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## New turn on fluorimetric sensor for direct detection of ultra-trace ferric ions in industrial wastewater and its application by test strips



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Keywords: Iron Detection Fluorescence Sensor	New 5-(4-(dimethylamino)phenyl)-4-(2-(4-methoxy-3-methylphenyl)-2-oxoethyl)-1H-pyrazol-3(2 H)-one (AAP) sensor was synthesized and well characterized. AAP sensor was developed for direct detection of ultra-traces of $Fe^{3+}$ ions in industrial wastewater and the obtained results were validated through comparison with flame atomic spectroscopy. The turn on fluorescent AAP sensor worked excellently at pH 4.0 and the detection limit was 1.59 nmol L <sup>-1</sup> through ESIPT inhibition mechanism. In addition, AAP exhibited high selectivity, sensitivity, fast, direct and efficient response towards $Fe^{3+}$ ions. The effect of interfering cations commonly present in water was also examined. Furthermore, AAP sensor was successfully integrated in test strips for fluorescent detection of $Fe^{3+}$ ions with no signal is recorded against interfering cations.

### 1. Introduction

Recently, metal ions detection attracted more attention due to their importance in the ecological and biological concern [1]. As worldwide industrialization advances, the amount of heavy metals found in the environment increase. Some of these metals are harmful and contaminate the soil and water [2,3]. The danger of tainted drinking water and food is expanding, and accordingly the health risks for many people are also increased. Continuous monitoring of heavy metals in industrial wastewater such as  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$  and  $Fe^{3+}$  is hence essential.

Levels of ferric ions (Fe<sup>3+</sup>) in nature were increasing, particularly industrial wastewater can causes ecological and health problems, consequently estimating Fe<sup>3+</sup> concentration is a critical for the assessment and confirmation quality of water [4]. High concentration of iron in plasma can cause several diseases, for example, Parkinson's, Alzheimer's, Huntington's and cancer [5]. In addition, iron prompts the generation of highly reactive oxygen species which can cause dangerous tissue damages including liver/heart fibrosis or diabetes [6].

There are different techniques used for  $\text{Fe}^{3+}$  ions detection like flame atomic absorption spectroscopy (FAAS), inductively coupled plasmamass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and cathodic striping voltammetry [7–15]. Although, these techniques are characterized by their sensitivity and selectivity, they are expensive instruments, complicated methodology and consuming time. While Optical sensors are incredibly valuable techniques for the specific recognition of clinical, chemical and environmental species [16–26]. The fluorescence technique is considered to be the best tool, due to its selectivity, sensitivity, fast response, easily operated and cheap technique [27–29] that offers preferences over different techniques.

Herein, a novel portable fluorescent sensor of 5-(4-(dimethylamino) phenyl)-4-(2-(4-methoxy-3-methylphenyl)-2-oxoethyl)-1H-pyrazol-3 (2 H)-one (AAP) has been synthesized and applied for selective and sensitive Fe<sup>3+</sup> ions detection in industrial waste water which is prime challenge to analytical chemists. This results in chemosensors that are less prone to interferences. The change of the fluorescence intensity linearly depended on the concentration of Fe<sup>3+</sup> in the range from 0 to 50  $\mu$ mol L<sup>-1</sup>. The proposed sensor has been applied to the industrial wastewater samples with acceptable results.

### 2. Experiments

### 2.1. Materials and solutions

The materials and organic solvents were purchased from Sigma chemical Co. and used as analytical grade with purity of  $\geq$  99.0 %.

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Received 9 December 2020; Received in revised form 6 February 2021; Accepted 17 February 2021 Available online 20 February 2021 1010-6030/© 2021 Elsevier B.V. All rights reserved. Stock solution of 1-amino-3-arylidene-2(3 H)-pyrrolone (AAP) was prepared by dissolving 8.70 mg in 25 mL DMF. Buffer solution pH 2.0, 4.0, 6.0, 8.0 and 10.0 was prepared using KCl / HCl, acetic acid / sodium acetate tri-hydrate, acetic acid / sodium acetate tri-hydrate, disodium hydrogen phosphate / HCl, disodium hydrogen phosphate / and KCl / NaOH respectively. Aqueous solutions of all cationic compounds of  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  ions, were purchased from Aldrich and used as received were prepared from their chlorate or nitrates salts.

