**RESEARCH ARTICLE**

# *Terminalia chebula*: a novel natural product colorimetric sensor for $Fe^{2+}$ and $Fe^{3+}$ ions

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## Abstract

Natural product like *Terminalia chebula* as $Fe^{2+}$ and $Fe^{3+}$ ions sensor was not reported in the literature till now. Herein, we first reported *Terminalia chebula* (*T. chebula*), a natural product used in Ayurveda, as a highly sensitive, simple, and cost-effective colorimetric sensor for the detection of $Fe^{2+}$ and $Fe^{3+}$ ions. *Terminalia chebula* showed a selective colorimetric sensing ability for iron (2+/3+) by changing color from green and pale yellow to blue, having limit of detection level of 43.7 μM and 60.8 μM for $Fe^{2+}$ and $Fe^{3+}$ ions, respectively. The concentration-dependent colorimetric determination of iron (2+/3+) was carried out, and the color change to distinguish between different concentrations was excellent. Using High Performance Liquid Chromatography, the fraction having sensing ability was isolated and purified. From the mass spectra of the purified fraction, it was concluded that, the major component responsible for the sensing ability was tri-*O*-galloyl-*β*-D-glucose. This chemosensor could be used to detect and quantify $Fe^{2+}$ and $Fe^{3+}$ in water samples, which is particularly a useful tool.

**Keywords:** *Terminalia chebula*, Iron sensing, Chemosensor, Colorimetric sensor

## Introduction

Detection and estimation of transition metal ions are extremely important in chemical, biological, and environmental sciences. Iron is one of the most important transition metal ions in living organisms; it is a key transition metal ion in the electron transport process, oxygen transport, and storage in higher organisms. Also, it plays an important role in different enzymes like catalase, peroxidase, superoxide dismutase, etc. by controlling reactive oxygen species generation (You et al. 2015; de Silva 2000; Jiang and Guo 2004). Therefore, regulation and maintenance of iron level in our body is very crucial; because both deficiency and excessive iron uptake can cause a number of disorders like anemia, hemochromatosis, etc. It was reported that iron shortage can lead to heart failure and diabetes (Tkaczyszyn et al. 2018; Madhu et al. 2017). On the other hand, excessive iron can cause disruption of blood vessels, inducing bloody vomitus/stools, liver and kidney failure, and even cause death (https://www.healthline.com/health/iron-poisoning; https://www.ncbi.nlm.nih.gov/books/NBK548214/). World Health Organization (WHO) recommended maximum allowed level of iron in drinking water is 0.3 mg/L, at this concentration drinking water sometimes acquires a reddish-brown color (http://www.idph.state.il.us/envhealth/factsheets/ironFS.htm). In water, iron is mostly found in two forms: soluble ferrous iron ($Fe^{2+}$) and less soluble ferric iron ($Fe^{3+}$) (http://www.saskh2o.ca/). In the northern parts of West Bengal, especially, in Alipurduar, Jalpaiguri, Cooch Behar, and Darjeeling districts, ground water is heavily contaminated with iron, which is one of the major contaminants of domestic and agricultural water resources (Rajmohan and Prathapar 2016). Iron can also be found in surface water due to natural deposits, industrial wastes, iron ore refining, and corrosion of iron-containing metal cans. As a result, a cost-effective,

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simple, highly sensitive, and selective iron chemosensor for households would be beneficial for commoners.

Many analytical techniques, including atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), inductively coupled plasma-mass spectroscopy (ICP-MS), electrochemical methods, and others, are being employed for the detection and quantitative estimation of iron (Welna et al. 2011; Hu 2011; Alberti et al. 2020). All of these methods are costly, time-consuming, and labor-intensive. These methods necessitate a well-trained analyst, pre-treatment of water samples, and in some cases, a specialized laboratory facility as well. Colorimetric detection using ion sensors, on the other hand, can be used to monitor target ions even with the naked eye. As a result, ion sensors have gained a lot of interest when it comes to detecting metal ions such as $Fe^{2+}$ and $Fe^{3+}$. Still, the iron sensors are not very easily accessible to the common people. Commercially available ion sensors are costly and chemically synthesized compounds are used as sensing materials, which may cause hazards to the environment if not disposed properly. That is why most of the ion sensors are not available for the general public. And previously, some natural products have been utilized in sensing applications (Pinyou et al. 2010; Saithongdee et al. 2014; Ballesteros et al. 2021). So, there are previous reports of natural products being utilized as a sensor.

