intensity fluctuations from the LED source. Interaction of dithizone with metal ions was characterised using UV/Vis absorption spectroscopy. A Perkin Elmer (Lambda 900) UV/Vis absorption spectrometer was used for characterization and comparison/calibration of the aqueous samples. A custom-made sample cell (as shown in Fig. 2(b)) was used for holding the samples for measurement.
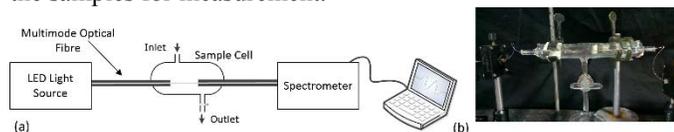
Fig. 2. A schematic diagram of the experimental setup (a) and a picture of the custom-made sample cell (b).

RESULTS AND DISCUSSIONS

Absorption study of mercury dithizonates at various mercury ions concentrations were carried out using UV-Vis absorption spectrometer by keeping the mercury dithizonate solution into the standard quartz cuvette (1 cm path-length). Fig. 3(a) shows the mercury dithizonate absorption trend for various concentrations of mercury ions measured at peak wavelength 490 nm. Absorption increases linearly with the concentration of mercury ions following the Beer-Lambert's Law. A similar experiment was carried out with the developed fibre optic sensor, where a mercury dithizonate solution was entered the sample cell and a change in output signal from the spectrometer was recorded at the peak wavelength of mercury dithizonates (490 nm). Fig. 3(b) shows the trend of the output signal (I) over the reference signal (I_{ref}) with mercury ions concentrations where the signal from water was considered as a reference signal. The measured output signal decreases exponentially with an increase in mercury ion concentration. The observed decrease in output signal can be attributed to the evanescent absorption by mercury dithizonate solution. An increase in the mercury ion concentration leads to increased absorption by mercury dithizonates which result into higher evanescent absorption. Consequently, the light intensity of the
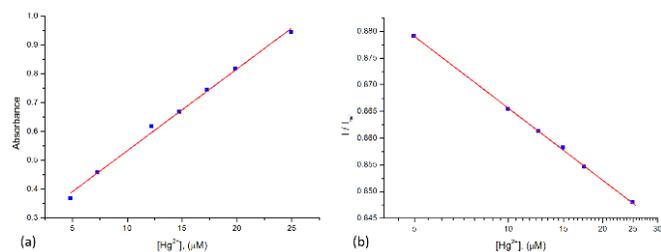
transmitted signal through the fibre decreases with an increase in the mercury ion concentrations.

Fig. 3. Measured mercury dithizonate absorption trend (a) and output signal trend from the fibre optic sensor with mercury concentrations.

A. Metal ions selectivity

The spectral response of copper, chromium and mercury ions with dithizone (78μM) was evaluated with 1μg/ml concentration of each and the corresponding normalized absorption spectra are shown in Fig. 4. The absorption peak observed for chromium, copper and mercury dithizonate were at 530, 438 and 490 nm respectively. The peak absorption wavelength of mercury ions was 40 and 52 nm away from the peak absorption wavelength of chromium and copper ions respectively. The wide spectral shift ($\Delta\lambda_{max}$) for copper and chromium ions evades the spectral overlap issues and enables the selective detection of each using principle component analysis (PCA) [15,16].
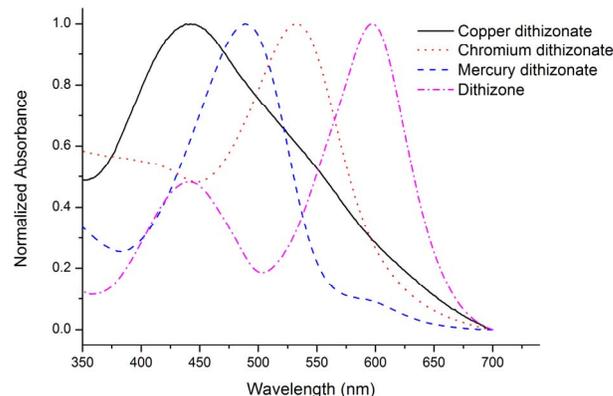
Fig. 4. Normalized absorption spectra of 1 μg/ml mercury, copper and chromium dithizonate in an aqueous solution.

