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RESEARCH

Poly(Azomethine-urethane)-based Fluorescent Chemosensor for the Detection of Cr^{3+} Cations in Different Water Samples

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Abstract

A highly selective, and effective poly(azomethine-urethane)-based chemosensor (HIMA) was prepared, and it used as a fluorescent sensor for the detection of Cr^{3+} cations in different solutions. The HIMA was prepared in two-step reactions by using hexamethylene diisocyanate, 2,4-dihydroxy benzaldehyde, and 2-aminophenol. The sensitivity and selectivity of the fluorescent probe were tested in the presence of different metal ions. The obtained findings indicated that the chemosensor exhibited a quenching effect against the only Cr^{3+} ion. The limit of detection (LOD) and limit of quantitation (LOQ) of the chemosensor HIMA were calculated as 7.98×10^{-7} M, and 2.42×10^{-6} M, respectively. In addition, the binding constant (Ka) of the chemosensor was calculated as 5.31×10^{5} M^{-1}.

Keywords Fluorescence · Chromium · Chemosensor · Polyurethane · Quenching

Introduction

Chromium is one of the important heavy elements in the focus of wastewater treatment due to its wide range of applications such as chromate production, electroplating, metal mining, textile industry, and wood corrosion resistance [1–3]. It is generally found as trivalent (Cr^{3+}), and hexavalent (Cr^{6+}) cations in aqueous media due to the stable oxidation states [4]. They can be found as different compounds such as $Cr(OH)_3$, CrO_4^{2-}, etc. depending on the temperature and pH value of the water, the reduction–oxidation potential, and the concentration of chromium [5, 6]. Among these species, $Cr^{3+}$is an essential element in daily human and animal nutrition, and it has a non-toxic behavior [7]. Besides, chromium plays an important role such as enzyme and RNA formation, accelerating blood coagulation, increasing β-glucuronidase activity, secretion of hormones and some vitamins, increasing immunity, feed intake, and energy efficiency in animals [8, 9].

Polyurethanes (PUs), which contain the urethane group in the main chain as their characteristic properties, are attracting more and more attention due to their structural flexibility, ion transportability, mechanical properties, thermal conductivity, flexibility, chemical and wear resistance [10, 11]. They have also exhibited superior compatibility with other polymers and inorganic materials, and poly(azomethine-urethane)s derivatives of polyurethane have been also reported in the literature due to these properties [12, 13]. To the best of our knowledge, there are very few studies reported in the literature regarding the development of poly(azomethine-urethanes) as fluorescence sensors for the detection of cations or analytes. Among these studies, they were used to detection of Mn^{2+} [14], Cd^{2+} [15], Zn^{2+} [16, 17], Cu^{2+} [18], Fe^{3+} [19, 20], and DNA [21] and PAMU-based fluorescence sensor for the detection of Cr^{3+} cations with good selectivity, and sensitivity has not been reported in the literature yet.

In the present paper, a poly(azomethine-urethane) (PAMU)-based fluorescent sensor was developed for the determination of Cr^{3+} cations in different solutions. For this purpose, PAMU was synthesized by two-step polymerization reactions. In the first reaction, polyurethane was prepared via copolymerization reaction of hexamethylene diisocyanate (HDI) with 2,4-dihydroxy benzaldehyde (HBA), and then the poly(azomethine-urethane) was obtained by the grafting of 2-aminophenol into the prepared pre-polymer. The fluorescence sensing behavior of the fluorescent chemosensor was tested in the presence of different cations such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, K^{+}, Li^{+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Zr^{4+}. According to the fluorescence measurements, the sensor responded as a quenching effect toward

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Cr(III) ions, and it has a good potential application for the detection of Cr(III) ions with high sensitivity and selectivity in different water samples.

Materials and Methods

Reagents

2-Aminophenol (2-AP), 2,4-dihydroxy benzaldehyde (HBA), hexamethylene diisocyanate (HDI), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), chloride salts of aluminum (III), barium (II), cadmium (II), chromium (III), cobalt (II), iron (III), nickel (II), potassium (I), and zirconium (IV), nitrate salts of lead (II), lithium (I), manganese (II), and zinc (II), and ethylenediaminetetraacetic acid (EDTA) were supplied as commercially from Sigma Aldrich, and they were used without any purification.

