

## Dual ion selective fluorescence sensor with potential applications in sample monitoring and membrane sensing

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### ARTICLE INFO

#### Article history:

Received 24 April 2016

Received in revised form 6 October 2016

Accepted 8 October 2016

Available online 11 October 2016

#### Keywords:

Chemosensor

Dual metal ion

Reversibility

Real sample

Al<sup>3+</sup>

Zn<sup>2+</sup>

### ABSTRACT

A new sensing functionalized chemosensor 3-hydroxy-2-(1H-indol-3-yl)-4H-chromen-4-one (**M1**) was readily prepared in facile reaction conditions and explored its sensing nature response towards metal ions in semi-aqueous medium. The chemosensor **M1** exhibited high selective and sensitive fluorescence turn “off-on” response for Al<sup>3+</sup> and Zn<sup>2+</sup> ions in the existence of several metal ions and the changes are enabled for naked-eye detection. These high selectivity expressed by high binding constants  $2.62 \times 10^4$  (Al<sup>3+</sup>) and  $1.92 \times 10^4$  M<sup>-1</sup> (Zn<sup>2+</sup>) calculated by the Benesi-Hildebrand equation based on the emission studies. The binding strategy was also supported by <sup>1</sup>H NMR titration.

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### 1. Introduction

Aluminium is the third most prevalent metal crust on earth and it has numerous application in different industries such as paper, textile, and alimentary industries [1–4]. Recently, the concentration of Al<sup>3+</sup> has increased in our food due to widespread expose of aluminium material in our daily life. According to WHO, long lasting intake of Al<sup>3+</sup> (more than 7 mg kg<sup>-1</sup>) can produced serious health problems like as damage the central nervous system, osteoporosis, Alzheimer's disease, anaemia, gastrointestinal ailments [5–11].

Zinc is second most abundant metal ions and it has high potential application in human bodies and plays a critical role in different disease control, gene transcription (DNA-binding proteins), regulation of brain function and pathological enzymes. It has also constructing functional strategies in molecule synthesis. But the high expose of Zn<sup>2+</sup> cause some toxic symptoms like neurodegenerative disorders [12–20]. Owing to high implication of Zn<sup>2+</sup> and Al<sup>3+</sup> in environmental and biological area, it has necessary to grow a device for trace level detection. At present, various analytical techniques like as voltammetry, atomic absorption spectroscopy, neutron activation analysis, inductively

coupled plasma-mass spectroscopy (ICP-MS) and chromatography are accessible for quantitative and qualitative analysis of various metal ions in numerous biological and industrial effluents [21–27]. However, most of these methods contain sophisticated techniques and high cost maintenance. Optical chemosensors have more attention over other techniques due to their simplicity, high sensitivity with quick response, low-cost value and bare-eye imaging [28–33].

Optical chemosensors are greatly valuable tools for the careful gratitude of several chemical and biological based species. There are many reported sensors based on coumarin, quinoline, rhodamine, Schiff base etc. for different analyte [34–44]. Design of dual or multi ion sensing receptors is a new area of research activity, due to their more potential application in recognize analyte and provides a divergent and measureable output changes in electrochemical/optical signal. Previously, J.-C. Qin et al., has expressed a multifunctional fluorescent chemosensor approach with coumarin based probe for Zn<sup>2+</sup>, Cu<sup>2+</sup> and S<sup>2-</sup> ions, similarly Y.R. Bhorge et al., also proposed pyrene-based optical chemosensor for Cu<sup>2+</sup> and Fe<sup>3+</sup> [45–49]. De Silva et al. well reviewed about the most two famous proposal mechanism of chemosensors (a) photoinduced electron transfer (PET) and (b) intermolecular charge transfer (ICT) [50]. Usually, the PET type optical probe exhibited selective response with a fluorescence enhancement, however, ICT based probe showed ratiometric sense. These two strategy are broadly used to design fluorescent chemosensors.

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Our group has previously investigated  $Zn^{2+}$  and  $Al^{3+}$  sensing abilities of flavanol and benzofuran derivative. In benzofuran derivative, we observed only two compound responded sensing behavior towards  $Al^{3+}$  ions over 14 synthesized compound [51]. Interestingly, both of these compounds were indole moiety. At other point, 3-hydroxy flavonol derivative is well known chromophore moiety responding sensing behavior towards  $Zn^{2+}$  ions via keto-enol tautomerism [52]. In this work, we introduced dual or multi ion sensing receptors approach and added both of sensing moiety in single scaffold and investigated their ability to metal binding/sensing. New fluorescent sensor 3-hydroxy-2-(1H-indol-3-yl)-4H-chromen-4-one (**M1**) was readily prepared in facile reaction conditions and characterised. Chemosensor **M1** showed high selectivity towards  $Al^{3+}$  and  $Zn^{2+}$  over a wide range of metal ions in semi-aqueous medium, mainly attributed PET (photoinduced electron transfer) and Keto-enol tautomerism process.

## 2. Experimental section

### 2.1. General experimental detail

All the reagent chemicals, solvent and metal salts were purchased from Sigma-Aldrich and were used without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol Resonance ECX-II spectrometer for compound characterisation (at 400 MHz for  $^1H$  NMR and 100 MHz for  $^{13}C$  NMR) and  $CDCl_3$  were used as a solvent with tetramethylsilane (internal reference). Spectra were plotted using MestReNova-6 software and Chemical shifts ( $\delta$ ) were reported in ppm. Mass spectrometry was collected by Bruker-daltronics-microTOF-QII® spectrometer using ESI, with <5 ppm error. UV-vis spectra were studied on a Shimadzu UV-2450 spectrophotometer. The emission spectra were recorded on a Horiba fluoromax-4 spectrofluorometer with 1.0 nm emission and excitation slit width. All pH of sample was measured with Eutech pH-510.