In this article, a natural product has been used to solve the problems. We have used *Terminalia chebula (T. chebula)*, which is a traditional medicine belonging to the genus *Terminalia*, family Combretaceae, and is mostly found in south east Asia (Kumar 2020). The mature dried fruit of *T. chebula* is an important Indian herb with homeostatic, antitussive, laxative, diuretic, and cardiotonic properties, widely used extensively in the indigenous system of medicine (ayurvedic) (Bag et al. 2013; Upadhyay et al. 2014; Afshari et al. 2016). *Terminalia chebula* has been reported to contain gallic acid, ellagic acid, tannic acid, ethyl gallate, chebulic acid, chebulagic acid, corilagin, mannitol, ascorbic acid, and other compounds (Grover and Bala 1992; Sheng et al. 2018; Chang and Lin 2012). *Terminalia chebula*, contains 32% tannin, which can bind to iron very efficiently (Bag et al. 2013; Fu and Chen 2019; South and Miller 1998; Sarkar et al. 2012). In this regard, *T. chebula* can be evaluated to be an excellent eco-friendly, easily available, and inexpensive colorimetric sensor for the detection of iron in the aqueous phase with a user-friendly method.

## Experiments
### Preparation of *Terminalia chebula* extract
Dried ripen fruits of *T. chebula* were collected from the local market and authenticated by a professor from the Botany Department, Cooch Behar Panchanan Barma University (CBPBU). Appropriate *T. chebula* fruits (those which are well ripened, not moldy or rotten and free from any kind of insect attack) were selected, then seeds were removed, grounded to coarse powder using a domestic grinder. The powder thus obtained was stored in vacuum desiccators for subsequent use.

At first 1.5 gm of *T. chebula* powder was weighed and, taken in a conical flask containing 100 mL of double distilled water. The mix was kept in the conical flask for 24 h at room temperature and filtered. The filtrate thus obtained was preserved in the refrigerator for further use.

### Characterization
The *T. chebula* raw extract was initially column chromatographed using RP-HPLC (reverse phase high performance liquid chromatography) [Shimadzu SPD-20A UV detector and Shimadzu LC-20AR series pumping system (Shimadzu Corporation, Kyoto, Japan) with Eclipse XDB-C18 (reverse phase) and C18 monochromatic column, respectively], then the active ingredient was identified by treatment of $Fe^{3+}$ and $Fe^{2+}$ solutions to different collected fractions from HPLC. The active ingredient of the raw extract for iron sensing was further purified by preparative RP-HPLC with MeOH as mobile phase (isocratic system) on a C18 column ($25 \times 250$ mm), at UV detector: 292 nm, flow rate: 1.0 ml/min with a runtime of 20 min. Subsequently, the purity of the isolated product was checked using the analytical column SB C18-column (ZORBAX SB-C18, $4.6 \times 250$ mm, 5 µm, UV detector: 292 nm, flow rate: 1.1 ml/min, tR = 2.5 min). Then the chemical structure of the isolated fraction was characterized and confirmed by FAB-MS spectroscopy (Fast Atom Bombardment Mass Spectrometry) (the Korea Basic Science Institute at Daegu, S. Korea) and was found to be $m/z$ 637.9 $[M+H]^+$, and calculated $m/z$ 636.1 for $C_{27}H_{24}O_{18}$.

### UV–Vis titration measurements of *Terminalia chebula* extract with $Fe^{2+}$ and $Fe^{3+}$
For the UV–Vis titration, the prepared extract was diluted with double distilled water in a ratio of 1:250. The desired concentrations of $FeSO_4$ and $FeCl_3$ solutions were prepared for the colorimetric estimation. 2.4 mL of the prepared *T. chebula* extract was taken and 100–1000 µL of the metal ion solution (final concentration $1.44 \times 10^{-5}$–$1.44 \times 10^{-4}$ M) was added to it. After mixing and keeping solutions for 5 min in the dark, UV–Vis spectra were measured at room temperature (You et al. 2015; Kang and Kim 2018).

## Competitive experiments

For this experiment, the extract was diluted in the ratio of 5:250 and metal ion solutions of $NiCl_2$, $CoCl_2$, $HgCl_2$, $CdCl_2$, $Al_2(SO_4)_3$, $MnSO_4$, $Cr_2O_3$, $LaCl_3$, $MgCl_2$, $CaCl_2$, NaCl, KCl were prepared in distilled water (0.004 M). 1 mL of each metal solution was taken in a test tube containing 1 mL 0.004 M of $Fe^{2+}$ or $Fe^{3+}$ solution, followed by addition of 1 mL of the extract. After mixing and keeping for 5 min in dark, the UV–visible spectra of each mixture were taken at room temperature (Gao et al. 2017).

## Determination of $Fe^{2+}$ and $Fe^{3+}$ in water samples

UV–Vis spectra of water samples containing $Fe^{2+}$ and $Fe^{3+}$ were carried out by adding 1 mL of diluted (5:250) stock solution of *T. chebula* extract and 2 mL of sample solutions. Mixed homogenously, the solutions were allowed to stand for 5 min at room temperature before recording UV–visible spectra (You et al. 2015).

## Colorimetric determination of iron concentration by naked eye

A colorimetric technique was utilized to determine the content of $Fe^{2+}$ and $Fe^{3+}$ in aqueous solution by the naked eye. Different concentrations of iron solutions (10, 50, and 100 ppm) were prepared, then 200 µL of *T. chebula* raw extract was added to each solution, to a final volume of 2.5 mL. Color changes were observed after 5 min of waiting. The same technique was performed using a paper strip, at first 200 µL *T. chebula* raw extract was added onto the strip and dried in the oven. Following that, $Fe^{2+}$ and $Fe^{3+}$ solution (50 µL) separately of various concentrations (10, 50, and 100 ppm) were added to the strips, dried and the colors for different concentrations of $Fe^{2+}$ and $Fe^{3+}$ were monitored.