Preparation of the Chemosensor (HIMA)

The chemosensor (*(E)-4-(((2-hydroxyphenyl)imino)methyl)-3-methoxyphenyl (6-acetamidohexyl)carbamate*, HIMA) was prepared in two steps as in the previous paper (Fig. 1) [22]:

In the first step, the prepolymer was prepared by the copolymerization reaction of HBA (0.276 g, 2 mmol) and HDI (0.336 g, 2 mmol) in THF under Argon atmosphere for 24 h around 70 °C. In the last step, the chemosensor was obtained by the grafting of 2-AP (0.218 g, 2 mmol) into the preformed prepolymer (0.615 g, 2 mmol) in DMF/MeOH mixture (1:3; *v:v*) at 60 °C for 3 h.

Yield 82% for **prepolymer**, 85% for **HIMA**.

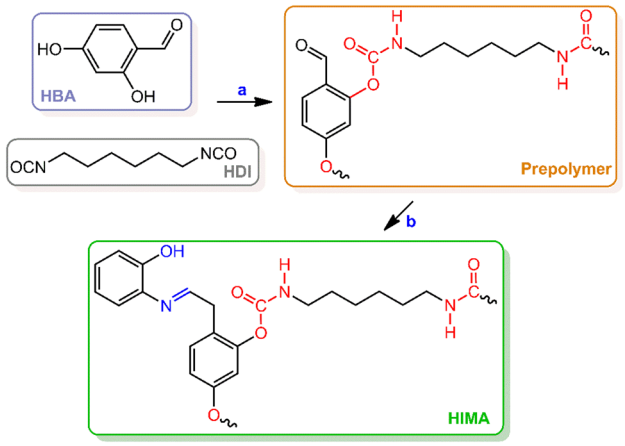

Fig. 1 Synthesis of the fluorescent probe (HIMA) (*Reaction conditions; a: THF, reflux, 6 h, Ar atmosphere, and 70 °C; b: THF/MeOH mixture (1:3; v:v), reflux, 3 h, 2-aminophenol (2-AP), and 60 °C*)

FT-IR (cm^{-1}, υ) 3321 (urethane –NH), 2936, 2861 (aliphatic -CH), 1705 (-CHO), and 1666 (urethane –C = O) for **prepolymer**, and 3320 (urethane –NH), 2932, 2858 (aliphatic -CH), 1645 (urethane –C = O), and 1588 (-N = CH) for **HIMA**.

^{1}H-NMR (400 MHz, DMSO-d_6, δ) 10.93 (-CHO), 7.90 (Ar–H), 7.67 (Ar–H), 7.65 (Ar–H), 6.76 (urethane -NH), 3.51 (Al-CH), 3.05 (Al-CH), and 1.33 (Al-CH) for **prepolymer**, and 9.83 (-OH), 7.86 (-N = CH), 6.93 (Al-CH), 6.71 (Al-CH), 6.79 (Al-CH), 6.77 (Al-CH), 6.73 (Al-CH), 6.68 (urethane –NH), 2.85 (Al-CH), 2.53 (Al-CH) and 1.35 (Al-CH) for **HIMA**.

GPC Mn = 3300 Da, Mw = 4700 Da, and PDI = 1.424 for **prepolymer**, and Mn = 18300 Da, Mw = 25500 Da, and PDI = 1.393 for **HIMA**.

Instruments

The polymer and fluorescent probe (HIMA) were characterized using FT-IR (Perkin-Elmer Spectrum Two Fourier Transform-Infrared Spectrometer), ^{1}H-NMR (Bruker AC FT-NMR 400 MHz Spectrometer), GPC (Shimadzu Gel Permeation Chromatography, eluent: DMF, standard: polystyrene) techniques.

