Spectrophotometric and Fluorometric Methods for the Determination of Fe(III) Ions in Water and Pharmaceutical Samples

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ABSTRACT: Chemical sensors based on mesoporous silica nanotubes (MSNTs) for the quick detection of Fe(III) ions have been developed. The nanotubes’ surface was chemically modified with phenolic groups by reaction of the silanol from the silica nanotubes surface with 3-aminopropyltriethoxysilane followed by reaction with 3-formylsalicylic acid (3-fsa) or 5-formylsalicylic acid (5-fsa) to produce the novel nanosensors. The color of the resultant 3-fsa-MSNT and 5-fsa-MSNT sensors changes once meeting a very low concentration of Fe(III) ions. Color changes can be seen by the naked eye and tracked with a smartphone or fluorometric or spectrophotometric techniques. Many experimental studies have been conducted to find out the optimum conditions for colorimetric and fluorometric determining of the Fe(III) ions by the two novel sensors. The response time, for the two sensors, that is necessary to achieve a steady spectroscopic signal was less than 15 s. The suggested methods were validated in terms of the lowest limit of detection (LOD), the lowest limit of quantification (LOQ), linearity, and precision according to International Conference on Harmonization (ICH) guidelines. The lowest limit of detection that was obtained from the spectrophotometric technique was 18 ppb for Fe(III) ions. In addition, the results showed that the two sensors can be used eight times after recycling using 0.1 M EDTA as eluent with high efficiency (90%). As a result, the two sensors were successfully used to determine Fe(III) in a variety of real samples (tap water, river water, seawater, and pharmaceutical samples) with great sensitivity and selectivity.

INTRODUCTION

Iron is the fourth most prevalent element in the earth’s crust, and it is widely spread throughout the ecosystem. It is most common in oxidation states II and III. Fe(II) and Fe(III) have different bioavailability and metabolism. The Fe(III) ion is a critical metal center in catalysis and biology, as well as in biotechnology. An adequate amount of Fe(III) intake prevents certain illnesses, for example, liver and pancreatic uptake. Once the concentration of the Fe(III) ions surpasses the capability of the organisms, they become toxic, although they can be detoxified via Strophariaceae. As a result, Fe(III) detection or sensing is critical for biological and environmental issues.

Many traditional analytical techniques were used in Fe determination, e.g., ICP-AES method, ion-selective membrane potentiometric sensor, flame atomic absorption spectrometry, and the combination of ultraviolet detection and capillary electrophoresis method. Also, UV–vis detection and micro-column ion chromatography, as well as atomic absorption spectrometry after solid-phase extraction, were also reported. When compared to alternative techniques like luminescence spectroscopy, these procedures are costly, are time-consuming, and need pretreatment or preconcentration.

It is worth mentioning that most power plants include a basic laboratory with low-cost devices like spectrophotometers. While spectrophotometric techniques are recognized for being uncomplicated, affordable, and quick methods of analysis, they typically require the selectivity and sensitivity needed for low-concentration analyte detection. However, combining them with a microextraction method with a high preconcentration factor can improve their sensitivity. Multivariate calibration approaches, for example, partial least squares (PLS) regression, principal component regression (PCR), and artificial neural networks, can help increase selectivity.

In the solid state, formylsalicylic acid derivatives have been demonstrated to form stable metal complexes with various metal ions. It was also found that the salicylic acid derivatives were more sensitive toward Fe(III) ions than other organic compounds containing the phenolic group. In pure and mixed solvents, Orabi studied the absorption spectra of 3-formylsalicylic acid and 5-formylsalicylic acid. He also used spectrophotometry to investigate the complex formation between the two formylsalicylic acids with the Fe(III) ions in a solution. The stoichiometric ratios of the two systems were
calculated using the slope-ratio, continuous variation, and mole-ratio approaches, all of which revealed a 1:1 type of complex. The 3-fsa and 5-fsa compounds have been immobilized on the surface of silica gel containing the amino group. The extraction of Fe(III) from the resultant materials was examined, and the exchange capacity was found to be 0.95–0.96 mmol g−1. However, there is no one using the immobilized formylsalicylic acids in the determination of Fe(III) using spectrophotometric and fluorometric methods.