B. Effect of pH on sensor

The effect of pH on the sensor was studied by varying the pH from 4 to 9 of the mercury dithizonate solution using nitric acid and ammonium hydroxide. Fig. 5 shows the effect of pH on the mercury dithizonate peak absorption measured at 490 nm. The higher absorption observed at pH 6 can be attributed to the availability of the maximum binding sites for the chelation. A similar effect was observed by Benounis and team for the calix(4)arene molecule [17]. The adsorption/binding site formed by S-C-N-N atoms was protonated by H$^+$ ions in highly acidic solutions while in the case of pH > 6, the formation of mercury hydroxide occurs which may result in a lower absorption observed in the trend.
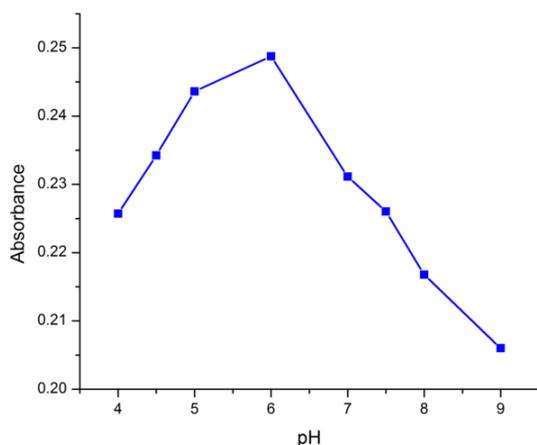
Fig. 5. Mercury dithizonate absorbance trend measured at the peak absorption wavelength with pH varying from 4 to 9.

C. Multi-ion detection

Simultaneous detection of copper and chromium ions along with mercury ions was evaluated by mixing the copper and chromium ions with mercury ions prior to adding the chelating agent dithizone. Absorption spectra of dithizone (78μM) in the presence of mercury, mercury and copper, mercury and chromium ions are shown in Fig. 6. Due to the stronger binding affinity of mercury, even in the presence of other metal ions, a strong mercury dithizonate peak can be seen. Table I shows the data analysis of each absorption peak of metal dithizonate.
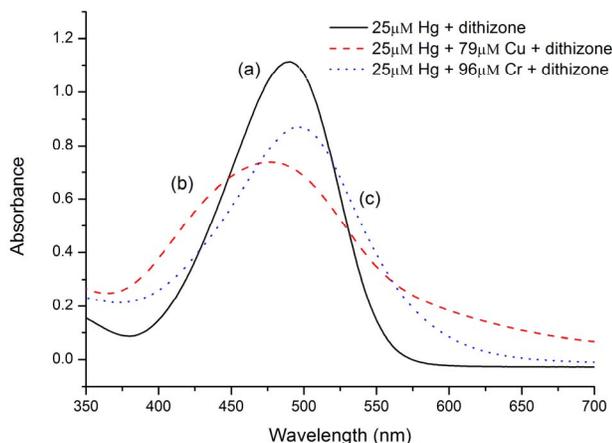
Fig. 6. Absorption spectra of metal dithizonates in an aqueous solution.