Preparation of the Stock Solutions

A 24 µM stock solution of HIMA (0.061 g) was prepared in 100 mL DMF/deionized water (1:2; *v:v*) mixture. The aqueous stock solutions of metal cations (72 µM) such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, K^{+}, Li^{+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Zr^{4+} were prepared in 10 mL deionized water by using their chloride or nitrate salts.

Optical Measurements

Absorption spectra of HIMA in the presence or absence of Cr^{3+} were measured using a Perkin-Elmer UV–Vis spectrophotometer between 250 and 800 nm. All fluorescence measurements were carried out by using a Perkin-Elmer LS 55 fluorescence spectrophotometer in the range from 500 to 800 nm in DMF/distilled water (1:2; *v:v*) mixture. Excitation and slit width were adjusted as 497 and 5 nm, respectively. In the tested absorption and fluorescence measurements solutions, the molar ratio of the HIMA and metal cations was 1:2 (*v:v*).

Results and Discussion

Absorption Measurements

Normalized absorption spectra of HIMA in the presence and absence of chromium (Cr^{3+}) solution were given in Fig. 2.

As can be seen in Fig. 2, the free HIMA chemosensor exhibited two absorbance bands at 347 and 423 nm due to $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ transitions, respectively [23, 24]. These transition bands were also recorded at 376, and 448 nm in the solution of the HIMA when added to Cr^{3+} cations, respectively. These results showed that the mentioned transition bands of HIMA with the addition of Cr^{3+} cations were shifted to 29 and 25 nm a bathochromic (red) shift. This was attributed to the inhibition of the internal charge transfer (ICT) with the addition of a Cr^{3+} ion into the HIMA solution [25].

Fluorescence Response of the Fluorescent Chemosensor

The fluorescence response of the developed chemosensor (HIMA) was studied in the presence of the stock solution of the HIMA chemosensor and different metal ions such as Al^{3+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, K^{+}, Li^{+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Zr^{4+} (Fig. 3). This measurement to recognize the selectivity of HIMA chemosensor towards cations was performed by the addition test solution of 1 mL fluorescent sensor solution (24 µM) in DMF/deionized water and 2 mL cations (72 µM) in deionized water. The developed PAMU-based chemosensor showed a strong emission band at 557 nm when excited at 497 nm, and its emission intensity was recorded as 47.442 a.u. With the addition of cations in the HIMA solution, emission intensities were measured as 15.058, 57.764, 69.914, 71.234, 83.363, 86.819, 93.935, 100.577, 106.744, 117.114, 124.772, 131.368, and 135.286 a.u. for Cr^{3+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ba^{2+}, Li^{+}, K^{+}, Al^{3+}, Cd^{2+}, Fe^{3+}, Ni^{2+}, and Zr^{4+}, respectively at the mentioned wavelength. These results indicated that the emission intensity of HIMA was dramatically changed in the presence of Cr^{3+} by the quenching effect while it was increased in the presence of the other tested metal ions. This quenching effect could be explained by the interaction of functional groups such as azomethine (-N = CH), hydroxyl (-OH), urethane –NH, and carbonyl (-C = O) in the structure of HIMA with Cr^{3+} ion [26].

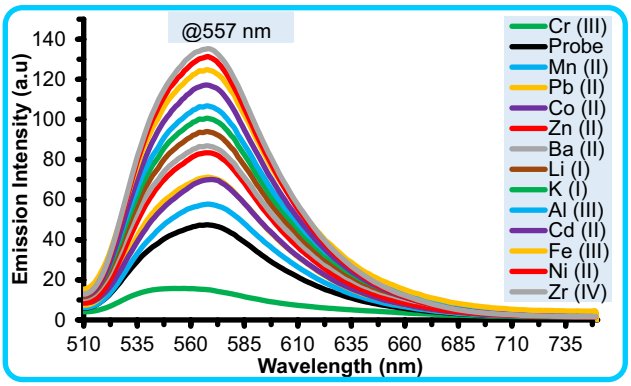

Fig. 3 Fluorescence spectra of HIMA in the presence of different concentrations of cations (Concentration: HIMA = 24 µM, metal ions = 72 µM, *v:v* = HIMA/cation: 1/2 in DMF/deionized water)