### 2.2. Apparatus

A Shimadzu-UV Probe Version 2.33 and JASCO FP-8300 were used for UV–vis. and fluorescence measurements respectively. Flame atomic absorption spectrophotometer was (FAAS; Perkin Elmer A Analyst 100)

## 2.3. Synthesis of 5-(4-(dimethylamino)phenyl)-4-(2-(4-methoxy-3-methylphenyl)-2-oxoethyl)-1H-pyrazol-3(2 H)-one (AAP) sensor

### 2.3.1. Synthesis of 5-[4-methoxy-3-methylphenyl]-2(3 H)-furanone (2)

A mixture of 4-[4-methoxy-3-methylphenyl]-4-oxobutanoic acid (1) (0.01 mol) and acetic anhydride (3 mL) in20 mL toluene was heated under reflux for 1 h, the reaction was then cooled, the solid product obtained after cooling was collected by filtration and recrystallized from ethanol to give 5-[4-methoxy-3-methylphenyl]-2(3 H)-furanone (2) as orange crystals.

### 2.3.2. Synthesis of 3-(4-(dimethylamino)benzylidene)-5-(4-methoxy-3methylphenyl)-2(3 H)-furanone (3)

To a solution of compound (2) (0.01 mol) in acetic anhydride (10 mL), we added the 4-(dimethylamino)benzaldehyde (0.01 mol) and anhydrous sodium acetate (0.01 mol). The reaction mixture was heated under reflux for 2 h, the solid compound was filtered after cooling then crystallized from the ethanol to give 3-arylidene-2(3 H)-furanone (3) as yellow crystals [30].

### 2.3.3. Formation of 2-(4-(dimethylamino)benzylidene)-4oxobutanhydrazide (4)

Hydrazine hydrate (0.02 mol) was added to a solution of compound (3) (0.01 mol) in ethanol (40 mL), after stirring for 4 h at room temperature and kept overnight. The resultant white solid was filtered and washed with diluted ethanol. The hydrazide was used directly in the next reaction.

# 2.3.4. Formation of 5-(4-(dimethylamino)phenyl)-4-(2-(4-methoxy-3-methylphenyl)-2-oxoethyl)-1H-pyrazol-3(2 H)-one (5)

A solution of the hydrazides **(4)** (0.01 mol) in ethanol (30 mL) was heated under reflux for 4 h. After cooling, the solid compound was filtered, dried and crystallized from the ethanol to give orange crystals of pyrazolone **(5)**, m.p. 160, yield 63.7 %. IR (ATR, u, cm<sup>-1</sup>): 1686(C = O), 3309 and 3208 (2 NH). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  12.96 (s, 1 H), 7.76 (s, 1 H), 7.59 (dd, J = 12.0, 3.5 Hz, 2 H), 7.16 (d, J =8.7 Hz, 2 H), 7.01 (d, J =8.6 Hz, 1 H), 6.67 (d, J =8.7 Hz, 2 H), 3.83 (s, 3 H), 3.72 (s, 2 H), 2.85 (s, 6 H), 2.20 (s, 3 H). Anal. Calcd (%) for C<sub>21</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub> (349.43): C, 72.18; H, 6.63; N, 12.03; Found C, 71.97; H, 6.49; N, 12.25 (SI: Scheme 1).

### 2.4. Spectrofluorimetric measurements

### 2.4.1. Fluorescence determination of $Fe^{3+}$ ions

To obtain the optimum sensing condition of  $Fe^{3+}$  ions, the fluorometric measurements were conducted at room temperature over a wide range of pH solutions from 2 to 10 using standard buffer solutions. The spectrofluorometric sensing of  $Fe^{3+}$  ions via AAP sensor was performed over a different concentration of  $Fe^{3+}$  ions adjusted at pH 4.0 at excitation and emission wavelength 370 nm and 470 nm respectively.

### 2.4.2. Binding constant calculation

The binding constant (K) calculated using Benesi-Hildebrand equation, where K result from the intercept to the slope ratio [31].

$$\frac{F^{\circ}}{F - F^{\circ}} = \alpha + \frac{\alpha}{K \left[Fe^{3+}\right]}, \ \alpha = \frac{1}{F_L - F^{\circ}}$$
(1)

Where [Fe] is  $Fe^{3+}$  ions concentration,  $F^{o}$  and F are the fluorescence intensity in the absence and presence of  $Fe^{3+}$  ions, respectively, and  $F_{L}$  is the limiting intensity of fluorescence.

### 2.4.3. Molar ratio method

The stoichiometry of AAP sensor with  $Fe^{3+}$  ions is evaluated using fluorescence measurements by using various concentrations of AAP sensor while the  $Fe^{3+}$  ions is kept constant, then recording the intensity of the emission peak at 470 nm.