### 2.2. Synthesis of chemosensor

The chemosensor (**M1**) was produced by the previously reported method with some variations [53]. 10 mmol of 2-hydroxyacetophenone, 10 mmol of aldehyde added in 15 ml methanol followed by 4 equiv NaOH and stirred for full night at room temperature, then reaction mixture make acidic with conc. HCl and the obtained solid product after filtration. In second step the filtrate product (4 mmol) was dissolved in methanol and added 4 equiv. NaOH and 10 equiv. of  $H_2O_2$  (30%). The reaction mixture stirred in ice bath for 5 h than reaction stop after addition of acid. The pure product was recrystallized from cold ethanol. Yield: 52%; Proton NMR (400 MHz,  $CDCl_3$ ):  $\delta$ , ppm ( $J$ , Hz) = 12.07 (s, 1H, -OH), 8.77 (s, 1H), 7.83–7.81 (d,  $J$ =3.5, 2H), 7.73–7.71 (d,  $J$ =7.5, 1H), 7.42–7.40 (d,  $J$ =3.5, 2H), 7.00–6.98 (d,  $J$ =8.5, 2H), 6.71 (s, 1H), 5.25 (s, 1 –NH.).  $^{13}C$  NMR spectrum (100 MHz,  $CDCl_3$ ),  $\delta$ , ppm: 176.95, 163.68, 162.63, 154.89, 138.94, 136.49, 133.77, 130.74, 128.30, 128.06, 125.22, 123.48, 119.93, 118.50, 114.54, 106.02, 100.08. ESI MS  $m/z$  (M+H): 278.0836, Calculated for  $C_{14}H_{11}O_3$  = 278.0817.

### 2.3. UV-vis and fluorescence sensing study

For photo fluorescence studies, main solution of probe (**M1**) and metal ions  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Nd^{3+}$ ,  $Hg^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Na^+$ ,  $Zn^{2+}$  and  $Pb^{2+}$  were prepared ( $1.0 \times 10^{-3}$  M) in  $MeOH:H_2O$  (9:1) solution and were further diluted for spectral recordings. All the spectra were obtained from 390 nm to 700 nm in a quartz cell (1 cm path length) at room temperature. All the fluorescence spectral studies were performed with emission and

excitation (1.0 nm) slit. Selectivity of probe **M1** to metal ions were measured through different experimental method.

### 2.4. Synthesis of polymeric membrane

Naked eye membrane sensing kit was synthesized with help of previous paper [54]. 2 mg of ionophore (**M1**), 30 mg PVC, 65 mg plasticizers 2-nitrophenyloctyl ether (o-NPOE) and 3 mg anionic additive NaTPB were dissolved in THF with continuous glass rode stirring and viscous oily substance was poured into a polyacrylate ring placed on a glass surface. After the full night solvent evaporation, about 0.5–0.6 mm thick flexible membrane were obtained, which were then used directly as a sensor kit in UV light. These PVC membrane based sensor kit are quite stable at room temperature. We can store membranes in 5% methanolic solution for around 20 days without loss of sensing ability.

### 2.5. Quantum yield calculations

Optical chemosensor **M1** showed turn on response with  $Al^{3+}$  and  $Zn^{2+}$  thus we measure quantum yields of **M1**, **M1**+ $Al^{3+}$  and **M1**+ $Zn^{2+}$  by using coumarin-1 ( $\Phi=0.99$  in ethyl acetate) as a standard reference solution and quantum yield is calculated by using standard equation.

$$\Phi_{\text{Sample}} = \Phi_{\text{Reference}} \times \frac{A_{\text{Sample}}}{A_{\text{Reference}}} \times \frac{(Abs)_{\text{Reference}}}{(Abs)_{\text{Sample}}} \times \frac{n_{\text{Sample}}}{n_{\text{Reference}}}^2$$

### 2.6. Determination of $Al^{3+}$ and $Zn^{2+}$ in semi aqueous samples

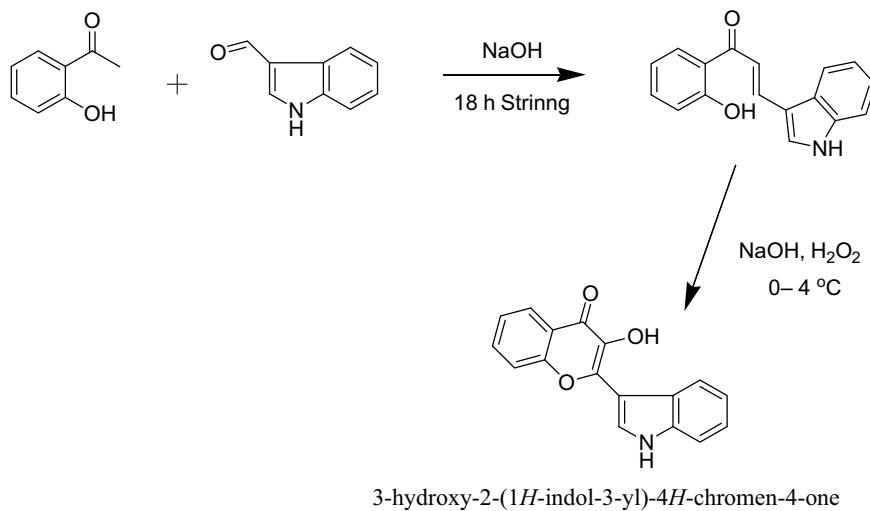
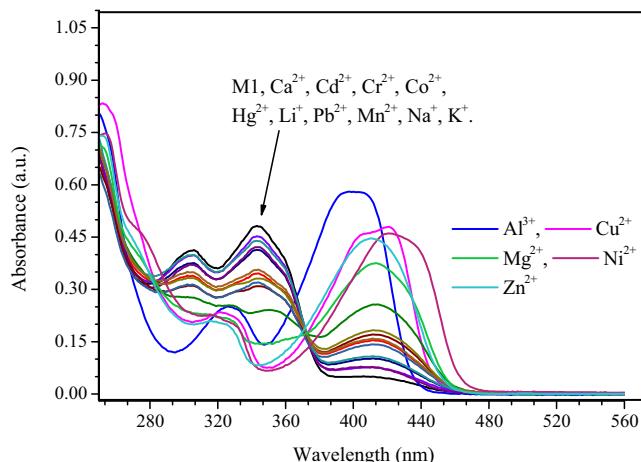
Samples were collected from different source of water supply and were passed through a standard 0.50  $\mu M$  filter. All the samples were spiked with different known concentration of  $Al^{3+}$  or  $Zn^{2+}$  ion, maintaining the near neutral pH of the medium using phosphate buffer. After well mixed, the solutions were allowed to stand at room temperature for 10 min before the all experimental test. Each experiment was performed three time and average values were used in standard addition method.