Cr^{3+} Cation Concentrations Effect

To investigate the potential spectral efficiency and applicability of the HIMA chemosensor, its emission intensity was measured in the presence of different Cr^{3+} cation concentrations under 497 nm excitation wavelength, and at the ambient conditions (Fig. 4). Emission intensities were recorded as 48.72, 45.42, 43.04, 41.15, 38.75, 36.45, 30.25, 24.58, 15.72, and 12.24 in the presence of 2, 4, 8, 12, 16, 24, 32, 48, 64, and 72 µM of Cr^{3+} concentrations, respectively. These results revealed that the emission intensity of the HIMA chemosensor was gradually decreased with the increasing Cr^{3+} cations concentrations.

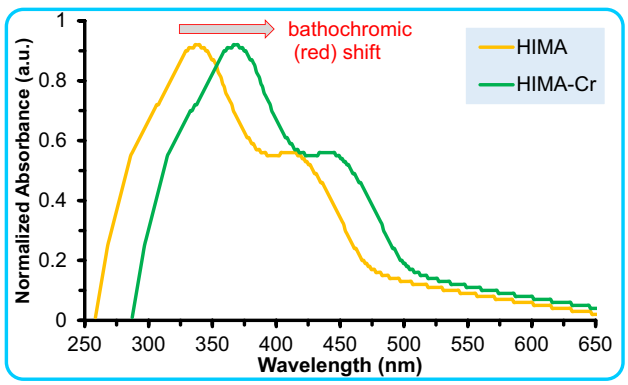

Fig. 2 UV–Vis spectra of HIMA and HIMA-Cr (Concentration: HIMA = 24 µM, Cr^{3+} = 72 µM; *v:v* = HIMA/$Cr.^{3+}$: 1/2 in DMF/deionized water)

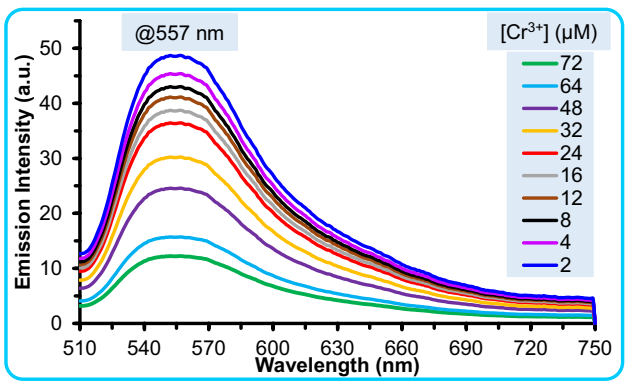

Fig. 4 Fluorescence spectra of HIMA in the presence of different Cr^{3+} concentrations (Concentration: HIMA = 24 µM, *v:v* = HIMA/Cr^{3+}: 1/2 in DMF/deionized water)

Limit of Detection (LOD) and Limit of Quantification (LOQ)

To test the practical applicability of the HIMA chemosensor, a calibration curve was obtained by plotting the emission intensities against the different chromium (III) concentrations (Fig. S1). As can be seen from the obtained calibration curve, the HIMA chemosensor showed a gradually decreasing linear response toward increasing Cr^{3+} cations concentrations. Also, this linearity value was detected as 0.9933.

The limit of detection (LOD) and the limit of quantification (LOQ) of the proposed chemosensor was calculated by using the following equations (Eqs. 1, and 2) and emission titration methods, respectively [27, 28]:

$$\mathrm{LOD} = \frac{3\,\sigma_{bi}}{m} \tag{1}$$

$$\mathrm{LOQ} = \frac{10\,\sigma_{bi}}{m} \tag{2}$$

where σbi and m are the standard deviations (0.012) of metal-free chemosensor solutions and slope (m = 0.4964) obtained from Fig. S1, respectively. The regression equation of HIMA in the presence of Cr^{3+} was found as $I = -0.4964[Cr^{3+}] + 47.629$. LOD and LOQ values of 7.98×10^{-8} M (0.0798 µM, 0.024 ppm), and 2.42×10^{-7} M (0.242 µM), respectively.