In this work, a facile and highly efficient strategy to prepare smart nanosensors based on the mesoporous silica nanotubes has been done. First, the mesoporous silica nanotubes were prepared by using nickel-hydrazine complex nanorods as a hard template. Second, the MSNTs were immobilized by 3-amino-propyltriethoxysilane. Third, the formyl salicylic acids were bonded chemically with 3-APTES@MSNTs. Fourth, the formed 3-fsa-MSNT and 5-fsa-MSNT sensors were found to have high sensitivity and selectivity for the determination of Fe(III). Fifth, the determination process can be tracked by the naked eye, a smartphone, or fluorometric and UV–vis spectrophotometric techniques. Sixth, the smart sensors were used for determining the Fe(III) in tap water, river water, seawater, and pharmaceutical samples.

### EXPERIMENTAL SECTION

#### Preparation of the 3-Formylsalicylic Acid (3-fsa) and 5-Formylsalicylic Acid (5-fsa).

The 3-fsa and 5-fsa were synthesized according to the literature. The purity was analyzed by CHNS elemental analyses—CH (3-fsa): C, 57.86; H, 3.66, and CH (5-fsa): C, 57.89; H, 3.61—as they are consistent with the C₈H₆O₄ molecular formula of both (molecular wt. 166.13), which required C, 57.84; H, 3.64%. The 3-fsa and 5-fsa were analyzed by using 1H and 13C NMR spectroscopy. The data of the 3-fsa were as follows: 1H NMR (300 MHz, DMSO-d₆): δ 7.30 (t, H, Ben-H), 7.95 (d, H, Ben-H), 8.38 (d, H, Ben-H), 10.19 (s, H, Ben-CHO), 12.04 (s, H, Ben-COOH), 12.15 (s, H, Ben-OH); 13C NMR (100 MHz, CDCl₃): δ 188.0 (CHO), 171.8 (COOH), 162.9 (Ben, OH), 137.8 (Ben, CHO), 137.5 (Ben, CH), 136.5 (Ben, CH), 121.7 (Ben, CH), 113.8 (Ben, COOH). The data of the 5-fsa were as follows: 1H NMR (300 MHz, DMSO-d₆): δ 7.21 (d, H, Ben-H), 7.84 (s, H, Ben-H), 8.05 (d, H, Ben-H), 9.88 (s, H, Ben-CHO), 12.04 (s, H, Ben-COOH), 15.2 (s, H, Ben-OH); 13C NMR (100 MHz, CDCl₃): δ 191.0 (CHO), 171.8 (COOH), 168.0 (Ben, OH), 129.4 (Ben, CHO), 137.9 (Ben, CH), 131.6 (Ben, CH), 118.4 (Ben, CH), 129.4 (Ben, COOH).

#### Synthesis of MSNT-Bound Amines (3-APTES@MSNTs)

Into a round-bottomed flask, 1.0 g of the grinded MSNTs was transferred. Then, 50 mL of anhydrous toluene (Sigma-Aldrich) was added followed by 3 mL of 3-amino-propyltriethoxysilane (3-APTES) (Sigma-Aldrich Co. Ltd., Dorset, United Kingdom) and refluxed overnight. The 3-APTES@MSNTs were filtered off; washed with ethanol, diethyl ether, and toluene; and then dried for 6 h at 60 °C.

#### Synthesis of MSNT-Bound Formylsalicylic Acid Sensors (3-fsa-MSNT and 5-fsa-MSNT Sensors)

For the synthesis of MSNT-bound formylsalicylic acid sensors (3-fsa-MSNT and 5-fsa-MSNT sensors), 1.0 g of grinded 3-APTES@MSNTs was added to the solution after 0.3 g of 3- or 5-formylsalicylic acid was dissolved in 50 mL of anhydrous toluene by heating. The mixture solution was refluxed for 6 h, left to cool, and filtered off. The precipitate was washed with diethyl ether, ethanol, and toluene and dried at 80 °C for 5 h under a vacuum. Scheme 1 shows the synthesis approach to the MSNT-immobilized formylsalicylic acid phases.

#### Determination of the Fe(III) Ions in the Real Samples

The suggested method was applied to determine the Fe(III) ions in water samples collected from different sources, as shown in Table 5. One drop was added from the 0.1 M HCl solution to 50 mL of the water samples after they were filtered using a 0.45 μm Super filter preceding the test. Then, they were spiked with different Fe(III) ions concentrations (25, 50, and 75 ppb). Also, the planned method was applied to determine the Fe(III) ions in the pharmaceutical sample (dietary supplement). Ten irolamin capsules were added to 50 mL of HNO₃ 50% (v/v) after removal of their caps. The solution was heated till it was nearly dry and transported to a 100 mL volumetric flask. The solution was made up to the mark, and then 1 mL was taken and diluted with the appropriate buffer in different 10 mL volumetric flasks. All the results of the determination by the 3-fsa-MSNT and 5-fsa-MSNT sensors were compared with results obtained using the ICP-OES technique.