## Results and discussions

### Characterization using HPLC and mass spectroscopy methods

To study the $Fe^{2+}$ and $Fe^{3+}$ active ingredient of *T. chebula*, water extract was purified using RP-HPLC. Initially, the extract was analyzed using preparative RP-HPLC and, out of all the fractions, only one fraction showed activity toward $Fe^{2+}$ or $Fe^{3+}$ ions. The single peak at 2.5 min was isolated and lyophilized [Fig. 1(inset)]. Subsequently, the mass spectrum of the isolated compound showed a *m/z* peak at 637.9 $(M+H)^+$, indicating the presence of tri-*O*-galloyl-β-D-glucose as a major component responsible for the iron detection (Fig. 1) (https://pubchem.ncbi.nlm. nih.gov/compound/1_3_6-Tri-O-galloyl-beta-D-gluco se; https://pubchem.ncbi.nlm.nih.gov/compound/1_ 2_3-Tri-O-galloyl-beta-D-glucose). This conclusion is based on previous report that tri-*O*-galloyl-β-D-glucose is one of the major components of *T. chebula.* And the
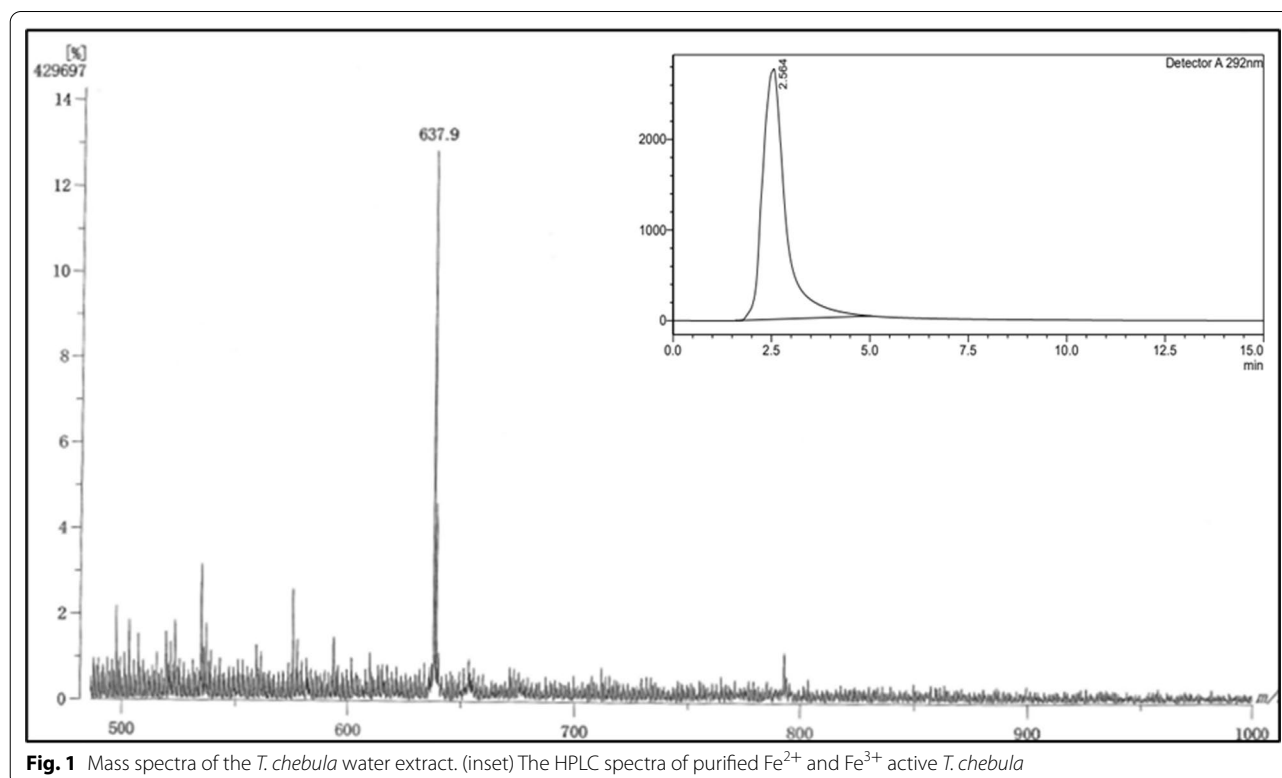


**Fig. 1** Mass spectra of the *T. chebula* water extract. (inset) The HPLC spectra of purified $Fe^{2+}$ and $Fe^{3+}$ active *T. chebula*

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mass spectral data also supported this, as the *m/z* value of 637.9 $(M+H)^+$ only matches with the tri-*O*-galloyl-*β*-D-glucose (Bag et al. 2013; Fu and Chen 2019; South and Miller 1998; Sarkar et al. 2012).