According to the World Health Organization (WHO) and the United States Environmental Protection Agency, the maximum amount of Cr^{3+} allowed in drinking water has been reported as 0.05 ppm (0.05 mg/L), and 0.015 ppm (0.015 mg/L), respectively [29]. As can be seen in the LOD value of the HIMA chemosensor in the presence of Cr^{3+}, it was calculated to be lower than the maximum amount in drinking water reported by WHO and USA Environmental Protection Agency.

To investigate the binding efficiency of the proposed chemosensor, the stoichiometry between HIMA chemosensor and Cr^{3+} cations was determined using Job's plot method (Fig. S2) [30]. The maximum emission intensity was obtained at the ratio $[Cr^{3+}] / ([Cr^{3+}] + [HIMA]) = 0.5$. This result showed that the host–guest interaction between HIMA chemosensor and Cr^{3+} cations was performed in a 1:1 stoichiometric ratio.

In addition, the binding constant (Ka) of the HIMA chemosensor with Cr^{3+} cations was calculated by using the following Benessi-Hildebrand equation (Eq. 3) [31]:

$$\frac{1}{I - I_O} = \frac{1}{K_a(I_{max} - I_o)[M]} + \frac{1}{I_{max} - I_o} \tag{3}$$

where I, I_o, and I_{max} are emission intensities of HIMA chemosensor with Cr^{3+}, without Cr^{3+}, and saturated solution in the presence of the maximum amount of cation, respectively. Also, [M] is the concentration of added $[Cr^{3+}]$ cations. Ka value was found as 5.31×10^5 M^{-1}. This calculated Ka value was compatible with the reported studies in the literature for the determination of trivalent cations [32, 33].

As demonstrated in Table S1, the HIMA chemosensor for the detection of Cr^{3+} cations was compared to the previously reported paper in the literature in terms of structure, LOD value, and media. It was clearly seen in the finding results that the developed chemosensor had a lower and satisfactory LOD value compared to the chemosensor in Table 1, and it was done progress in the LOD value according to the other studies.

To examine the complex interaction between the prepared HIMA chemosensor with Cr^{3+} cation, the ^{1}H-NMR titration method was used and ^{1}H-NMR spectra of HIMA in the absence and presence of Cr^{3+} cation were given in Fig. 5a. As can be seen in Fig. 5a, urethane –N<u>H</u>, hydroxyl (-O<u>H</u>), and imine (-N = C<u>H</u>) protons were detected at 9.71, 8.44, and 7.88 ppm for the HIMA, and 9.92, 8.50, and 7.95 ppm for HIMA-Cr complex. These results revealed that the proton peak values of the complex were shifted to the higher values, and they were weakened. According to these results, the possible complexation was carried out with Cr^{3+} ions between urethane, hydroxyl, and imine functional groups (Fig. 5b) [34, 35].

Interference

To investigate the performance and selectivity of the chemosensor, the possible interference effect of the tested cations (Mn^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ba^{2+}, Li^{+}, K^{+}, Al^{3+}, Cd^{2+}, Fe^{3+}, Ni^{2+}, and Zr^{4+}) (72 µM) on the fluorescence intensity of the HIMA (24 µM) was evaluated in the presence of Cr^{3+} cations (72 µM) (Fig. 6). As represented in Fig. 6, the tested metal cations did not have any significant interference effect on the sensor developed to detect Cr^{3+} cations. This was attributed to the strong complexation between the HIMA

Table 1 Determination of Cr^{3+} cations in different water samples

Water sample	Spiked cation (µM)	Determined cation concentration (µM)	Recovery (%)	[a] RSD (%)
Drinking water	20	20.23	101.15	1.89
Drinking water	50	50.47	100.94	1.77
Seawater	20	20.35	101.75	2.07
Seawater	50	50.57	101.14	1.85
Tap water	20	20.49	102.45	2.11
Tap water	50	50.63	101.26	1.93