### RESULTS AND DISCUSSION

#### Characterization of the 3-fsa-MSNT and 5-fsa-MSNT Sensors

The Fourier transform infrared (FTIR) spectra of the MSNT, 3-APTES@MSNT, 3-fsa-MSNT and 5-fsa-MSNT sensors were collected by using a Bruker Alpha(II) spectrometer (equipped with a diamond ATR crystal) and given in Figure S1. The OH bending vibration at 809 cm⁻¹ and the Si–O–Si asymmetric stretching vibration at 1067–1037 cm⁻¹ appeared in the four spectra. After the immobilization of the 3-APTES, a new band at 2941–2929 cm⁻¹ that signified C–H stretching vibration appeared in the spectrum of 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT samples. The presence of a new band at 1558–1565 cm⁻¹...
Figure 1. FE-SEM images of the (A) MSNT, (B) 3-APTES@MSNT, (C) 3-fsa-MSNT, and (D) 5-fsa-MSNT sensors.

Figure 2. HR-TEM images of the (A) MSNT, (B) 3-APTES@MSNT, (C) 3-fsa-MSNT, and (D) 5-fsa-MSNT sensors.
consistently with the bond (C=O) in the spectrum of 5-fsa-MSNT and 5-fsa-MSNT sensors shows that the formylsalicylic acids were covalently bonded to the 3-APTES@MSNTs through Schiff base bond formation. In addition, the NH2 bands that appeared in 3-APTES@MSNTs at 3160 and 3240 ppm were absent in the IR spectra of 3-fsa-MSNT and 5-fsa-MSNT sensors. The characteristic (C=O) band at 1639–1612 cm\(^{-1}\) in the 3-fsa-MSNT and 5-fsa-MSNT sensors was additional proof of the occurrence of a carboxyl group in their structures. The phenolic (OH) band of the formylsalicylic acids appeared at 3377–3389 in the spectra of 3-fsa-MSNT and 5-fsa-MSNT sensors.

Because of its unique surface functioning, biocompatibility, and hydrophilic design, the silica nanotube has gotten a lot of attention. It was previously synthesized with carefully regulated dimensions.\(^{21}\) In this paper, to synthesize mesoporous silica nanotubes and increase their surface area, the CATAB as a surfactant was used in its preparation. The structure of MSNT, 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensors was verified by the XRD analysis. The low-angle XRD patterns of the MSNT, 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensors were carried out using an XPERT PRO PANalytical (made in Netherlands). They displayed a shoulder peak at 2\(^0\) ≈ 1.55\(^0\) confirming the presence of ordered mesopores in the wall of the silica nanotubes, as shown in Figure S2A. The wide-angle XRD of the MSNT, 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT samples displayed a typical broad peak over the range 15–37\(^0\), as shown in Figure S2B. This can be attributed to the fact that the nanotubes’ wall was found to be made of amorphous silica. It appears that the MSNTs’ structure morphology was kept after the modification by 3-APTES and also after the condensation of the formylsalicylic acids with 3-APTES@MSNTs.

Figures 1 and 2 show the morphologies of the MSNTs, 3-APTES@MSNTs, 3-fsa-MSNTs, and 5-fsa-MSNTs by the FE-SEM (Hitachi S-4300) and HR-TEM (Tecnai G20, made in Netherlands). They speculated that the substance comprises nanotubes with a diameter of 32 nm. In addition, the MSNTs’ structure morphology was kept after the modification by 3-APTES and also after the reaction of the formylsalicylic acids with 3-APTES@MSNTs.

The nitrogen adsorption–desorption isotherm measurements of the MSNT, 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensors were performed at 77 K using a CHEMBET NOVA 3000-Quanta chrome instrument with a pore size and surface area analyzer. As shown from Figure 3A, all samples showed a type IV isotherm, which displays pore condensation with hysteresis loop at p/p0 = 0.4–1.0 relative pressure. In addition, the (BET) surface area of the MSNTs was 825.17 m\(^2\) g\(^{-1}\), which is higher than the surface area of the 3-APTES@MSNTs (660.13 m\(^2\) g\(^{-1}\)). The surface areas of the two sensors were slightly decreased than the surface area of the 3-APTES@MSNTs (618.87 and 602.75 m\(^2\) g\(^{-1}\) for the 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively). Consequently, the pore volume of the 3-APTES@MSNTs was 0.666 cm\(^3\) g\(^{-1}\), while the pore volumes of the 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensors were 0.532, 0.504, and 0.507, respectively. The decrease in surface areas and pore volumes of the 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensors can be attributed to the attaching of 3-APTES, 3-fsa, and 5-fsa molecules outside and inside the wall of the nanotube.