### 2.4.4. Calculation quantum yield and brightness for AAP sensor

The quantum yield (QY) of AAP sensor was determined in DMF using the following equation at concentration  $10 \,\mu$ mol L<sup>-1</sup>. The QY was calculated with coumarin 6 in ethanol (QY = 0.78) as the reference [32]:

$$Q_X = Q_R \frac{A_R \ I_X \ .n^2_X}{A_X \ .I_R \ .n^2_R}$$
(2)

Where Q is the quantum yield, A is the absorbance value at the excitation wavelength, I is the integrated area of the emission spectra, n is the refractive index of the responding solvent and subscripts R and X denote the of the reference and AAP sensor, respectively. While the brightness was determined by multiplying molar absorbance ( $\varepsilon$ ) and quantum yield (Q) of AAP sensor.

### 3. Results & discussion

### 3.1. Characterization of 5-(4-(dimethylamino)phenyl)-4-(2-(4-methoxy-3-methylphenyl)-2-oxoethyl)-1H-pyrazol-3(2 H)-one (AAP) sensor

The starting 5-[4-methoxy-3-methylphenyl]-2(3 H)-furanone (2), was synthesized by Friedel-Crafts acylation of o-cresyl methyl ether with succininc anhydride in the presence of anhydrous aluminium chloride, and subsequent cyclization of the intermediate,4-(4-methoxy-3-methylphenyl)-4-oxo-butanoic acid (1) with acetic anhydride.

3-(4-(Dimethylamino)benzylidene)-5-(4-methoxy-3-methylphenyl)-2(3 H)-furanone (3) was synthesised from the condensation reaction of 5-[4-methoxy-3-methyl phenyl]-2(3 H)-furanone with 4-(dimethylamino)benzaldehyde in the presence of anhydrous sodium acetate under perkin reaction conditions.

The synthesis of hydrazide (**4**), was accomplished by stirring of a mixture of 5-[4-methoxy-3-methylphenyl]-3-substituted-2(3 H)-furanone (**3**) and hydrazine hydrate. The reaction was carried out by stirring the reaction mixture in ethanol on cold.

Heating the hydrazide (4) in refluxing ethanol provided mainly the pyrazolone (5). The formation of the pyrazolone (5) was assumed to proceed via the intramolecular Michael addition according to the reaction mechanism outlined in (Scheme 1), where the nitrogen atom of NH<sub>2</sub> group could attack onto the  $\beta$ -carbon of the unsaturated carbonyl group followed by dehydrogenation with the formation of the corresponding pyrazolone.

The structure of pyrazolone **(5)** (AAP sensor) was confirmed by IR and <sup>1</sup>H-NMR (SI: Figs. 1 and 2). The IR spectrum revealed the presence of two absorption bands corresponding to the 2NH groups at  $3309 \text{ cm}^{-1}$  and  $3208 \text{ cm}^{-1}$ . The absorption band of carbonyl group appeared at  $1686 \text{ cm}^{-1}$ .

The <sup>1</sup>H-NMR spectrum (DMSO- $d_6$ ) of the pyrazolone **(5)** showed the presence of four singlets in the aliphatic region at 2.20, 2.85, 3.72 and 3.83 ppm corresponding to Ar–CH<sub>3</sub>, CH<sub>2</sub> of side chain, N(CH<sub>3</sub>)<sub>2</sub>, and Ar–OCH<sub>3</sub>, respectively. The signals of the aromatic protons were



Scheme 1. Proposed mechanism for the formation of compound (5).

observed at 6.67–7.76 ppm. The signal for NH group of pyrazole ring was observed as merged with the signals of aromatic protons in aromatic region. The signal characteristic for the NH proton adjacent to the keto group of the pyrazole ring was observed at 12.96 ppm as singlet.

### 3.1.1. Steady UV-vis and fluorescence spectroscopy

AAP sensor containing (-NH-C = O-) group which makes it susceptible to lactam –lactim tautomerism [27] (Scheme 2). The UV spectrum of  $1 \times 10^{-4}$  mol L<sup>-1</sup> AAP sensor in different solvents was examined (SI: Fig. 3). The absorption spectrum of AAP shows two peaks (band I and band II) band I can be found in 360–380 nm range correspond to lactim form and band II found in 460 nm–470 nm correspond lactam form [33–36]. Band I assigned to  $\pi$ - $\pi$ \* transition of C=C of lactim while band II assigned to n- $\pi$ \* transitions of n-electrons of the carbonyl group of lactam form [36].