In the presence of copper ions, mercury dithizonate absorption peak was shifted to 478 nm, while in the presence of chromium ions, the absorption peak was shifted to 498 nm. The full-width half-maximum (FWHM) value indicates the peak broadening in the presence of copper and chromium ions. The larger value of the area under the peak (b) and (c) indicates that even after 25 μM of mercury ions were consumed in chelating with dithizone, there were still some binding sites available. As the copper ions have the next higher binding affinity after mercury ions, the few binding sites which were left then used by the copper ions to chelate with dithizone. Therefore, the reduction in available binding sites for the mercury ions cause the reduction in absorption peak height and the introduction of copper dithizonates cause the peak broadening. A similar effect can be seen for the chromium ion. The difference observed in the peak height was due to the lower binding affinity of chromium ions. Observed FWHM value for peak (b) was higher than the peak (c) because the wavelength shift ($\Delta\lambda_{max}$) of copper dithizonate was higher than the chromium dithizonate with respect to the peak wavelength of mercury dithizonate. The higher FWHM value observed for peak (b) and peak (c) compared to peak (a) and shift of the central wavelength both supports the detection of copper and chromium ions along with mercury ions simultaneously.

TABLE I. ABSORPTION PEAK ANALYSIS OF METAL DITHIZONATE.

Peak	Peak Area	FWHM	Central Wavelength	Peak Height
(a) Hg	103.21	85.28	490.00	1.08
(b) Cu + Hg	127.28	119.46	478.00	0.54
(c) Cr + Hg	114.13	97.87	498.00	0.75

These results indicate that a lower concentration of interfering metal ions may not affect the mercury ion detection due to the strong binding affinity of mercury. In a similar way, detection of copper and chromium ions may not be affected if a very low concentration of mercury ions are present. Also, the analysis based on the area under the peak indicates the possibility of simultaneous multi-ions detection.

D. Dithizone immobilisation and sensor development

A standard multimode step index silica fibre with core and cladding diameter 200 and 230 µm respectively was used to develop the sensor. The polymer coating (jacket) of the fibre was removed mechanically using a commercially available optical fibre stripper for the length of about 5 cm. Cladding (3 cm in length) of the fibre was removed using acetone. An uncladded fibre was coated with a layer of PMMA (1 mg/ml) by dip coating with the help of a dip coater unit, at a pulling rate of 37.5 mm/min. After the fibre was fully immersed in the PMMA solution, 1 min settling time was allowed and thereafter, removed from the solution at the same speed. The coated fibre was dried at room temperature for 2 hours. Thereafter, the same process was repeated by replacing the PMMA solution with dithizone (1 mM). The coated fibre was immersed in dithizone solution for 2 hours to allow the binding process, and thereafter removed from the solution and dried at room temperature.

A similar experiment was performed using the dithizone coated silica fibre. Prior to each sample of copper ions, a reference spectrum was collected in water. Fig. 7 shows the plot of I/I_{ref} with copper ion concentrations. It was observed that with an increase in copper ion concentrations, I/I_{ref} decreases exponentially as observed in the previous results with mercury.
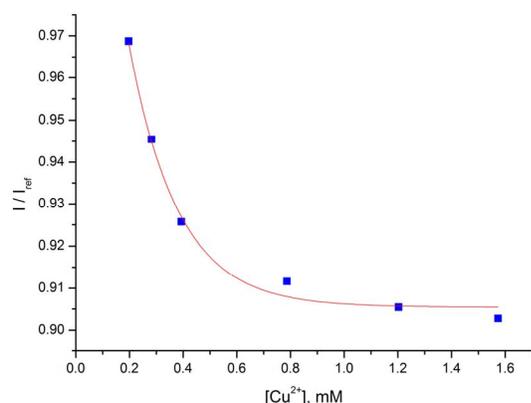
Fig. 7. Output signal trend of the developed fibre optic sensor with copper ion concentrations.

CONCLUSION

Fibre optic sensor was developed to detect heavy metal ions in water environments. Results have shown that very low concentrations of mercury and copper ions can be detected using the developed fibre optic sensor. Obtained results on simultaneous detection of copper, chromium and mercury ion using dithizone have provided the possibility of multi-ions detection using the developed sensor. Further work is being carried out to develop an integrated multi-ion sensor for onsite monitoring for the agricultural, environmental and marine industries.

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