## 3. Results and discussion

### 3.1. Metal sensing ability of the synthesized probe

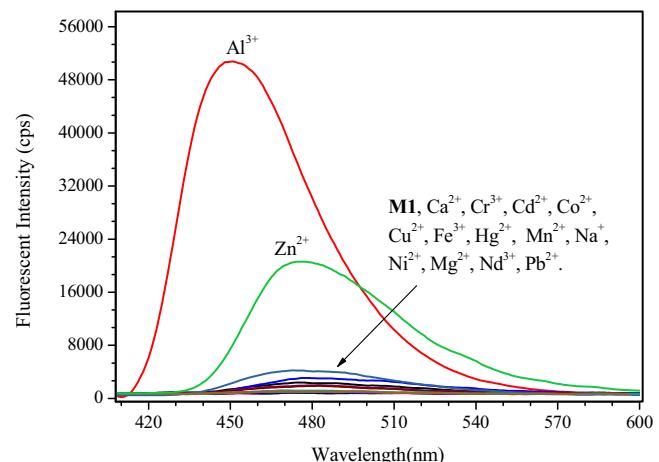
In an initial analysis, the metal ion sensing abilities of optical chemosensor was examined through absorbance study. Dilute solution of chemosensor **M1** ( $2.0 \times 10^{-5}$  M) in  $MeOH:H_2O$  (v/v, 9:1) displayed four strong absorbance band located at 207, 247, 305 and 345 nm. After the addition of diverse metal ion like as  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Nd^{3+}$ ,  $Hg^{2+}$ ,  $Na^+$ ,  $Pb^{2+}$  and  $Ca^{2+}$  ions didn't produce any significant changes in absorbance band. While in the presence of  $Cu^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  ions, absorbance band centred at 305 and 345 nm shifted to high wavelength, that result showed binding affinity of chemosensors with these metal ions (Fig. 1). But it was not produced specific character for particular metal ions so we can't identified exact metal ion through absorbance study (Scheme 1).

Fluorescence spectra of chemosensor **M1** ( $20 \mu M$ ) were also performed alone and with the diverse metal ions to investigate the metal recognition abilities in  $MeOH:H_2O$  (v/v, 9:1). Chemosensor **M1** exhibited a feeble fluorescence band after the excitation at 390 nm. These fluorescence emission band intensity retain unchanged after the addition of diverse metal ions like as  $Ca^{2+}$ ,  $Cr^{3+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Cd^{2+}$ ,  $Nd^{3+}$ ,  $Cu^{2+}$ ,  $Hg^{2+}$ ,  $Ni^{2+}$ ,  $Na^+$ ,  $Pb^{2+}$  and  $Mg^{2+}$  (Fig. 2). Interestingly, subsequently addition of  $Al^{3+}$  and  $Zn^{2+}$  ions fluorescence emission intensity was dramatically increased,

**Scheme 1.** Synthesis of chemosensors **M1**.**Fig. 1.** UV-vis spectrum of **M1** (20  $\mu\text{M}$ ) in methanol:H<sub>2</sub>O (v/v, 9:1) solution with various metal ions (20  $\mu\text{M}$ ) such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ .

this “turn on” fluorescence response was evidently obvious under UV light (**Fig. 3**). In the presence of equimolar amount of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  a sharp turn on fluorescence enhancement rise at 450 and 474 nm, respectively.