Effect of different solvents (ethanol, DMF, benzene and water) on UV–vis spectra for AAP sensor is shown in (SI: Fig. 3). Band II shifted to higher wavelength as the polarity of solvent increase, following the order water > ethanol > DMF > benzene at 470 nm, 466 nm, 463 nm and 460 nm, respectively, this may be due to more solvation, which indicates that, the absorption bands of AAP are significantly dependent on solvent polarity [36,37]. In polar protic solvent such ethanol, it was noticed that the absorption of band I assigned to lactim form was higher than the lactam band (band II). This refers to the formation of the ion pair in the polar protic solvent that is involved in hydrogen bonding with the solvent, making it less available to the hydrogen bond with the

lactam form. While in nonpolar solvent (benzene), the absorption of the lactim tautomer band is lower than that of the lactam band [38]

After excitation at 370 nm (lactim form of AAP sensor) (SI: Fig. 4), one emission band were recorded at 470 nm attributed to lactam form (high emission intensity) analogues to 2-hydoxypyridine (2HP) not salicylic acid (SA) [39–41]. This assigned to the presence of an ultrafast lactim-lactam crossover on the excited state prior to emission (no dual emission) [42]. While excitation at longer wavelength ( $\lambda_{exc}$  470 nm) very weak emission is produced at 560 nm of lactim form only (SI: Fig. 5). All further studies concerning Fe<sup>3+</sup> ions determination proceed at  $\lambda_{exc}$  370 nm.

### 3.1.2. Photophysical properties

The photophysical properties such as absorption ( $\lambda_{max}$ ), emission ( $\lambda_{em}$ ), molar extinction coefficient ( $\epsilon$ ) and Stokes shift of 5-(4-(dimethylamino)phenyl)-4-(2-(4-methoxy-3-methylphenyl)-2-oxoethyl)-1H-pyrazol-3(2 H)-one (AAP) sensor were evaluated and the results are presented in Table 1. It was obvious that the hydrogen-bond interactions between carbonyl group of lactam form (hydrogen-bond acceptor) and protic solvents (hydrogen-bond donor) caused high Stokes shifts [43]. The quantum yield and brightness of AAP sensor in DMF at  $\lambda = 360$  nm was 0.03 and 444 respectively.



Scheme 2. Lactam -lactim tautomerism.

#### Table 1

Photophysical aspects of AAP sensor in different solvents.

Solvent	λ <sub>abs</sub> (nm)	λ <sub>exc</sub> (nm)	λ <sub>em</sub> (nm)	$\epsilon \ (mol^{-1} cm^{-1} L) x \ 10^3$	Stock shift (cm <sup>-1</sup> ) $\Delta \upsilon = \upsilon_{exc} - \upsilon_{em}$
Benzene	460, 380	370	425	13.4, 10.1	3497.6
DMF	470, 360	370	450	1.99, 14.8	4804.8
Ethanol	465, 363	370	463	4.15, 14.1	5428.8
Water	470, 365	370	475	7.62, 85.2	5974.4

### 3.2. Detection of $Fe^{3+}$ ions using of AAP sensor

### 3.2.1. pH effect

Fig. 1 shows the fluorescence response of probe as a function of pH. The results show that the maximum intensity of the AAP sensor was at a pH of 4.0 (Fig. 1). It was obvious that the fluorescence intensity was very weak in acidic medium due to the protonation of the carbonyl oxygen. Higher pH is avoided to prevent precipitation of metal hydroxide.

### 3.2.2. Calibration curve and detection limit

The effect of Fe<sup>3+</sup> concentration on the emission spectrum of AAP sensor was performed (from 0 to 50  $\mu$ mol L<sup>-1</sup>) in aqueous solution at pH 4 (Fig. 2), it is obvious that the intensity of AAP sensor at  $\lambda_{em} = 470$  nm is gradually increased with increasing Fe<sup>3+</sup> concentration (Fig. 2).

Calibration plots for Fe<sup>3+</sup> in pH 4.0,  $\lambda_{ex} = 370$  nm,  $\lambda_{em} = 472$  nm, at 25 °C are depicted in Fig. 3. Where the detection limit ( $D_L = 3\sigma$ /slope) and quantitation limit ( $Q_L = 10 \sigma$ /slope) for sensing of Fe<sup>3+</sup> ions via AAP sensor estimated to be 1.59 nmol L<sup>-1</sup> and 5.31 nmol L<sup>-1</sup>, respectively with a good linearity of Fe(III) concentration is found from 2 nmol L<sup>-1</sup> to 0.4 µmol L<sup>-1</sup> (Table 2). This limit of detection is 160 times lower than the limit value ( $\approx 5.5$  M) allowed by the U.S. Environmental Protection Agency in drinkable water [44] also it was lower than those for previously reported methods [45–54] (Table 3).