**UV–Vis Studies on the 3-fsa-MSNT and 5-fsa-MSNT Sensors.** To find out the ideal conditions for colorimetric and fluorometric determining of the Fe(III) ions by the 3-fsa-MSNT and 5-fsa-MSNT sensors, many experimental studies have been conducted.\(^{22}\) To determine the optimum pH, about 30 mg of each sensor was added to solutions containing 0.1 ppm Fe(III) ions (ferric nitrate nonahydrate [Fe(NO\(_3\)]\(_3\)·9H\(_2\)O) (98%, Merck)) and diverse pHs (pH 1–9). Figure S3 shows that the optimum pH was obtained at pH 4 and 2 for the 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively. These values were coincident with the pK\(_a\) and the optimum pH values for the complexation of the two acids with Fe(III) ions investigated by Orabi.\(^{16}\) The optimum amount of each 3-fsa-MSNT and 5-fsa-MSNT sensor for the detection of the Fe(III) ions was investigated. The absorbance of different solutions containing 0.1 ppm Fe(III) ions and different amounts of the 3-fsa-MSNT or 5-fsa-MSNT sensors from 10 to 70 mg at their optimum pHs was measured. Figure S4 shows that the absorbance of each solution rose gradually with the rise in the amount of each sensor and plateaued starting from 20 and 30 mg for 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively. Therefore, these working amounts (20 mg for the 3-fsa-MSNT sensor and 30 mg for the 5-fsa-MSNT sensor) were utilized for the next investigations.

The response time of reacting 0.1 ppm Fe(III) ions with 20 mg of the 3-fsa-MSNT sensor or 30 mg of the 5-fsa-MSNT sensor at their optimum pHs had been checked. It was found that the response time became constant after 10 s to achieve...
the steady-state response. Furthermore, 20 s was found to be the reaction time needed for determining the concentrations of Fe(III) ion lower than 0.02 ppm. The fast response of the 3-fsa-MSNT and 5-fsa-MSNT sensors may be attributed to using a nanomaterial having a high surface area (mesoporous silica nanotubes) as a scaffold.

The change in color and the absorption spectra of the reaction of the 3-fsa-MSNT and 5-fsa-MSNT sensors, at their optimum conditions, with different Fe(III) ion concentrations (from 0.0 to 2.0 ppm) are shown in Figure 4 and Scheme 2. It was observed that the absorbance signal at 378 and 495 nm for 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively, increased when the concentration of the Fe(III) ions increased, as shown in Figure 5. In general, the 3-fsa-MSNT sensor’s color changed from pale yellow to red, while the 5-fsa-MSNT sensor’s color switched to violet from pale yellow. The highest concentration of Fe(III) ions that can be determined was 1.3 and 2.0 ppm for the 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively. The calibration plots represented in Figure 6 showed that the Fe(III) ions can be determined over a wide range of concentrations (0.0–0.56 ppm by using the 3-fsa-MSNT sensor and 0.0–1.52 ppm by using the 5-fsa-MSNT sensor).

According to International Conference on Harmonization (ICH) guidelines, the figures of merit have been calculated and listed in Table 1. The calculated limits of detection (LODs) using the two sensors were very low (0.026 ppm by using the 3-fsa-MSNT sensor and 0.023 ppm by using the 5-fsa-MSNT sensor). Consequently, it is possible to determine ultra-traces of Fe(III) ions using the two sensors with high sensitivity better than other spectrophotometric methods as shown in Table 2. This may be attributed to the use of mesoporous silica nanotube nanomaterial as a carrier that boosted the sensitive property of the immobilized reagents (formylsalicylic acids), resulting in the high sensitivity of the 3-fsa-MSNT and 5-fsa-MSNT sensors.

It appears from Table 1 that the 5-fsa-MSNT sensor has a lower LOD than the 3-fsa-MSNT sensor, and this may be because the positions of the hydroxyl and carboxylic groups are farther from the formyl group in the 5-fsa-MSNT structure than in the 3-fsa-MSNT structure. This makes the hydroxylic and carboxylic groups in the 5-fsa-MSNTs directed to the solution and easily react with the Fe(III) ions.