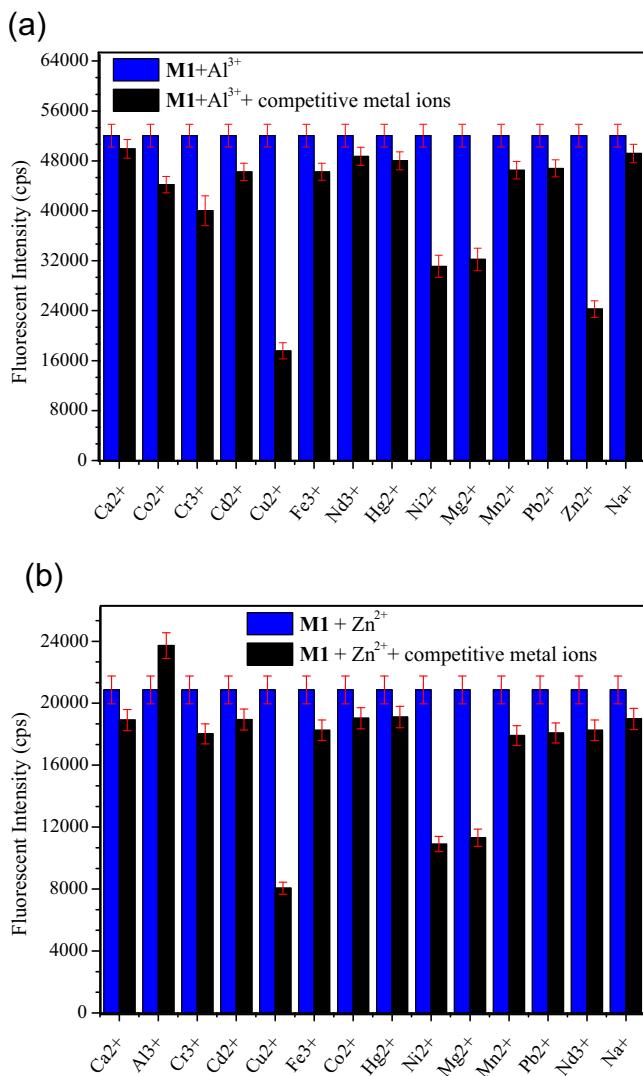
For a high chemosensor, selectivity to a precise ion should be remain largely unaffected by additional competitive species. The selectivity of chemosensor **M1** for  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  were examined through the fluorescence competitive experiment in the occurrence of diverse metal ions (20  $\mu\text{M}$ ) like as  $\text{Ca}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$  at the room temperature (**Fig. 4**). Gratifyingly, the chemosensor was able to hold their selectivity toward  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$ . This experiment showed that selected coexistent metal ions (other than  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$ ) did

**Fig. 2.** Fluorescence emission spectra of chemosensor **M1** (20  $\mu\text{M}$ , MeOH) in presence of equimolar amount of different metal ions (20  $\mu\text{M}$ ) like as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ( $\lambda_{\text{ex}} = 375 \text{ nm}$ ).

not exhibit any interfere. However  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  exhibited notable interference but optical chemosensor **M1** was applicable to detected  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  in presence of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$ . During sample analysis these interference effect could be decreased if experiment were performed with high concentration of optical probe and it can be applied for environment analysis.

Sensitivity of chemosensor with  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  metal ions were determined by titration method. This experiment was performed with the continuing addition (0, 0.5, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 30, 40  $\mu\text{M}$ ) of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  to the **M1** solution. In **Fig. 5**, a regular fluorescence upgrading occurred at 450 nm and 474 nm upon progressive addition of  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  ion, respectively. The results exposed good linear relationship ( $R^2 > 0.99$  for both  $\text{Al}^{3+}$  and

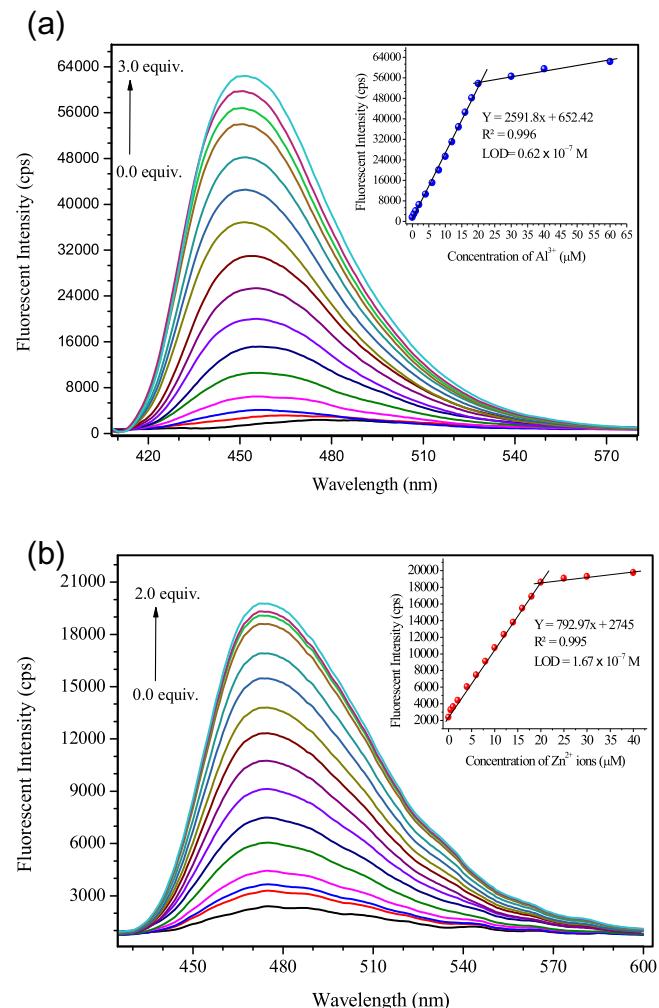
**Fig. 3.** Naked eye fluorescence responses of **M1** in the appearance of different metal ion in MeOH: H<sub>2</sub>O (v/v, 9:1) solution.



**Fig. 4.** Examination of selectivity of chemosensor **M1** [20  $\mu$ M in MeOH: H<sub>2</sub>O (v/v, 9:1)] toward (a) Al<sup>3+</sup> at 450 nm and (b) Zn<sup>2+</sup> at 474 nm in the presence of various metal ions (with error bar).