Benesi-Hildebrand Eq. (1) was used to calculate the binding constant of Fe<sup>3+</sup> with AAP sensor (Fig. 4). The binding constant  $K_D$  equals  $2.69 \times 10^5 \text{ mol}^{-1}$  L. The obtained data revealed that the AAP sensor exhibited a very good binding to Fe<sup>3+</sup> ions. The best stoichiometry is found to be 1:2 which confirmed through molar ratio method (SI: Fig. 6).

### 3.2.3. Mechanism of fluorometric $Fe^{3+}$ ion sensing

AAP sensor contains a strongly electron-donating group (N—N dimethylamino) conjugated to an electron-withdrawing group (carbonyl oxygen) in addition to excited-state intramolecular proton-transfer





Fig. 2. Emission spectra for the AAP sensor with increasing concentration of  $Fe^{3+}$  ion at pH 4,  $\lambda_{em}=470$  nm.



Fig. 3. Calibration plot for the AAP sensor with emission measured at  $\lambda_{em}=470$  nm with different Fe $^{3+}$  ion concentrations.

### Table 2

The linear range, correlation coefficients,  $D_L$  (detection limit),  $Q_L$  (quantitation limit) and  $K_D$  (binding constant) for determination of Fe<sup>3+</sup> ions using AAP sensor at  $\lambda_{\rm em}$  470 nm,  $\lambda_{\rm exc}$  370 nm and at pH 4.0.

Linear range (µmol $L^{-1}$ )	R	$D_L \text{ (nmol } L^{-1}\text{)}$	$Q_L \text{ (nmol } L^{-1}\text{)}$	$K_D (\mathrm{mol}^{-1}\mathrm{L})$
0.002 - 0.4	0.9588	1.59	5.31	$2.69\times 10^5$

(ESIPT) effect due to lactam-lactim tautomerism, so AAP sensor is poorly fluorescent. Upon chelation of  $Fe^{3+}$  ions with two carbonyl oxygen of AAP sensor, the (ESIPT) effect is reduced, leading to fluorescence enhancement [55,56]. In addition chelation with  $Fe^{3+}$  induces the rigidity in the resulting compound and increases the chelation enhanced fluorescence (CHEF) effect [57].

### 3.3. Interference study

The selectivity of AAP sensor against different interfering cations has been investigated in the absence of Fe<sup>3+</sup> ions (Fig. 5). It is obvious that, there is no significant change on the intensity at  $\lambda_{em}$  470 nm after addition of 10 µmol L<sup>-1</sup> of interfering cations to AAP sensor as shown in Fig. 6, which confirm the high selectivity towards Fe<sup>3+</sup> ions.

Fig. 1. Emission intensity at  $\lambda_{em}=470$  nm for  $Fe^{3+}$  ion detection as a function of pH using the AAP sensor.

#### Table 3

Comparison between AAP sensor and the reported methods for  $\mbox{Fe}^{+3}$  ions detection.

Sensor	Detection Limit (nmol L <sup>-1</sup> )	Refs.
N-doped carbon dots (CDs)	$50 \text{ nmolL}^{-1}$	[45]
Nitrogen-doped carbon quantum dots (N-CQDs) with urea and ophenylenediamine	$39\mathrm{nmol}\mathrm{L}^{-1}$	[46]
Pyrazole bearing imidazole derivative (DIBI sensor)	$1.73\times 10^3 \text{ nmolL}^{-1}$	[47]
Boron doped carbon dots (B-CDs) starting from glucose and boric acid.	$242\mathrm{nmolL}^{-1}$	[48]
fluorescein–reduced graphene oxide functionalized with polyethyleneimine	$1.12\times 10^3 \text{ nmolL}^{-1}$	[49]
Rhodamine 6 G hydrazide derivative (R6 GD)	$50 \text{ nmolL}^{-1}$	[50]
Rhodamine amide (RHA)	$300 \text{ nmolL}^{-1}$	[51]
9,10-bis((2-(4-((naphthalen-2-yloxy)methyl)-1H- 1,2,3-triazol-1-yl) ethoxy)methyl) anthracene	$314 \text{ nmolL}^{-1}$	[52]
Carbon quantum dots (CQDs) modified ZnO/CdS nanoparticles	$172\mathrm{nmolL}^{-1}$	[53]
Tb-MOF of 1,3-di(3', 5'- dicarboxylphenyl) benzene	$936 \mathrm{nmol}\mathrm{L}^{-1}$	[54]
AAP sensor	$1.59\mathrm{nmolL}^{-1}$	Our work



Fig. 4. Benesi-Hildebrand relation for the interaction of different concentrations of Fe<sup>3+</sup> with AAP sensor at  $\lambda_{ex} = 370$  nm.