## Sensing property toward $Fe^{2+}$ and $Fe^{3+}$

The selectivity of the sensor for the detection of $Fe^{2+}$ and $Fe^{3+}$ was investigated with different metal ions such as $Co^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $Hg^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $Ca^{2+}$, $Al^{3+}$, $Mn^{2+}$, $La^{3+}$, $Cd^{2+}$. The absorption spectra of the extract with different cations are shown in Fig. 2. Colors of iron with the extract changed instantly from faint green to deep blue and pale yellow to blue for $Fe^{2+}$ and $Fe^{3+}$ ions, respectively, and there were no detectable color changes of other metal ions with the extract ($Cr^{3+}$ and $Mg^{2+}$

showed very faint yellow color but in comparison to $Fe^{3+}$ or $Fe^{2+}$, it is negligible and did not interfere in iron detection). These findings suggested that *T. chebula* extract could be used as a colorimetric chemosensor for $Fe^{2+}$ and $Fe^{3+}$ ions with high selectivity in aqueous medium.

UV–Vis titration was used to investigate the sensing characteristics of the extract with $Fe^{2+}$ and $Fe^{3+}$ (Fig. 3). An aqueous solution of *T. chebula* extract showed absorbance peaks at 215 and 274 nm. On successive addition of $Fe^{2+}$ aliquots, the absorbance peak of *T. chebula* decreased and a new absorption peak appeared at 576 nm that increased with the gradual addition of ferrous ion ($Fe^{+2}$) solution with an isosbestic point at 308 nm. In the presence of ferric ion ($Fe^{+3}$), characteristic new absorption peak appeared at 576 nm, and that
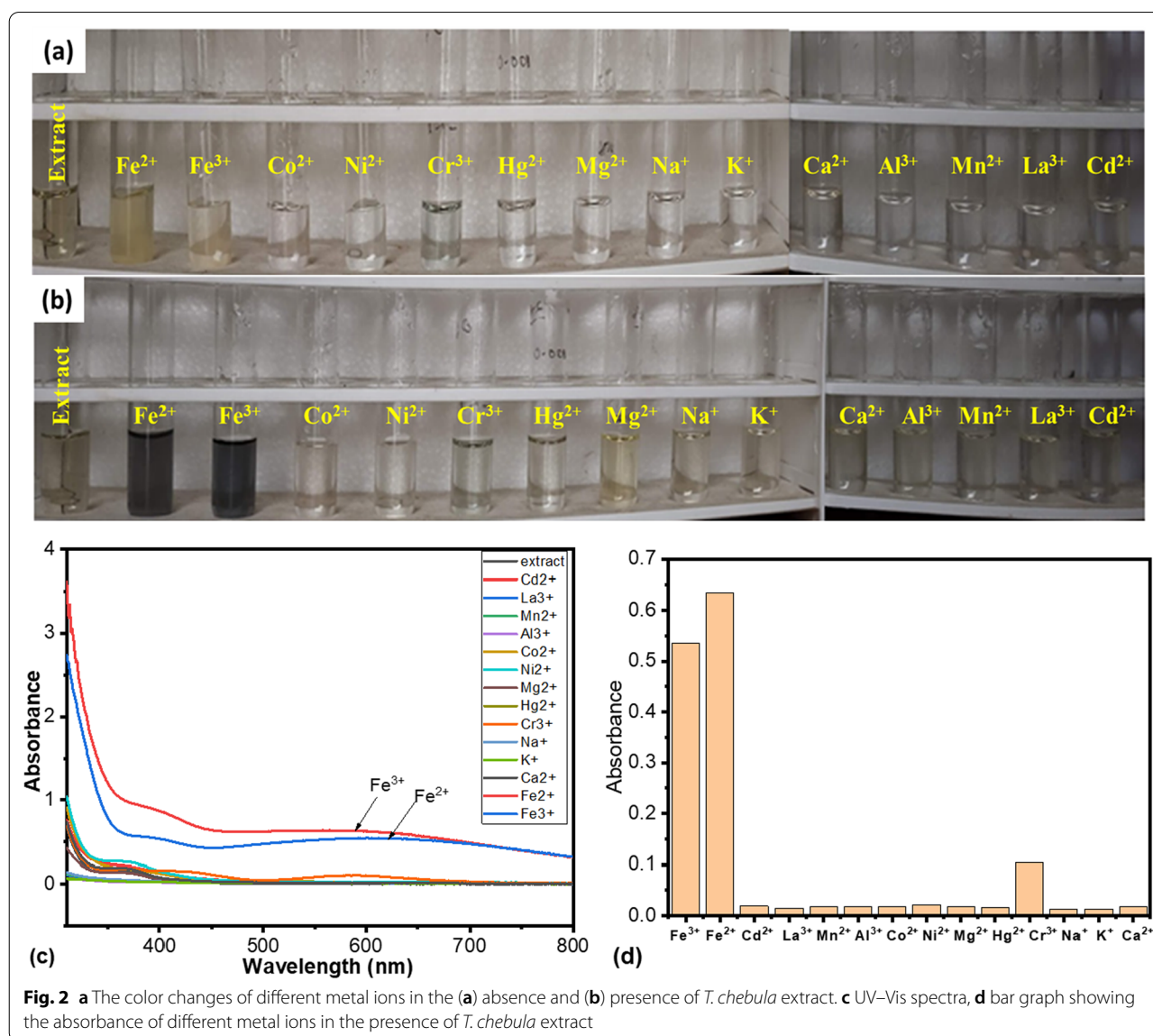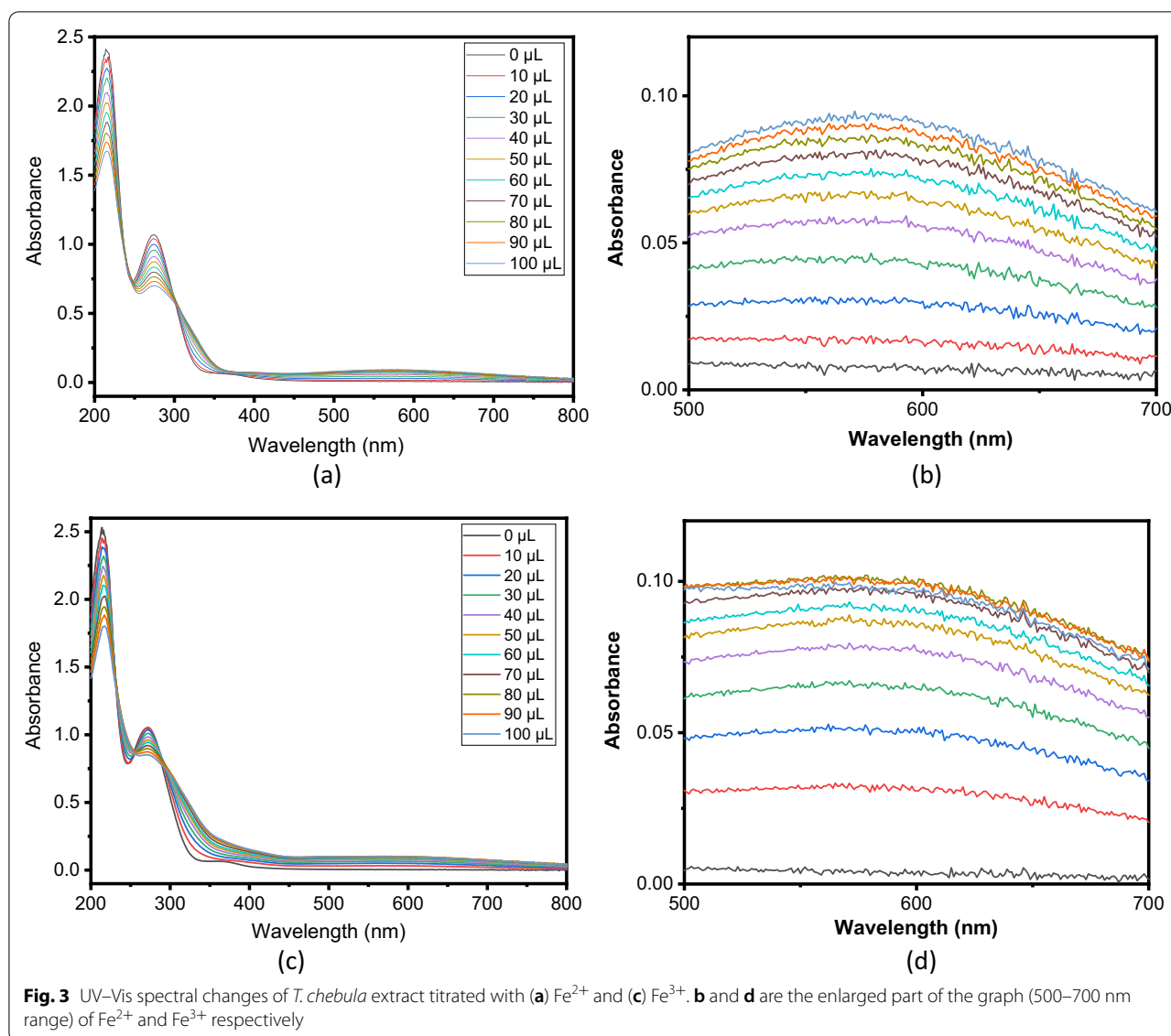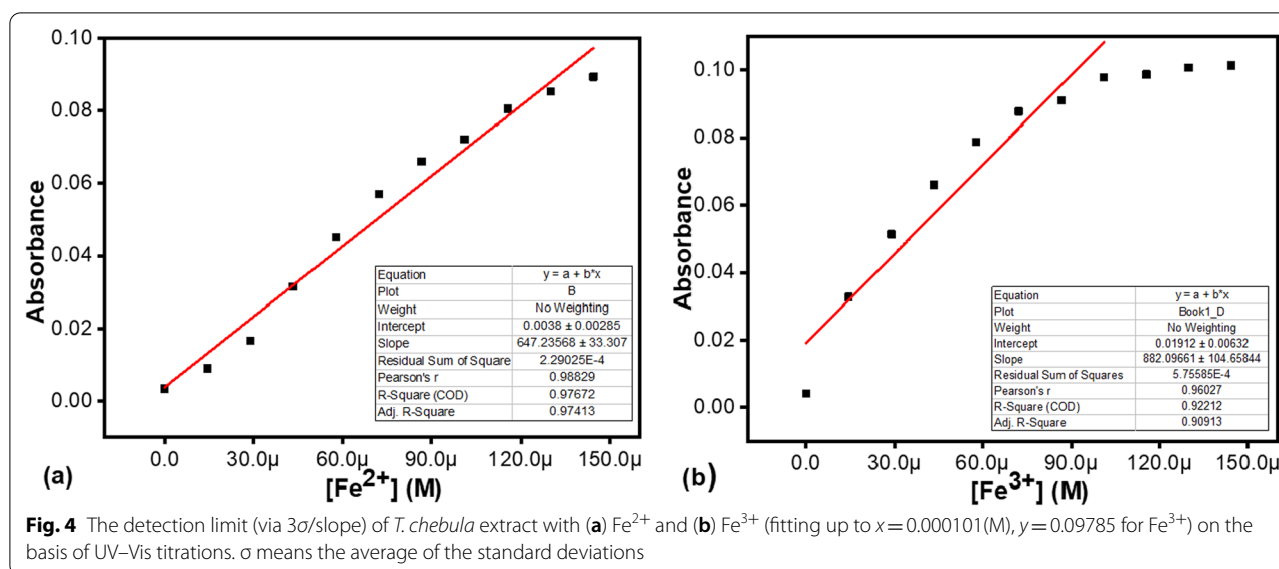


