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New Ratiometric Luminescent Probe for Detection of Phenol in industrial Effluents*

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Abstract

Due to the high toxicity of phenols, the World Health Organization (WHO) recommended that, the maximal acceptable phenol content in drinkable water should be less than 0.001 μg/mL. This article aims to employ the first red luminous [Eu(III)-$(TAN)_2$-Phen]Cl complex as a luminescent probe to detect the phenols in industrial effluents (TAN = 1,3-Butanedione, 4,4,4-trifluoro-1-(2-naphthalenyl) and Phen=1,10 phenanthroline). Under optimal operating parameters, the quenching of the luminescence intensity of Eu(III) complex is directly proportional to the concentration of phenol in the range of 1.4 to 8.6 μg/mL. The limit of detection (LOD) is 1.2 μg/mL using ratiometric fluorescence. Moreover, the method was applied successfully for the detection of phenol in real industrial effluents with satisfied recovery and validated by standard method (4-AAP) to yield very closely similar concentrations of both methods. Therefore, this method can help for a simple quality control of total phenol content in industrial effluents.

Keywords: Phenol, Detection, Eu(III) complex, luminescent, quenching

1. Introduction

The existence of phenolic compounds in aquatic environment is due to industrial and agricultural activities. When phenolic compounds interact with water, some changes may occur that make the resulting moieties potentially more toxic than the original compounds [1]. These compounds have the potential to harm both humans and animals since they are poisonous and carcinogenic [2]. Phenolic compounds have been recorded as priority pollutants by the European Union and the United States Environmental Protection Agency (USEPA) [3], [4]. The first step in detection of phenolic compounds is the extraction process using liquid–liquid extraction (LLE), solid-phase extraction or steam-distillation extraction followed by quantification using numerous techniques including chromatography (HPLC) [5], photometry and fluorometry [6], [7] are just a few of the techniques that have recently been conducted in this area to establish a direct and easy technique for the identification of phenolic chemicals.

HPLC provides high sensitivity, yet technique, photometry is simple, but displays too little sensitivity. HPLC provides superb identification and separation ability, particularly when together with MS detection. However, HPLC instruments are quite expensive to purchase and need systematic maintenance, whereas luminescence provides a similarly sensitive detection with less instrumental demand. If luminescence is combined with an appropriate probe that shows high binding constants to its target and high brightness, trace analysis is achieved even with inexpensive instruments. Therefore, new probes and luminescent methods could signify a promising way for quantitation of phenolic compounds. The analytical application of

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lanthanide-sensitized luminescence has fashioned great interest for a long time. The chief benefit of lanthanide chelates as probes in luminescence spectrometry include large Stokes' shifts, narrow emission bands, and long luminescence lifetimes. Moreover, their luminescence can be considerably increased by coordination of so-called antenna ligands with high molar absorbance and high quantum yield [8]– [10]. Lanthanide complexes are ideal probes for luminescence assays based on changes of luminescence intensity or lifetime. In the last years, the analytical use of sensitized lanthanide luminescence as well as its response with decrease or enhancement of luminescence intensity or lifetime towards the presence of relevant molecules demonstrated their potential as useful probes [11]– [13].

Herein the ratiometric fluorescence technology was applied using a luminescent Eu(III) complex for determination of phenol ,and the fluorescence technique used for testing determination of phenol content in real industrial wastewater samples giving high recoveries with lower relative standard deviation and comparing the concentration within the standard method for phenolic compound determination using 4-aminoantipyrine [14]

2. Materials and Methods

2.1. Reagents

All the used chemicals were of analytical grade or chemically pure and doubly distilled water was used, throughout. The standard solution of Eu (III) complex (100.0 μmol/L) was prepared by dissolving 9.3 mg of the complex in acetone up to 100 mL in volumetric flask. An accurately weighted standard sample of 5.0 mg of phenol [**Figure 1**] was dissolved 1 mL methanol and diluted to 10 mL with distilled water in volumetric flask (500 μmol/L). The PIPES buffer (10 mmol/L) was prepared by the dissolving of 0.30 g of piperazine-N,N'-bis(2-ethanesulfonic acid (Sigma Aldrich) in 90 mL of distilled water and adjusting pH to 7.5 with NaOH and/or HCl and then diluting with water to 100 mL. Ammonia buffer was prepared by dissolution of 6.76 g of NH_4Cl in 10 mL distilled water, addition of 57.2 mL of NH_4OH and then completed to 100 mL with distilled water. 2 % 4-aminoantipyrine (4AAP) from Merck was prepared by dissolving 0.2 g of 4-aminoantipyrine in distilled water and then completed the volume to 10 mL. A stock solution of 8% Potassium ferricyanide was prepared by dissolving 0.8 g of potassium ferricyanide in distilled water and then completing the volume to 10 mL. The stock solutions of NaCl, KCl, $NiSO_4.7H_2O$, $CaCl_2.2H_2O$, $CuCl_2.2H_2O$, $MgSO_4.7H_2O$, $Pb(NO_3)_2$, NaH_2PO_4 and Na_2CO_3 and phenolic compounds (p.cresol, m.cresol, pyrogallol and α-naphthol) were prepared by dissolving 5 mg of each interfering compound in 100 mL distilled water and the other phenol dissolved in10 mL methanol and completed to 100 mL with distilled water.