Zn<sup>2+</sup> ion) between fluorescence intensity and concentration suggests that sensor **M1** is useful for quantitative analysis of Al<sup>3+</sup> and Zn<sup>2+</sup> at 450 and 474 nm, respectively. Furthermore, the detection limit for Al<sup>3+</sup> and Zn<sup>2+</sup> was determined to the emission titration as  $0.62 \times 10^{-7}$  M and  $1.67 \times 10^{-7}$  M, respectively (Fig. 5, inset), based on blank standard equation ( $LOD = 3\sigma/\text{slope}$ ). Quantum yield of optical probe **M1** was examined with coumarin-1 as a standard. Optical probe **M1** exhibited low quantum yield ( $\Phi = 0.0208$ ) and it improved with both metal ion Al<sup>3+</sup> and Zn<sup>2+</sup> after excited at 375 nm  $\Phi = 0.3413$  (**M1+Al<sup>3+</sup>**) and 0.2841 (**M1+Zn<sup>2+</sup>**) (Fig. 6).

Furthermore, association constants (Ka) value for **M1+Al<sup>3+</sup>** and **M1+Zn<sup>2+</sup>** complex was estimated through the linearly enhanced value at 450 nm and 474 nm, respectively, in fluorescence titration. Benesi-Hildebrand equation based association constants



**Fig. 5.** The fluorescence enhancement of **M1** at 450 nm and 474 nm upon progressive addition (0 to 2 equiv.) of (a) Al<sup>3+</sup> and (b) Zn<sup>2+</sup> ion, respectively. Inset: linear response spectra with LOD.

(Ka) was calculated  $2.62 \times 10^4 \text{ M}^{-1}$  (**M1+Al<sup>3+</sup>**) and  $1.92 \times 10^4 \text{ M}^{-1}$  (**M1+Zn<sup>2+</sup>**), respectively [55]. All aspects of these binding behavior including maximum emission wavelength, binding constant, detection limit and fluorescence enhancement factor were determined by emission spectra were compiled in Table 1. A comparative binding response, selectivity towards diverse metal ions and sensitivity studies was performed in Table 2. Results showed present works is highly acceptable in optical sensing.

Moreover, the pH effect on the emission response of optical probe **M1** was examined in MeOH: H<sub>2</sub>O (v/v, 9:1). The emission intensity of **M1+Al<sup>3+</sup>** and **M1+Zn<sup>2+</sup>** centred respectively at 450 nm and 474 nm were recorded at different pH values (3.0–9.0). The results showed that metal complex of chemosensor **M1** did not exhibited any distinct and characteristic emission band in high acidic and high pH medium due to formation of ammonium

**Table 1**

Photophysical properties of optical sensor **M1** in semi-aqueous medium.

|                           | $\lambda_{\text{abs.}}$ (nm) | $\lambda_{\text{flu.}}$ (nm) | FEF <sup>a</sup> | LOD ( $\mu$ M) | $K_a (10^4, \text{M}^{-1})$ |
|---------------------------|------------------------------|------------------------------|------------------|----------------|-----------------------------|
| <b>M1</b>                 | 207/247/305/345              | 479                          | –                | –              | –                           |
| <b>M1+Al<sup>3+</sup></b> | 203/246/327/400              | 450                          | 32.10            | 0.62           | 2.62                        |
| <b>M1+Zn<sup>2+</sup></b> | 204/254/324/410              | 474                          | 8.74             | 1.67           | 1.92                        |

<sup>a</sup> FEF = Fluorescence Enhancement Factor.

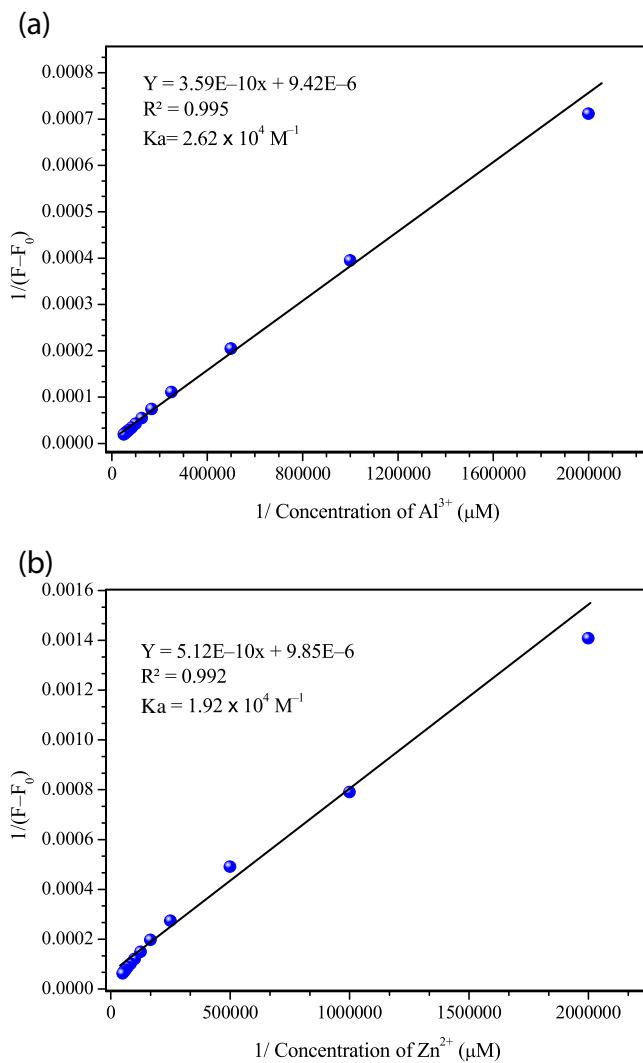


Fig. 6. Benesi-Hilderbrand plots between  $1/I - I_0$  vs  $1/[Al^{3+}]$  and  $1/[Zn^{2+}]$  at  $\lambda_{max} = 450$  and  $470$  nm, respectively.

salt and enolate structure. Thus, optimum naked-eye response of chemosensor obtained only in near neutral pH range (Fig. 7).