Fig. 5. The emission spectra of AAP sensor at  $pH\,{=}\,4.0$  in the presence of different metal ions at  $\lambda_{exc}$  370 nm.



Fig. 6. The luminescence intensity at  $\lambda_{em}$  470 nm of AAP sensor in presence of 10 µmol L<sup>-1</sup> different metal ions at  $\lambda_{ex}$  370 nm and pH 4.0.

### 3.4. Test-Strip fabrication

Test-Strip of AAP sensor was fabricated for detection of Fe<sup>3+</sup> ions in real field. The filter paper was immersed in  $1\times 10^{-3}$  mol L<sup>-1</sup>AAP solution for 30 min and then dried [58]. After irradiation of a UV lamp (365 nm) we can use these test strips to detect Fe<sup>3+</sup> ions. The fluorescence responses of these test strips to Fe<sup>3+</sup> and other interfering cations have been shown in Fig. 7. As expected, no color changes were observed for all cations except Fe<sup>3+</sup>, which indicated that AAP could be integrated in a filter paper-based fluorescence sensor for fluorometric detection of Fe<sup>3+</sup> ions, which was low-cost, simple and convenient.

### 3.4.1. Reusability

The reusability of AAP-test strips was studied by eluting  $10 \,\mu\text{mol L}^{-1}$  of Fe<sup>3+</sup> ions with ethylenediaminetetraacetic acid (EDTA) (0.01 mol L<sup>-1</sup>) through the decomplexation of Fe<sup>3+</sup> ions from AAP-test strips. The results indicated that AAP-test strips can be reused for Fe<sup>3+</sup> ions for about 5 times (SI: Fig. 7).

### 3.5. Real application

The wastewater samples were collected from two points (inlet and outlet) of the main combined drainage line of Aladabiyah wastewater treatment plant, Suez Gulf. Wastewater samples were pre-concentrated using the standard methods with APDC-MIBK extraction procedure. Fe<sup>3+</sup> concentrations in wastewater samples were measured using flame atomic absorption spectrophotometer [59].

The Fe<sup>3+</sup> ion was quantitatively determined by fluorescence spectroscopy with aid of the obtained calibration curve. The results of wastewaters were examined by AAP sensor and this was found to be in good agreement with those obtained by flame atomic absorption spectrophotometer Table 4.

### 4. Conclusion

AAP sensor was synthesized, characterized and applied for direct fluorometric detection of Fe<sup>3+</sup> ions. The results indicate that, the sensing mechanism is based on ESIPT inhibition mechanism. When compared with other fluorescent sensors, the present sensor shows low limit of detection. The formation of 1:2 complex is confirmed by molar ratio method. The binding constant is also calculated for the sensor-Fe<sup>3+</sup> ions as  $2.69 \times 10^5$  mol<sup>-1</sup> L. The competition study of the proposed method was examined and indicated the selectivity of AAP sensor towards Fe<sup>3+</sup> ions. The promising results can be encouraging for detection of Fe<sup>3+</sup> in industrial wastewater samples. More impressing, test strips have been successfully fabricated for fast and convenient sensing of Fe<sup>3+</sup>.



Fig. 7. The test strips for the visual detection of  $Fe^{3+}$  ions and different interfering cations under UV light.

### Table 4

Concentrations (mg/L) of Fe(III) ion in waste water samples.

Comple	Concentration of proposed method ppm (mg/l)			
Sample	FAA AAP sensor Method			
Inlet sample	91.32	91.29		
Outlet sample	83.88	83.80		

### CRediT authorship contribution statement

Rasha M. Kamel: Data curation, Writing - original draft, Supervision, Conceptualization, Visualization, Methodology, Investigation. Sahar S. El-Sakka: Supervision. Khaled Bahgat: Supervision. Marina R. Monir: Investigation, Methodology. M.H.A. Soliman: Data curation, Methodology, Investigation.

### **Declaration of Competing Interest**

The authors report no declarations of interest.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2021. 113218.

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