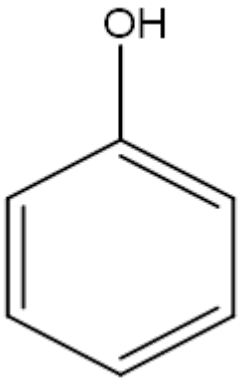

Figure 1: The chemical structure of the phenol

2.2. Characterization and measurement instrumentation

All luminescence measurements (luminescence spectra, excitation spectra and lifetimes) were carried out on Jasco FP-6300 Spectrofluorometer in the range (200–700 nm) equipped with a 150W xenon flash lamp in a 1.00 cm quartz cuvette. The excitation and emission monochromator band widths were 5 nm. The excitation wavelength was set at 365 nm, and the luminescence was measured using the peak height at 590 and 614 nm. All measurements were performed at room temperature (25 $\pm$ 0.1 °C) which should be kept at this level. Absorption spectra were recorded with a Shimadzu-UV 1800 UV–visible spectrophotometer with a 1 cm quartz cell. A pH meter (Lab 850, Schott Instruments GmbH, Germany) was used for pH adjustment.

2.3. Complex Preparation

The Complex was prepared previously as mentioned method [15]. The complex was characterized by IR, thermal and elemental analysis and the obtained results are of good agreement with the reported characterization results [15]. The Chemical Structure of the [Eu(III)$(TAN)_2$(Phen)]Cl complex as shown in **Figure 2.**

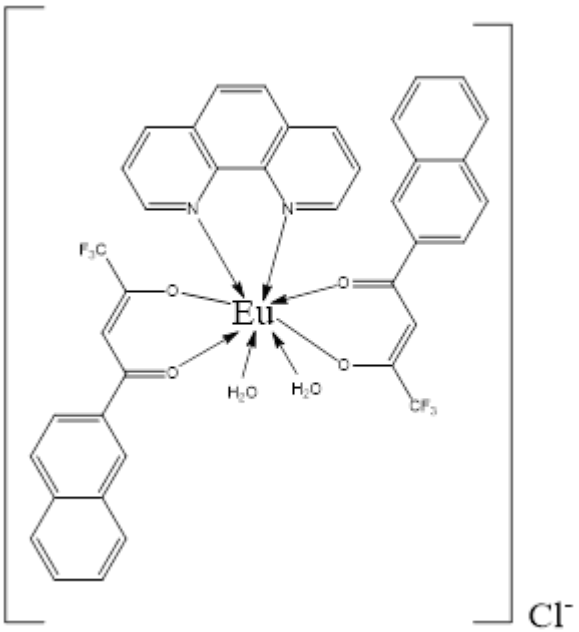

Figure 2: The proposed chemical structure of the Eu(III) complex

2.4. Luminescence measurements of free [Eu(III)$(TAN)_2$(phen)]Cl and in its interaction of phenol

For estimation the luminescence intensity of the complex free :100 μL of Eu(III)-$(TAN)_2$-(Phen) complex (100 μM) to get a final concentration of complex to be (2μM), then completed to 5mL with PIPES buffer).

For estimation the luminescence intensity of the complex and phenol (1:1):100 μL of Eu(III)-$(TAN)_2$-(Phen) complex (100 μM) to get a final concentration of complex to be (2μM) and (2μM) of phenol then completed to 5mL with PIPES buffer.

2.5. Ratiometric detection of phenol

A range of phenol between 1.4 - 21.4 μg/mL of phenol working solution (500 μg/mL), were added into volumetric flasks. 100 μL of a working Eu(III)-complex solution (2 μmol/L) and the volume was completed up to 5 mL with PIPES buffer (pH=7.5) to each of these volumetric flasks. The luminescence intensity (F) was measured at λ_{ex}/ λ_{em} = 365/(590,614) nm after 5 min. Concentrations of the samples were derived from the related ratiometric calibration curve.