**Fig. 2 a** The color changes of different metal ions in the (**a**) absence and (**b**) presence of *T. chebula* extract. **c** UV–Vis spectra, **d** bar graph showing the absorbance of different metal ions in the presence of *T. chebula* extract

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**Fig. 3** UV–Vis spectral changes of *T. chebula* extract titrated with (**a**) $Fe^{2+}$ and (**c**) $Fe^{3+}$. **b** and **d** are the enlarged part of the graph (500–700 nm range) of $Fe^{2+}$ and $Fe^{3+}$ respectively

increased with the gradual addition of $Fe^{+3}$ aliquots, $Fe^{+3}$ with *T. chebula* extract exhibited three isosbestic points at 232 nm, 255 nm, and 289 nm. The absorption peaks at 576 nm (characteristics of $Fe^{+2}$ and $Fe^{+3}$ complex with *T. chebula* extract) have molar extinction coefficients of $6.2 \times 10^2$ $M^{-1}$ $cm^{-1}$ and $2.2 \times 10^3$ $M^{-1}$ $cm^{-1}$ respectively, and these values are too large for d-d transitions. Thus, the new peak could be attributed to a metal-to-ligand charge transfer (MLCT), which is responsible for the intense color of the solutions (You et al. 2015). By using $3\sigma$/slope, the detection limit of $Fe^{2+}$ and $Fe^{3+}$ with *T. chebula* extract was determined and the values are 43.7 μM and 60.8 μM respectively (Fig. 4) (Kang and Kim 2018; Tsui et al. 2012). From Fig. 4, correlation coefficient (*R*)

values were found to be 0.988292 and 0.91661, respectively, for $Fe^{2+}$ and $Fe^{3+}$, which indicates both variables move in the same direction. The $P(T <= t)$ value for one-tail and two-tail was found to be 0.0163% and 0.0327% for $Fe^{2+}$ and 0.000431% and 0.000863% for $Fe^{3+}$, which are lower than 5%. The UV–Visible competitive experiments with $Fe^{2+}$ and $Fe^{3+}$ in the presence of other transition and common group metal ions were conducted to examine the selectivity for $Fe^{2+}$ and $Fe^{3+}$ as shown in Additional file 1: Fig. S1. The detection of both $Fe^{2+}$ and $Fe^{3+}$ with the naked eye was unaffected in presence of competing metal ions. In this experiment, the total concentration of the metal ions (iron and other competitive ions) was maintained constant in each test tube, the color