Figure 4. The absorption spectra and color change of different Fe(III) ion concentrations with the 3-fsa-MSNT sensor at pH 4 (A) and with the 5-fsa-MSNT sensor at pH 2 (B).
groups of the formylsalicylic acids, while the formyl oxygen is not involved in the binding. The findings revealed a proportionate relationship between the Fe(III) concentration and emission intensity, meaning that as the concentration of the Fe(III) ions increased, the emission intensities of the two sensors declined (Figure 8).

The sequential addition of Fe(III) ions (0.0−2.5 ppm) diminished the fluorescence intensity of the 3-fsa-MSNT and 5-fsa-MSNT sensors (Figure 7). The fluorometric titrations were performed at optimum conditions to assess the detection limit for the Fe(III) ions. The correlation between the comparative fluorescence intensity of the 3-fsa-MSNT and 5-fsa-MSNT sensors was plotted against Fe(III) ion concentration at $\lambda_{em} = 490$ and 474 nm, respectively (Figure 8). The LOD and limit of quantification (LOQ) for sensing of Fe(III) ions were determined (Table 1). The linear curves of the two sensors indicated that Fe(III) ions could be detected with great sensitivity throughout a wide concentration range (Figure 9).

The results showed that the fluorometric method is more

Table 1. The Figure of Merits for the Determination of the Fe(III) Ions by the Spectrophotometric, Fluorometric, and Image Analysis Methods Using the 3-fsa-MSNT and 5-fsa-MSNT Sensors

| parameter                  | 3-fsa-MSNT sensor | 5-fsa-MSNT sensor |
|---------------------------|-------------------|-------------------|
| detection range (ppm)     |                   |                   |
| LOD (ppm)                 | 0.026             | 0.018             |
| LOQ (ppm)                 | 0.079             | 0.057             |
| slope                     | 1.709             | 0.577             |
| intercept                 | 1.045             | 0.139             |
| correlation coefficient ($R^2$) | 0.9973           | 0.0 9995          |

Table 2. A Comparison of Different Reagent Features Used in the Literature for Spectrophotometric Detection of Fe(III)

| sensor or reagent                          | linearity range (ppm) | LOD (ppb) | ref |
|--------------------------------------------|-----------------------|-----------|-----|
| quercetin                                  | 0.1−15                | 60        | 24  |
| morin                                      | 0.4−15                | 380       |     |
| $N,N$-dimethyl-p-phenylenediammonium dichloride | 0.1−0.5               | 5         | 25  |
| mixture of sulfosalic acid and 1,10-phenanthroline | 0.09−1.0             | 80        | 26  |
| 3,5,7,2′,4′-pentahydroxyflavone             | 0.008−0.027           | 0.11      | 27  |
| phenanthroline                             | 0.040−1.0             | 3.09      | 28  |
| ferron                                     | 0.01−0.1              | 10        | 29  |
| casein-capped gold nanoparticles           | 0.01−0.05             | 25        | 30  |
| 3-fsa-MSNT sensor                          | 0.0−0.56              | 26        | this|
| 5-fsa-MSNT sensor                          | 0.0−1.52              | 18        | work|

groups of the formylsalicylic acids, while the formyl oxygen is not involved in the binding. The findings revealed a proportionate relationship between the Fe(III) concentration and emission intensity, meaning that as the concentration of the Fe(III) ions increased, the emission intensities of the two sensors declined (Figure 8).

The sequential addition of Fe(III) ions (0.0−2.5 ppm) diminished the fluorescence intensity of the 3-fsa-MSNT and 5-fsa-MSNT sensors (Figure 7). The fluorometric titrations were performed at optimum conditions to assess the detection limit for the Fe(III) ions. The correlation between the comparative fluorescence intensity of the 3-fsa-MSNT and 5-fsa-MSNT sensors was plotted against Fe(III) ion concentration at $\lambda_{em} = 490$ and 474 nm, respectively (Figure 8). The LOD and limit of quantification (LOQ) for sensing of Fe(III) ions were determined (Table 1). The linear curves of the two sensors indicated that Fe(III) ions could be detected with great sensitivity throughout a wide concentration range (Figure 9). The results showed that the fluorometric method is more

Figure 5. Response curves of 3-fa-MSNT and 5-fsa-MSNT sensors with different Fe(III) ion concentrations at the wavelength of 378 nm and pH 4 for the 3-fsa-MSNT sensor (A) and 495 nm and pH 2 for the 5-fsa-MSNT sensor (B).