### 3.2. Binding mode of chemosensor

Furthermore, the binding stoichiometry of **M1** with  $Al^{3+}$  and  $Zn^{2+}$  was achieved by the emission Job's plot method. Job's plot was recorded at maximum emission wavelength by continuously varied mole fraction of metal ions ( $Al^{3+}$  or  $Zn^{2+}$ ) in a solution of chemosensor **M1** and total concentration of solution ( $20 \mu\text{M}$ ) retain constant. The results explored that highest emission intensity was obtained around the 0.5 fraction for both metal ions, that was specified a 1:1 stoichiometry behavior of **M1+Zn<sup>2+</sup>** and **M1+Al<sup>3+</sup>** complex (Fig. 8).

To develop a clear thoughtful of binding events, proton NMR titration spectra was performed. The chemosensor **M1** has two possible binding site: **site A** (with furan oxygen and indole nitrogen) and **site B** (3-Hydroxy flavonol keto oxygen) as shown in Fig. 9. By comparative study of proton NMR of chemosensor **M1** with  $Al^{3+}$  and  $Zn^{2+}$ , some vital conclusions about binding can be drawn. In the experiment metal salt of  $Al^{3+}$  and  $Zn^{2+}$  was gradually added in separately in the  $DMSO-d_6$  solution of chemosensor **M1**. NH proton (indole group) of **M1** at  $5.3 \text{ ppm}$  and aromatic proton at  $6.5$ – $8.5 \text{ ppm}$  (furan oxygen) showed significant changes with gradual addition of  $Al^{3+}$ . In other case, signal of OH proton (3-hydroxy flavone group) of

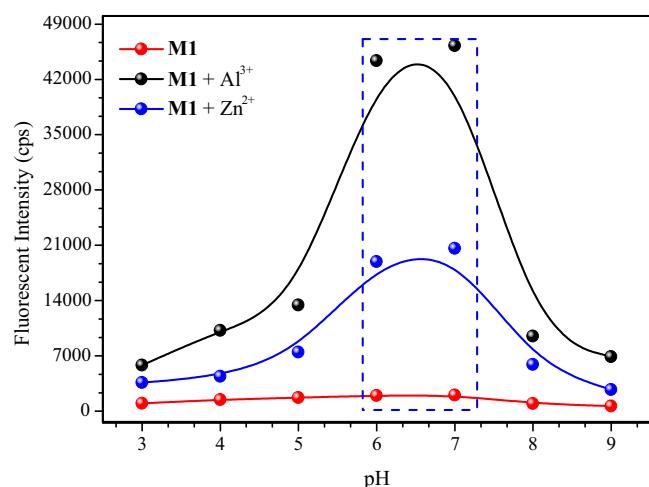


Fig. 7. Dependence of fluorescence response of **M1** towards  $Al^{3+}$  and  $Zn^{2+}$  over variable pH medium ( $\lambda_{max} = 450$  and  $470$  nm, respectively for  $Al^{3+}$  and  $Zn^{2+}$ ).

**M1** at  $12.2 \text{ ppm}$  showed downfield shift with continues disappearance after gradual addition of  $Zn^{2+}$ . The titration has clear evidence that **site A** of optical probe was directly involved in coordinating with  $Al^{3+}$  and **site B** was involved with  $Zn^{2+}$  (Fig. 10).

### 3.3. Reversible sensing nature

Reversibility is additional significant characteristic behavior of a molecular optode. As shown in Fig. 11, the fluorescence nature of **M1** was quenched upon addition of EDTA, we can understand it through displaced of  $Al^{3+}$  and  $Zn^{2+}$  from its binding interactions with EDTA. In result optical probe **M1** became freed from coordination sites and exhibited quenching behavior. This free chemosensor could be reclaimed in appropriate organic phase and can be applied several times for sensing.

### 3.4. Applications of the proposed dual ion sensor

#### 3.4.1. Naked eye detection of $Al^{3+}$ and $Zn^{2+}$ in solution phase

As mentioned formerly, optical chemosensor **M1** exposed distinct and careful response towards  $Al^{3+}$  and  $Zn^{2+}$  ions in long UV light. In contrast, additional various metal ions didn't give any marked fluorescent change (Fig. 3). This selective behavior was observed in  $MeOH/H_2O$  (v/v, 9:1).

#### 3.4.2. Membrane sensor for aluminium and zinc

Homogenous polymeric membranes were synthesized with suitable ratio of ionophore (**M1**): PVC: plasticizers (o-NPOE): NaTPB 3 mg: 30 mg: 65 mg: 3 mg (see Experimental section for more detail). Remarkably, these membranes exhibited their sensing response towards  $Al^{3+}$  and  $Zn^{2+}$  ions under UV light and using these membrane one can determine presence or absence of zinc and aluminium ion above a threshold concentration (Fig. 12). These PVC membranes sensor kit has several advantages such as easy preparation, light weight, high portability, and long life and low cost.