**Fig. 4** The detection limit (via $3\sigma$/slope) of *T. chebula* extract with (**a**) $Fe^{2+}$ and (**b**) $Fe^{3+}$ (fitting up to $x = 0.000101(M)$, $y = 0.09785$ for $Fe^{3+}$) on the basis of UV–Vis titrations. $\sigma$ means the average of the standard deviations

intensity in this experiment decreased in the presence of competing ions. In the absence of other metal ions, just iron was present in its entirety. However, when other metals are present, the concentration of iron was only 50% of the total ion concentration. This is what caused the color intensity to change. These findings suggest that the extract may function as a specific chromogenic chemosensor for iron ions. We have conducted experiments to monitor the effect of pH on the iron sensing properties of *T. chebula* extract over a wide range of pH from 2 to 10. The absorbance at 576 nm increased considerably with increasing pH from 2 to 10, as shown in Additional file 1: Fig. S2 (Ahmed et al. 2020), which can be explained by the presence of acidic hydrogen in tri-*O*-galloyl-*β*-D-glucose. As with the increase in pH value, the hydrogen abstraction from the phenolic -OH group will enhance the concentration of the deprotonated form of tri-*O*-galloyl-*β*-D-glucose, which will increase the rate of complexation with $Fe^{2+}$ and $Fe^{3+}$, resulting an increase in the absorbance values. The iron sensing effect of *T. chebula* in the presence of $Fe^{2+}$ and $Fe^{3+}$ ions were tested in the temperature range of 20–60 °C. Interestingly, the absorbance at 576 nm increases with increasing temperature (Additional file 1: Fig. S2) which may be due to the kinetic effect. The rate of complex formation increases with increasing temperature. In order to check the applicability of *T. chebula* in extract for the detection of $Fe^{2+}$ and $Fe^{3+}$ in unknown water samples, calibration curves for both $Fe^{2+}$ and $Fe^{3+}$ ions were drawn. In Additional file 1: Fig. S3 the calibration curve showed a straight line with the suitable recoveries and permissible R.S.D. (Relative Standard Deviation)

**Table 1** Determination of $Fe^{2+}$ and $Fe^{3+}$ in water samples

| Metal ion | Added (M) | Recovered (M) | Recovery (%) | R.S.D ($n=3$) (%) |
|---|---|---|---|---|
| $Fe^{2+}$ | 0 | 0 | | |
| | $1.50 \times 10^{-4}$ | $1.48 \times 10^{-4}$ | 98.66 | 1.71 |
| | $3.0 \times 10^{-4}$ | $2.97 \times 10^{-4}$ | 99 | 1.69 |
| $Fe^{3+}$ | 0 | 0 | | |
| | $1.50 \times 10^{-4}$ | $1.47 \times 10^{-4}$ | 98 | 1.84 |
| | $3.0 \times 10^{-4}$ | $2.95 \times 10^{-4}$ | 98.33 | 1.81 |

values (Table 1). The colorimetric assessment of iron concentration using only the naked eye produced excellent results. The color shift between the solutions can be seen very clearly in Fig. 5, and different levels of iron can be easily distinguished using the reported color which may be considered one of the major findings for iron sensing by the naked eye, in both solutions and paper strips (Whatman 41 filter paper strips) (Additional file 1: Fig. S4), thus, this will aid the common people in determining the iron content. Though naked eye detection is not a confirmatory result, yet it can give a qualitative idea. Previously, similar method of detection for iron and also other metals had been reported in the literature (Suresh et al. 2010; Wei et al. 2011; Sun et al. 2020), which proved that naked eye detection is also becoming a major tool for metal ion detection. Therefore, the naked eye detection can be treated as one of the secondary methods. These results warranted that *T. chebula* could be applied as a detector for iron in real water samples.
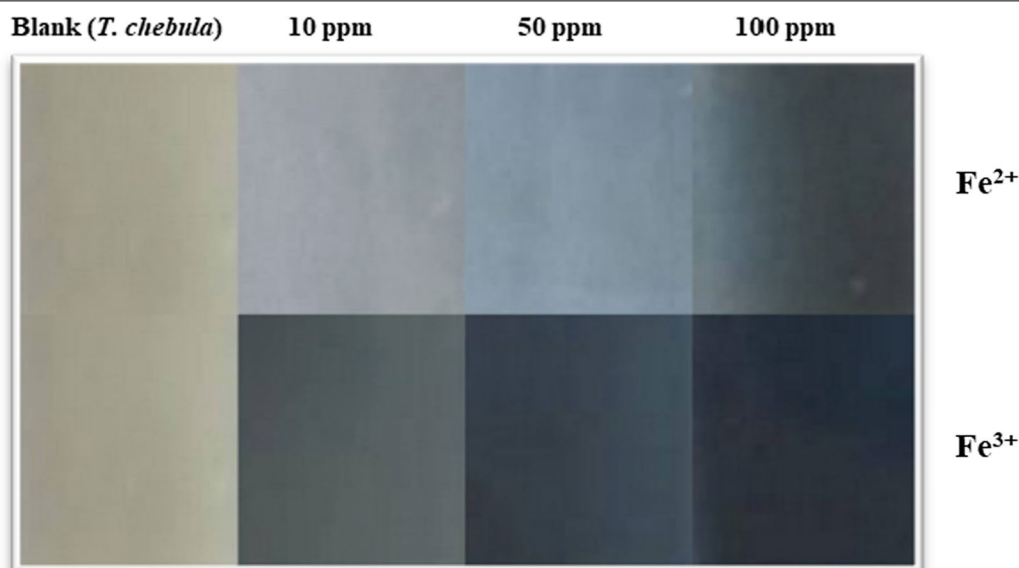
**Fig. 5** Colorimetric response of different concentrations of $Fe^{2+}$ and $Fe^{3+}$