Figure 6. Calibration plots of the 3-fsa-MSNT sensor (A) and 5-fsa-MSNT sensor (B) with different Fe(III) concentrations were measured at absorbances of 378 and 495 nm, respectively.

Table 2. A Comparison of Different Reagent Features Used in the Literature for Spectrophotometric Detection of Fe(III)
sensitive than the UV−vis spectrophotometric method. Also, they showed that the 3-fsa-MSNT and 5-fsa-MSNT sensors have a relatively low limit of detection compared to other previously reported fluorometric sensors (Table 3).41−47

To analyze the interaction between the 3-fsa-MSNT and 5-fsa-MSNT sensors and the Fe(III) ions, the quenching constant ($K_{SV}$) was determined at 298 K from the Stern−Volmer equation ($F_0/F = 1 + K_{SV}[Q]$, where $[Q]$ is the Fe(III) concentration). It was found that the quenching constants were 3.538 and 4.6735 mg$^{-1}$ L for the 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively. Because of the dynamical quenching, these data show that Fe(III) ions have a high quenching capability.

**Digital Image Analysis.** The digital images of the colored 3-fsa-MSNT and 5-fsa-MSNT sensors taken by a Samsung Galaxy A71 smartphone camera after adding the Fe(III) ions, as already described above, were measured by the Just Color Picker Software (Scheme 2). All the pixels (column by column) of these color images were scanned to collect the RGB component intensities. These intensities can be expressed in absorbance using the equation $A = -\log(I/I_0)$,22,48 where $I_0$ and $I$ are the intensity values of the blue component for the blank and the sample with the 3-fsa-MSNT and 5-fsa-MSNT sensors, respectively. The blue component was chosen because it supplied the maximum color intensity, as shown in Figure 10. It was noticed that as the concentration of Fe(III) ions increased, so did the absorbance of the blue component of the 3-fsa-MSNT and 5-fsa-MSNT sensors. Using the ideal conditions stated above for the spectrophotometric approach, the linear concentration ranges of the Fe(III) ions with the 3-fsa-MSNT and 5-fsa-MSNT sensors were found (Figure 11). The LOD and the LOQ of this method were calculated and

Figure 7. Emission spectra for the 3-fsa-MSNT and 5-fsa-MSNT sensors with increasing concentrations of Fe(III) ions at $\lambda_{exc} = 400$.

Figure 8. Response curves from the reaction of 3-fsa-MSNT and 5-fsa-MSNT sensors with different Fe(III) ion concentrations at emission measured at $\lambda_{em} = 490$ nm for the 3-fsa-MSNT sensor (A) and at $\lambda_{em} = 474$ nm for the 5-fsa-MSNT sensor (B).

Figure 9. Calibration plots of the 3-fsa-MSNT sensor (A) and 5-fsa-MSNT sensor (B) with different Fe(III) concentrations measured at emission measured at $\lambda_{em} = 490$ and 474 nm, respectively.
listed in Table 1. The image analysis method showed relatively great sensitivity compared to the fluorometric and spectrophotometric methods.

**Selectivity 3-fsa-MSNT and 5-fsa-MSNT Sensors.** To discover the possibility of the 3-fsa-MSNT and 5-fsa-MSNT sensors for detection of ions, the responses of absorption spectroscopy and the fluorescence emission of the 3-fsa-MSNT and 5-fsa-MSNT sensors to various anions and cations were examined. Among the tested metal ions, both 3-fsa-MSNT and 5-fsa-MSNT sensors only show significant responses to Fe(III) ions. The existence of Fe(III) ions drastically increases the absorbance and decreases the fluorescence emission of the 3-fsa-MSNT and 5-fsa-MSNT sensors. The quenching of the 3-fsa-MSNT and 5-fsa-MSNT sensors maybe because of the selective reaction of the Fe(III) ions with the carboxylic and phenolic groups of the formyl salicylic acids as mentioned above.