2.6. Luminescence determination of phenol in presence of diverse species

To investigate the effect of diverse species on the luminescence intensity of Eu(III) complex -phenol, certain concentration of each interfering species was added to 2μM of Eu(III)-$(TAN)_2$-(Phen) complex and 10 μg/ mL of phenol solution at tolerance limit of ±10% using PIPES buffer (pH =7.5).

2.7. Luminescence determination of phenol industrial wastewater samples

Three industrial wastewater samples were collected from Al-Nasr Petroleum Company, Suez Oil Processing Company, and Suez Steel Company, filtered and stored in refrigerator before analysis. Within 24 h the samples measured by both standard method by 4- AAP reagent and the proposed luminescent analysis. A 5 mL of each sample of industrial wastewater, 2 mL of ammonia buffer, 200 μL of (4AAP), 200 μL of potassium ferricyanide and ammonia buffer (pH =10) were mixed and diluted to 10 mL of distilled water in 10 mL volumetric flask as the standard method reported for phenolic compound detection. For the proposed luminescent analysis (1 mL of each sample, 100 μL of Eu(III)-$(TAN)_2$-(Phen) complex (2μM) were mixed and then completed to 5mL of PIPES buffer). In addition to, The concentration of phenol in the industrial wastewater samples were also determined using the standard addition method as follow: 1mL of the industrial wastewater sample ,100 μL of Eu(III)-$(TAN)_2$-(Phen) complex (2μM) and then completed to 5mL of PIPES buffer with different concentrations of phenol of 10,15,20 μg/mL. Each solution's fluorescence intensity was measured, and the phenol concentration was calculated.

3. Results and discussion

3.1. Luminescence characteristics of Eu(III - complex

3.1.1. Spectral features

Figure 3 displays the excitation of the Eu(III)-$(TAN)_2$-(Phen) complex was found at 365 and the emission wavelength at 614 nm. The hypersensitive transition ($^5D_0$-$^7F_2$), with its center at 614 nm, is the strongest and most coordination environment-sensitive transition. Magnetic and electric dipole transitions are prohibited in four extremely weak bands at 580, 590, 650, 690, and 710 nm, which correspond to the $^5D_0$-$^7F_{0,1,3,4,5}$ transitions. Due to its magnetic properties, the $^5D_0$-$^7F_1$ transition in the band at 590 nm is unaffected by the coordination environment [16]. The quantum yield (QY) was found to be 0.71 for Eu(III)-$(TAN)_2$-(Phen) complex as reported in the literature [15]. The influence of pH on the fluorescence intensity of the Eu(III)$(TAN)_2$(Phen) complex was tested, and PIPES buffer was selected as **In Ref** [15] it was selected for further analytical experiments. In dissimilarity to distilled water, methanol, and ethanol, the use of PIPES buffer has no noted impact on the complex's fluorescence spectra.

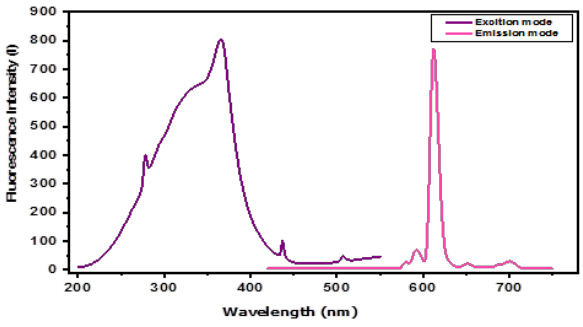

Figure 3: Excitation and emission spectra for Eu(III)-$(TAN)_2$-(Phen) complex in solid state as powder at room temperature, sensitivity is low, (λ_{ex} = 365 nm) and λ_{em} =614 nm at room temperature at room temperature

3.2. Spectral measurements for the interaction of the Eu(III) -$(TAN)_2$-(Phen) complex and phenol

The influence of phenol concentrations on the fluorescence intensity of Eu(III)-(TAN)-Phen complex showed a significant change in luminescence intensity as shown in **(Figure 4).** The addition of phenol to the Eu(III)-(TAN)-Phen system reduced the luminescence intensity of Eu(III) complex, indicating the successful coordination of phenol with the complex. According to the experimental findings, phenol can quench the intrinsic fluorescence of Eu(III)-$(TAN)_2$-Phen complex without producing any conformational change in it.