[a] RSD: The relative standard deviation

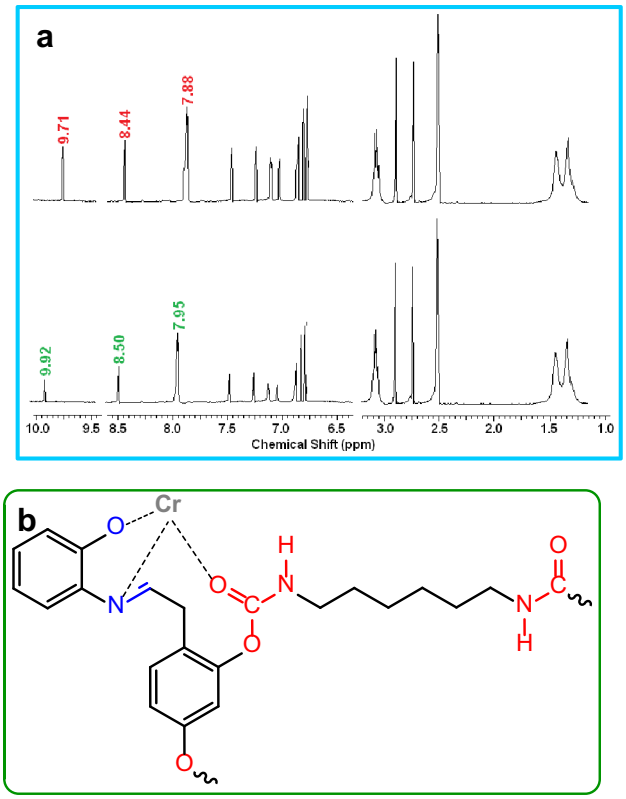

Fig. 5 ^{1}H-NMR spectra of HIMA in the absence and presence of Cr^{3+} (**a**), and the proposed sensing mechanism (**b**)

and Cr^{3+}, and the paramagnetic quenching effect of the mentioned cation due to the paramagnetic nature [36].

Reversibility

In order to test the reversibility of the developed PAMU-based fluorescent sensor, Cr^{3+} and EDTA were sequentially added to the HIMA chemosensor solution in DMF (Fig. 7). According

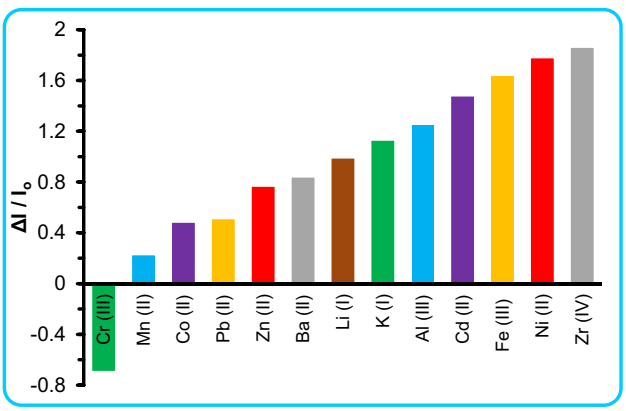

Fig. 6 Interference of different cations effect on the emission intensity of HIMA (Concentration: HIMA = 24 μM, cation = 72 μM; *v:v* = HIMA/Cr^{3+}: 1/2 in DMF/deionized water)

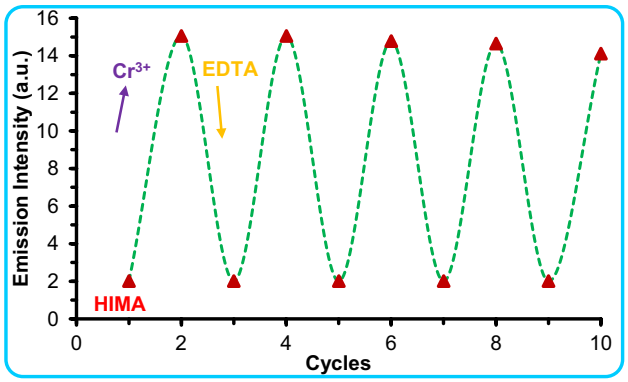

Fig. 7 Fluorescence spectra of HIMA (24 μM) after the sequential addition of Cr^{3+} (72 μM) and EDTA (72 μM)

to the results of the finding, the emission intensity of the HIMA chemosensor was slightly decreased after the 6th cycle and the sequential addition of cation and EDTA. This finding indicated that the developed PAMU-based chemosensor has been potentially applied for the determination and identification of Cr^{3+} cations as a selective and sensitive fluorescent sensor.