Also, Fe$^{3+}$ (100 ppm), Mg$^{2+}$ (500 ppm), Ca$^{2+}$ (500 ppm), Ba$^{2+}$ (500 ppm), Co$^{2+}$ (200 ppm), Ni$^{2+}$ (200 ppm), Cu$^{2+}$ (50 ppm), Zn$^{2+}$ (100 ppm), Pb$^{2+}$ (100 ppm), Hg$^{2+}$ (100 ppm), Cd$^{2+}$ (100 ppm), Cl$^{-}$ (500 ppm), NO$_3^-$ (500 ppm), and SO$_4^{2-}$ (100 ppm) were used to test their influence on the determination of Fe(III) (0.2 ppm) by the two sensors. According to the results, no major interferences (more than 5%) from these ions were detected during the determination process (Table 4).

**Recycling of the 3-fsa-MSNT and 5-fsa-MSNT Sensors.** The reusability of the 3-fsa-MSNT and 5-fsa-MSNT sensors after sensing the Fe(III) has been tested. Many substances have been tested to be the best eluents, but EDTA was found as a perfect recycling reagent. This could be because of its great capacity to remove metal ions from complexes. The used 3-fsa-MSNT and 5-fsa-MSNT sensors can recover their functionality after stirring them with 0.1 M EDTA for 1 h. The recycled 3-fsa-MSNT and 5-fsa-MSNT sensors were exposed again to a solution of Fe(III) ions. This procedure was repeated eight times. The 3-fsa-MSNT and 5-fsa-MSNT sensors’ sensing efficiency was estimated from the equation ($A/A_o$)% during the detection of the Fe(III) ions in each recycle, where $A$ is the absorbance of 3-fsa-MSNT and 5-fsa-MSNT sensors after reusability and $A_o$ is the initial absorbance. The findings (Figure S5) showed that the 3-fsa-MSNT and 5-fsa-MSNT sensors kept their efficiency (90%) even after eight-time recycling.

**Determination of the Fe(III) Ions in the Real Sample.** As the 3-fsa-MSNT and 5-fsa-MSNT sensors have high selectivity and sensitivity, they were checked to determine the Fe(III) ions in the real samples (tap water, river water, seawater, and pharmaceutical sample). The spectrophotometric and fluorometric methods were selected to determine the Fe(III) ions in all samples as they were more sensitive. All the results of the determination by the 3-fsa-MSNT and 5-fsa-MSNT sensors were compared with those obtained using the ICP-OES technique. Table 5 shows that the recoveries of the Fe(III) ions were between 83 and 116%. The spiked Fe(III) ions can be recovered with high precision from these samples, although the real samples are complex and contain components that can be a conflict with calculations. This indicates that the proposed method can be used for the determination of the Fe(III) ions with high selectivity and sensitivity in the real samples.

**CONCLUSIONS**

In this work, novel chemical sensors based on mesoporous silica nanotubes have been used to detect Fe(III) ions in

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**Table 3. An Overview of the Literature-Reported Nanomaterial-Based Approaches for Fluorometric Detection of Fe(III)**

| fluorophore                                    | linearity range (ppm) | LOD (ppb) | ref |
|-----------------------------------------------|-----------------------|-----------|-----|
| SUMOF-7II                                     | 0.92−9.3              | 927       | 41  |
| MIL-53(Al)                                    | 0.168−11.2            | 50.3      | 42  |
| boron-doped carbon dots                       | 0.0−0.893             | 13.51     | 43  |
| carbon polymer dots                           | 0.011−0.558           | 5.58      | 44  |
| nitrogen-doped and amino acid functionalized grapheme quantum dots | 0.027−27.92 | 5.58  | 45  |
| nitrogen-doped graphene quantum dots          | 0.27−27.92            | 10,000    | 46  |
| Gd(III)−5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin | 0.027−5.58 | 5.47    | 47  |
| 3-fsa-MSNT sensor                             | 0.0−0.56              | 17.2      |     |
| 5-fsa-MSNT sensor                             | 0.0−1.52              | 9.4       |     |

**Figure 10.** Response curves using the smartphone of 3-fsa-MSNT and 5-fsa-MSNT sensors with different Fe(III) ion concentrations at pH 4 for the 3-fsa-MSNT sensor (A) and pH 2 for the 5-fsa-MSNT sensor (B).
aqueous media. The Fe(III) ions were determined with remarkable sensitivity by the 3-fsa-MSNT and 5-fsa-MSNT sensors that resulted. The time it took to reach a reliable signal was minimal (less than 15 s). The color of the resultant 3-fsa-MSNT and 5-fsa-MSNT sensors changed after meeting a very low concentration of Fe(III) ions. Color changes can be seen by the naked eye and tracked with a smartphone or fluorometric or spectrophotometric techniques. The suggested methods were validated in terms of LOD, LOQ, linearity, and precision according to ICH guidelines. The lowest limit of detection obtained from the spectrophotometric technique was 18 ppb for Fe(III) ions. In addition, the results showed that the two sensors can be used eight times after recycling using 0.1 M EDTA as eluent with high efficiency (90%). As a result, the two sensors were successfully used to determine Fe(III) in a variety of real samples (tap water, river water, seawater, and pharmaceutical samples) with great sensitivity and selectivity.