#### 3.4.3. Estimation of $Zn^{2+}$ and $Al^{3+}$ concentration in environment sample

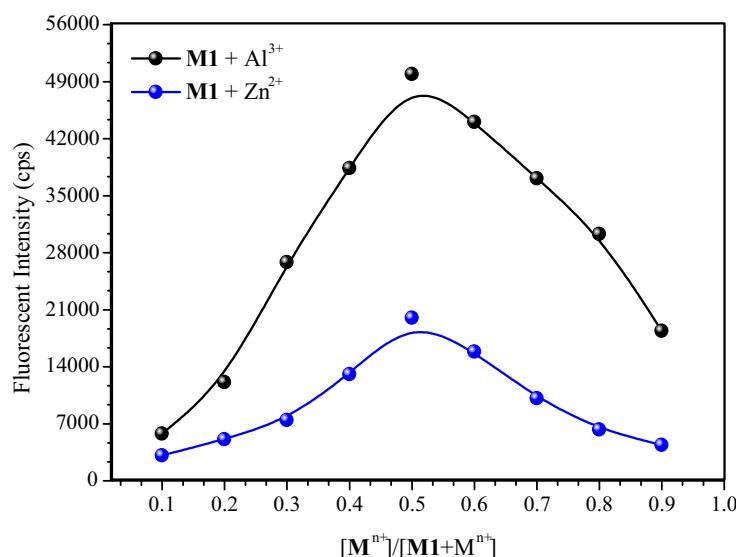
Since Chemosensor **M1** displayed a strong binding towards  $Zn^{2+}$  and  $Al^{3+}$  and this behavior is not much affected by existence of other metal ions (as confirmed by cross-selectivity examinations), hence the synthesized probe can be applied for trace level quantification of  $Zn^{2+}$  and  $Al^{3+}$  ion in environmental samples. For the calculation of accuracy, concentration of sample were also determined by

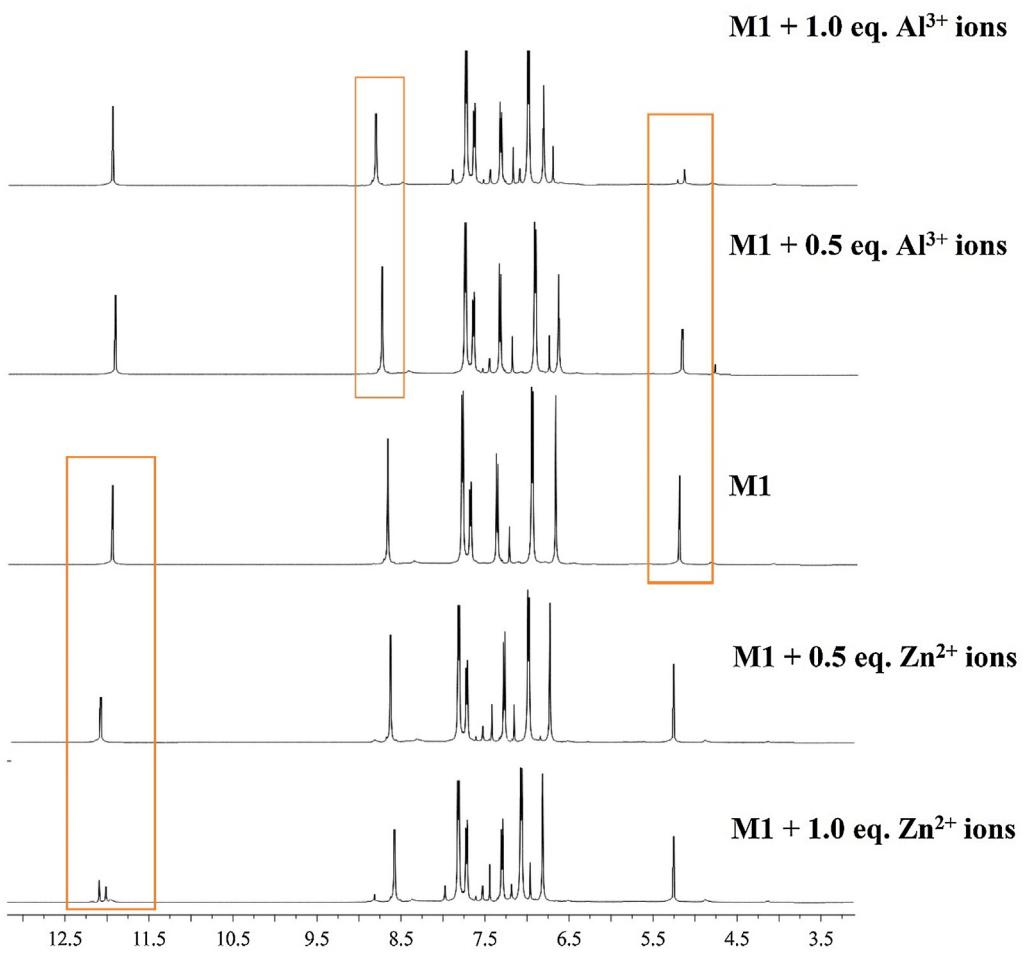
**Table 2**Comparative response of optical probe **M1** with previously reported probe.

| S.No.  | Sensor/probe          | Interference                     | Association constant ( $K_a$ )   | LOD in M                                       | pH range |
|--------|-----------------------|----------------------------------|--|--|----------|
| 1      | <b>M1 (This work)</b> | $\text{Cu}^{2+}$                 | $(\text{Al}^{3+}) 2.62 \times 10^4 \text{ M}^{-1}$<br>$(\text{Zn}^{2+}) 1.92 \times 10^4 \text{ M}^{-1}$ | $0.62 \times 10^{-7}$<br>$1.67 \times 10^{-7}$ | 6–7      |
| 2 [56] |                       | $\text{Cd}^{2+}, \text{Mg}^{2+}$ | –  | $1.72 \times 10^{-7}$                          | –        |
| 3 [33] |                       | $\text{F}^-, \text{OAc}^-$       | $2.6 \times 10^5 \text{ M}^{-2}$   | $3.6 \times 10^{-6}$                           | 7–8.4    |
| 4 [39] |                       | $\text{Cu}^{2+}, \text{Co}^{2+}$ | $5.85 \times 10^4 \text{ M}^{-1}$  | $1.3 \times 10^{-7}$                           | 6–9      |
| 5 [38] |                       | $\text{Cu}^{2+}$                 | $1.95 \times 10^5 \text{ M}^{-1}$  | $2.5 \times 10^{-6}$                           | 7–10     |
| 6 [4]  |                       | $\text{Ni}^{2+}, \text{Cu}^{2+}$ | –  | $7.5 \times 10^{-7}$                           | 5–13     |
| 7 [44] |                       | $\text{Cd}^{2+}$                 | –  | $5.0 \times 10^{-6}$                           | 7.5      |