Photostability

Another parameter used to evaluate the efficiency of the fluorescence chemosensor is photostability. To investigate the photostability of the HIMA chemosensor, its emission intensity was measured in the presence of a 1 mL fluorescent probe and 2 mL of Cr for 60 min (Fig. 8). As can be seen in Fig. 8, HIMA lost its emission intensity value at 0.87, 2.34, 3.00, 3.55, 4.89, and 5.82% after 10, 20, 30, 40, 50, and 60 min, respectively. Also, the proposed sensor lost its emission intensity at 0.52, 2.24, 2.71, 3.37, 4.04, and 4.70% at the mentioned times. These findings indicated that the HIMA chemosensor exhibited excellent photostability.

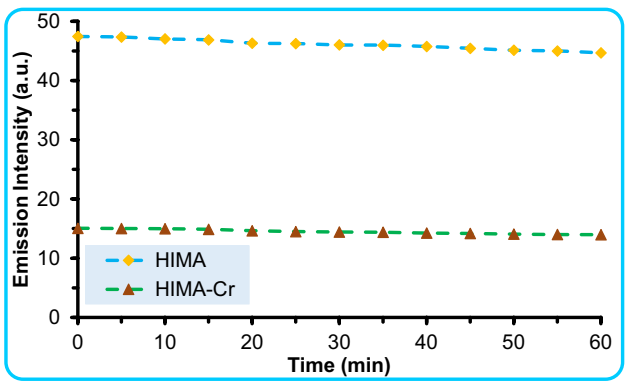

Fig. 8 Photostability of HIMA with/without Cr^{3+} (Concentration: HIMA = 24 μM, cation = 72 μM; *v:v* = HIMA/Cr^{3+}: 1/2 in DMF/deionized water)

Real Sample Applications

To test the applicability of the HIMA chemosensor in different water samples, it was tested with Cr^{3+} fluorescence and UV–Vis measurements in the drinking, sea, and tap water samples (Table 1). Cation concentrations were found as 20.23, 20.35, and 20.49 µM in the presence of 20 µM spiked Cr^{3+} cations, and 50.47, 50.57, 50.63 µM in the presence of 20 µM spiked Cr^{3+} cations for drinking, sea, and tap water samples. Recovery and RSD values were also recorded in the range from 100.94 to 102.45%, and 1.89 to 2.11%. These results exhibited that the HIMA chemosensor was successfully applied in the determination of Cr^{3+} cations amount in the different water samples.

Conclusion

In the present paper, an effective and highly selective fluorescent chemosensor based on poly(azomethine-urethane) (HIMA) was developed for the detection of Cr^{3+} cations in different water samples. The limit of detection (LOD) and quantitation (LOQ) of the HIMA sensor were calculated as 7.98×10^{-7}, and 2.42×10^{-6} M respectively, and they were found to be lower than the maximum amount in drinking water reported by WHO and USA Environmental Protection Agency. Also, stoichiometry between the HIMA and Cr^{3+} cations was found as 1:1, and the binding constant (Ka) was calculated as 5.31×10^{5} M^{-1}. These findings indicated that the proposed HIMA chemosensor could be found to potential application for the determination of Cr^{3+} cations in different water samples with satisfying, reliable, practical, and accuracy.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10895-022-03037-7.

Author Contributions Musa Kamaci is the single author of this manuscript. He has solely designed the manuscript.

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Data Availability All data generated or analyzed during this study are included in this published article.

Code Availability Not applicable.

Declarations

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Conflict of Interest The author also declares that there is no conflict of interest.

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