Table 4. The Tolerance Concentration for Interfering Matrix Species during Detection of [0.2 Ppm] Fe(III) Ions Using the 3-fsa-MSNT and 5-fsa-MSNT Sensors

| sensor       | specific pH | Fe(II) | Mg(II) | Ca(II) | Ba(II) | Co(II) | Ni(II) | Zn(II) | Cu(II) | Pb(II) | Hg(II) | Cd(II) | Cl− | NO3 | SO4 | tolerance limit for foreign ions (ppm) |
|--------------|-------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-----|-----|-----|--------------------------------------|
| 3-fsa-MSNTs  | 4           | 10     | 500    | 500    | 500    | 20     | 20     | 20     | 5      | 50     | 50     | 50    | 50  | 100| 200 |
| 5-fsa-MSNTs  | 2           | 10     | 500    | 500    | 500    | 20     | 20     | 20     | 10     | 50     | 50     | 50    | 50  | 100| 200 |

*aIon-sensing system with addition of masking agent of 0.1 M sodium citrate.

Table 5. The Fluorometric Method Results for the Determination of the Fe(III) Ions in the Tap Water, River Water, Sea Water, and Pharmaceutical Samples Using the 3-fsa-MSNT and 5-fsa-MSNT Sensors

| samples         | founda (ppb) | foundb (ppb) | SDa | RSD% | recovery (%) |
|-----------------|--------------|--------------|-----|------|--------------|
|                 | ICPOES       | 3-fsa-MSNT sensor | 5-fsa-MSNT sensor | 3-fsa-MSNT sensor | 5-fsa-MSNT sensor | 3-fsa-MSNT sensor | 5-fsa-MSNT sensor | 3-fsa-MSNT sensor | 5-fsa-MSNT sensor | sample source |
| tap water       |              |              |     |      |              |
| 25              | 31           | 32           | 31  | 0.0219| 0.0096       | 3.69            | 5.11            | 116         | 100          | Suez (Egypt) |
| 75              | 82           | 82           | 83  | 0.0212| 0.0092       | 3.77            | 9.32            | 100         | 114          |
| river water     |              |              |     |      |              |
| 25              | 67           | 66           | 68  | 0.0214| 0.0093       | 3.74            | 7.44            | 98          | 102          | Ismailia Canal (Egypt) |
| 75              | 118          | 117          | 117 | 0.0208| 0.0090       | 3.83            | 15.78           | 98          | 98           |
| sea water       |              |              |     |      |              |
| 25              | 31           | 31           | 32  | 0.0219| 0.0096       | 3.69            | 5.11            | 100         | 116          | Red Sea (Egypt) |
| 75              | 82           | 81           | 82  | 0.0212| 0.0092       | 3.77            | 9.17            | 86          | 100          |
| dietary supplement | 25         | 27           | 27  | 0.0219| 0.0096       | 3.68            | 4.90            | 100         | irolamin capsules |

*aAverage of three replicate determinations.

Figure 11. Calibration plots of the 3-fsa-MSNT sensor (A) and 5-fsa-MSNT sensor (B) with different Fe(III) concentrations were measured by the image analysis method.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05899.

Detailed procedure for the synthesis of the mesoporous silica nanotubes; the reaction between the 3-fsa-MSNT and 5-fsa-MSNT sensors with the Fe(III) ions; the image processing; FTIR spectra of the MSNT, 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensors; low-angle XRD patterns and wide-angle X-ray diffraction patterns of the MSNT, 3-APTES@MSNT, 3-fsa-MSNT, and 5-fsa-MSNT sensor samples; the effect of pH on the complexation of the Fe(III) with 3-fsa-MSNT and 5-fsa-MSNT sensors at the maximum wavelengths of 378 and 495 nm, respectively; the effect of the amount of 3-fsa-MSNT and 5-fsa-MSNT sensors with 0.1 ppm Fe(III) ions on the signal response at the wavelengths of 378 and 495 nm, respectively; and reusability study of the 3-fsa-MSNT and 5-fsa-MSNT sensors.
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