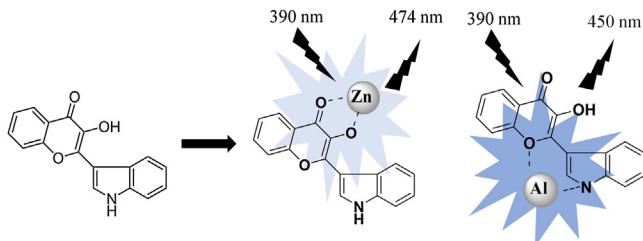
**Table 3**Real time analysis of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  concentration in MeOH:  $\text{H}_2\text{O}$  (v/v, 9:1) solution via. proposed sensor and AAS.

| Sample Methanol: Water (9:1) | Concentration of metal sample ( $\mu\text{g/L}$ )(AAS) |                  | Concentration of metal sample ( $\mu\text{g/L}$ )(Sensor M1) |                  |
|------------------------------|--|------------------|--|------------------|
|                              | $\text{Al}^{3+}$                                       | $\text{Zn}^{2+}$ | $\text{Al}^{3+}$   | $\text{Zn}^{2+}$ |
| Drinking water               | 9.15   | 14.92            | 9.29   | 15.18            |
| Rain water                   | 39.64  | 24.65            | 39.37  | 25.20            |
| Industrial water             | 92.12  | 88.54            | 93.08  | 90.12            |

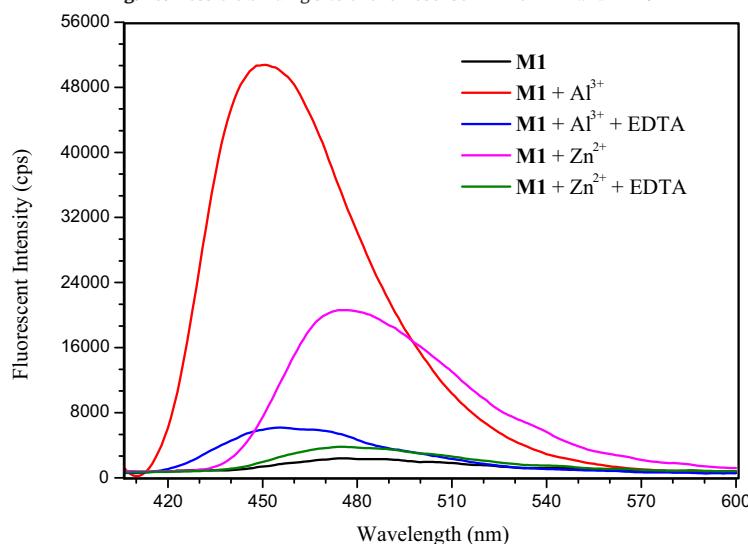
**Fig. 8.** Job's plot titration of chemosensor **M1** with  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  at maximum emission wavelength 450 and 474 nm, respectively.



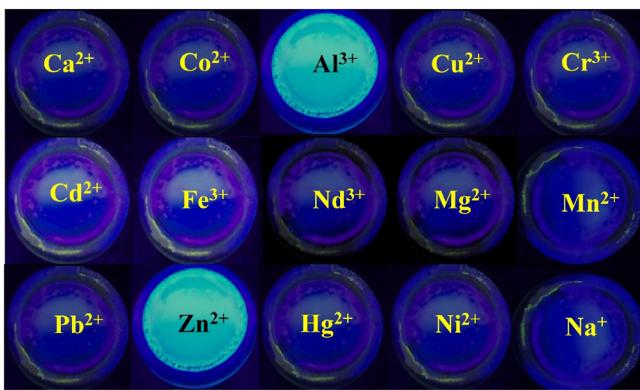
**Fig. 9.**  $^1\text{H}$  NMR titration spectra changes upon addition of  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$  (DMSO- $d_6$  used as NMR solvent).



**Fig. 10.** Possible binding site of chemosensor M1 for  $\text{Al}^{3+}$  and  $\text{Zn}^{2+}$ .



**Fig. 11.** Reversible sensing response of chemosensor M1 with EDTA.



**Fig. 12.** Fluorescence response of membrane based chemosensor toward different metal ion.

AAS. Comparison of both data, indicating the applicability of the proposed optical sensor in on spot sample monitoring ([Table 3](#)).

#### 4. Conclusion

In summary, we were rationally produced a simple dual ion selective fluorescence probe 3-hydroxy-2-(1H-indol-3-yl)-4H-chromen-4-one (**M1**) in facile reaction conditions. Chemosensor displayed a specific turn “off-on” fluorescence response towards Al<sup>3+</sup> and Zn<sup>2+</sup> at different wavelength 450 and 474 nm, respectively, under mild conditions. Chemosensor **M1** displayed excellent selectivity over various metal ions with low detection limit ~10<sup>-7</sup> mol L<sup>-1</sup>. Results showed that probe is highly favorable for real time analysis of environmental sample.

#### Acknowledgements

The author L.K. Kumawat would like to thank UJ-GES (South Africa) for the postdoctoral research fellowship. The authors are also grateful to Departmental Instrumentation lab (UJ) for provided that the instrumental facilities. M. Asif appreciates the support of the Deanship of Scientific Research at King Saud University for the Prolific Research Group PRG-1437-31.

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