In Eu(III)-$(TAN)_2$-Phen itself is fluorescent. In the presence of phenol, the luminescence intensity is reduced due to its binding to the receptor unit of the sensor and formation of a non-fluorescent complex, and therefore, the net fluorescence is quenched.

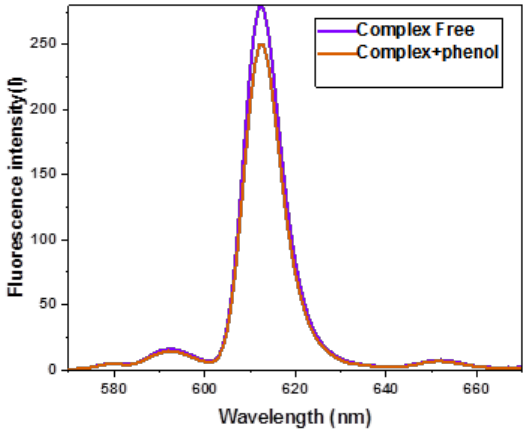

Figure 4: Fluorescence spectra of the reaction of 2μM of Eu(III)-$(TAN)_2$-(Phen) complex with 2μM of phenol λ_{ex}=365 nm and λ_{em} =614 nm a troom temperature

3.3. Analytical performance of ratiometric Eu(III -complex for quantification of phenol in wastewater samples

For the ratiometric probe, as the concentration of phenol increased, the fluorescence intensity gradually recovered at 614 nm and almost unchanged at 590 nm. Moreover, the fluorescence intensity of Eu(III) decreases as the phenol concentration increases. As shown in **Figure 5**, the F_{590}/F_{614} value linearly decreased as the phenol concentration increased, which could be expressed by the following linear relationship Y = 20.048X+ 0.983 (R^2 = 0.977) in the range of 1.4 to 8.6 μg/mL,

The limit of detection (LOD) is 1.2 μg/mL, where Y= F_{590}/F_{614}, X= concentration of phenol. The ratiometric calibration plot as shown in **Figure 6**.

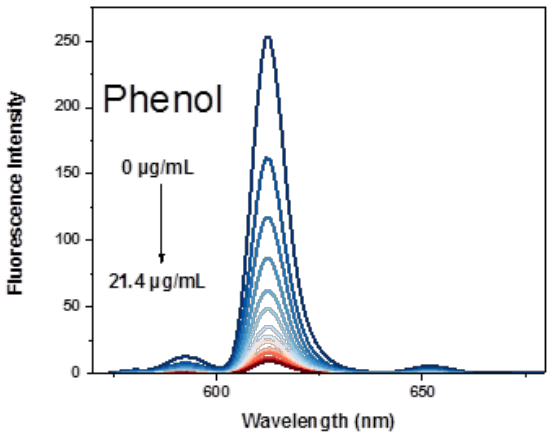

Figure 5: The emission spectra for the interaction of 100 μM of Eu(III)-$(TAN)_2$-(Phen) complex with different concentrations of phenol in using λ_{ex} = 365 nm at room temperature

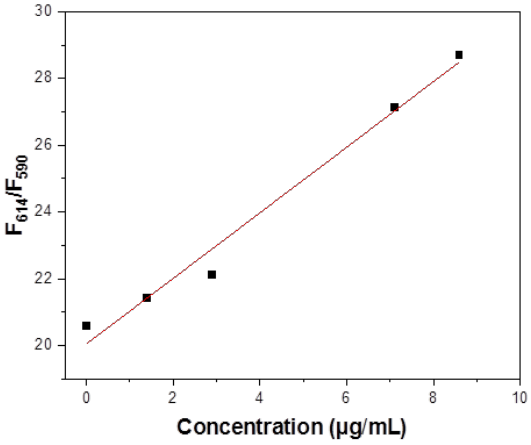

Figure 6: Calibration plot for the interaction of Eu(III)-$(TAN)_2$-(Phen) complex with different concentrations of phenol in at λ_{ex} = 365 nm, λ_{em} = 614 nm, at room temperature

3.4. *Diverse species effect*

The interferences of some cations, anions and some phenolic compounds such as p.cresol, m.cresol ,pyrogallol and α-naphthol that are already present in water and wastewater was studied by addition of these compounds to a solution of 10 μg/mL of phenol. Then, this mixture was added to a solution of the Eu(III) complex, and the change of the luminescence intensity (ΔF) was determined as compared to a solution of phenol and Eu(III) complex with the same concentrations, and without the interfering species being present at optimal conditions. As shown in **Table1**, the interfering species has a very little effect on the luminescent determination of phenol at about 10% is the tolerance limit. Hence, a high specificity is achieved by the proposed method. This suggests that the Eu(III) complex is a reliable luminescent probe to determine phenol in wastewater**.**

Table 1: Tolerance limit of interfering species affecting on detection of phenolic compounds using Eu(III)-$(TAN)_2$-(Phen) complex

Interfering species	Tolerance
Na+	0.68 ^{Q} μg/mL
K+	1.49 ^{Q} μg/mL
Ca2+	0.78 ^{Q} μg/mL
Cu2+	1.12 ^{Q} μg/mL
Pb2+	1.79 ^{Q} μg/mL
Ni2+	0.48 ^{Q} μg/mL
Mg2+	0.14 ^{Q} μg/mL
Cl-	1.36 ^{Q} μg/mL
SO42-	0.78 ^{Q} μg/mL
NO3-	0.54 ^{Q} μg/mL
PO43-	2.83 ^{Q} μg/mL
CO32-	1.21 ^{Q} μg/mL
p.Cresol	1.50 ^{Q} μg/mL
m.Cresol	2.00 ^{Q} μg/mL
α-naphthol	1.00 ^{Q} μg/mL
Pyrogallol	0.50 ^{Q} μg/mL

^{Q}: quenchingeffect

3.5. *Detection of phenol in wastewater effluents*

A comparison of the related concentrations of phenol in mg/mL found in the three wastewater samples by luminescence quenching and standard method is shown in **Table 2**. The concentrations of phenol obtained match very well within the range of errors of the individual methods. Importantly, the standard deviations are very low, even though the number of samples (n = 3) was not very high.

This demonstrates that both methods work precisely and that the detection of phenol with Eu(III) complex also works reliably in industrial effluents.

Table 2: Detection of phenol in wastewater samples

Sample	Standard method (4AAP) (μg/mL)	Eu(III)-$(TAN)_2$-(Phen) Complex (μg/mL)	Recovery (%)
Sample (I)	2.4	2.5	104 %
Sample (II)	6.4	6.02	94 %
Sample (III)	0.76	0.72	95 %

Sample (I)Al-Nasr Petroleum Company
Sample (II)Suez Petroleum Company
Sample (III) Suez Steel Company

Additionally, the standard addition method was applied in suggested method, in which the wastewater samples were added to Eu(III)-$(TAN)_2$-(Phen) complex at pH=7.5 using PIPES buffer. The comparison between the results acquired from both proposed and standard method of the (4AAP) methods were in perfect agreement **[Table 2]**.

Table 3: Determination of Phenolic Compounds in different types of wastewater samples using StandardAddition method

	Added (μg/mL)	Found (μg/mL)	Recovery (%)	RSD (n=3) %
Sample (I)	10	10.8	108%	1.7%
	15	15.2	102%	1.1%
	20	18.9	95%	0.3%
Sample (II)	10	9.5	95%	1.8%
	15	13.7	91%	2.9%
	20	21.1	105%	1.9%
Sample (III)	10	10.4	104%	1.9%
	15	14.9	99.9%	2.5%
	20	19.6	98.0%	2%

Real water samples are often difficult to analyze because of a high molecular weight matrix and various organic or inorganic components. The impacts of such interferences are compensated for by using the Standard Addition Approach [17].

To check the accuracy and precision of the suggested approach for determining phenol content, it was utilized to calculate the total phenol levels in wastewater sample. The recovery percentages are displayed in **[Table 3].** Curves for standard calibration (SC) and standard addition calibration (AC) were plotted. We note that the recovery-related results were satisfactory.

4. Conclusion

Eu(III)$(TAN)_2$(Phen) complex has been used as a fluorescent probe in a highly sensitive, quick fluorescence technique that has been designed to measure phenol concentration in the presence of PIPES buffer (pH=7.5). The luminescence intensity of the Eu(III)$(TAN)_2$(Phen) complex was quenched by phenol, the calibration curve using ratiometric fluorescence covering the range from 1.4 to 8.6 μg/mL, The limit of detection (LOD) is 1.2 μg/mL. The proposed approach was used to determine the phenolic content in three industrial effluents from three separate sources using standard addition method, and the findings were compared with the standard method for phenol content determination using 4-AAP method giving excellent recoveries. In the same samples, phenol was also determined by the standard addition method within concentrations of 10,15,20 μg/mL. This resulted in a lower relative standard deviation and good recoveries.

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