## Conclusion

*Terminalia chebula* may be the simplest, most selective, efficient, and least expensive chemosensor for $Fe^{2+}$ and $Fe^{3+}$ in aqueous conditions, with excellent selectivity for both cations over relevant competing metal ions. The presence of iron was detected by the sensor changing color from a very light green ($Fe^{2+}$) and pale yellow ($Fe^{3+}$) to a blue color with a LOD limit of 43.7 μM and 60.8 μM towards $Fe^{2+}$ and $Fe^{3+}$, respectively. Furthermore, the sensor might be utilized to measure iron in real-world water samples. Most importantly, the concentration of iron can be measured quickly and simply by comparing it with the reported color, which is a significant result and very valuable for the layperson. As a result of the findings presented here, a novel approach for selective recognition of the most abundant transition metal ions ($Fe^{2+}$ and $Fe^{3+}$) in the presence of various common metal ions has been developed. Most importantly, this method can be used for the quantitative estimation of $Fe^{2+}$ and $Fe^{3+}$ in water samples and may be accessible to the masses for routine iron detection. Though we cannot quantify $Fe^{2+}$ and $Fe^{3+}$ in a mixture. But this method is novel in determining both the ground water and surface water iron content individually, as mostly in ground water iron present as $Fe^{2+}$ state, while in surface water iron present as $Fe^{3+}$ (Gülay et al. 2018). The process of turning this analytical approach into a practical and easy-to-use procedure is in progress. The mechanism responsible for this color change as well as the influence of other metal ions of the periodic table on the *T. chebula* extract will be studied further in the future.

## Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40543-022-00348-z.

**Additional file 1**. **Figure S1**: The colour changes $Fe^{2+}$ in presence of different metal ions in the (a) absence and (b) presence of T. chebula extract; The colour changes $Fe^{3+}$ in presence of different metal ions in the (c) absence and (d) presence of T. chebula extract; Bar graph showing the absorbance of T. chebula extract with (e) $Fe^{2+}$ and (f) $Fe^{3+}$ in presence of various metal ions. **Figure S2**: Absorbance of T. chebula extract with $Fe^{2+}$. and $Fe^{3+}$ at different (a) pH (b) temperature. **Figure S3**: The calibration curve (at 576 nm) of T. chebula extract upon the addition of (a) $Fe^{2+}$.and (b) $Fe^{3+}$. [$Fe^{2+}$] and [$Fe^{3+}$] = $2.29\times10^{-5}$ – $2.29\times10^{-3}$ M. **Figure S4**: Colorimetric response of $Fe^{3+}$ in paper.

### Author contributions

SS performed all the experiments; TJ performed the Mass spectra and HPLC; SS written the manuscript; GB, DD and JI reviewed and edited the manuscript; GB, DD and JI supervised the entire project. All authors read and approved the final manuscript.

### Data availability

Not applicable.

## Declarations

### Competing interests

The authors declare no competing financial interest.

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**References**
1,2,3-Tri-O-galloyl-beta-D-glucose|C27H24O18 - PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/1_2_3-Tri-O-galloyl-beta-D-glucose. Accessed 2 Mar 2022.

1,3,6-tri-O-galloyl-beta-D-glucose | C27H24O18 - PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/1_3_6-Tri-O-galloyl-beta-D-glucose. Accessed 27 Feb 2022.

Afshari AR, Sadeghnia HR, Mollazadeh H. A Review on Potential Mechanisms of *Terminalia chebula* in Alzheimer's Disease. Adv Pharmacol Sci. 2016;2016:1–14. https://doi.org/10.1155/2016/8964849.

Ahmed F, Kabir H, Xiong H. Dual colorimetric sensor for $Hg^{2+}/Pb^{2+}$ and an efficient catalyst based on silver nanoparticles mediating by the root extract of *Bistorta amplexicaulis*. Front Chem. 2020;8:591958. https://doi.org/10.3389/fchem.2020.591958.

Alberti G, Zanoni C, Magnaghi LR, Biesuz R. Low-cost, disposable colourimetric sensors for metal ions detection. J Anal Sci Technol. 2020;11:30. https://doi.org/10.1186/s40543-020-00221-x.

Bag A, Bhattacharyya SK, Chattopadhyay RR. The development of *Terminalia chebula* Retz. (Combretaceae) in clinical research. Asian Pac J Trop Biomed. 2013;3:244–52. https://doi.org/10.1016/S2221-1691(13)60059-3.

Ballesteros JI, Caleja-Ballesteros HJR, Villena MC. Digital image-based method for iron detection using green tea (*Camellia sinensis*) extract as natural colorimetric reagent. Microchem J. 2021;160:105652. https://doi.org/10.1016/j.microc.2020.105652.

Chang CL, Lin CS. Phytochemical composition, antioxidant activity, and neuroprotective effect of *Terminalia chebula* Retzius extracts. Evid Based Complement Alternat Med. 2012;2012:1–7. https://doi.org/10.1155/2012/125247.

de Silva A. Combining luminescence, coordination and electron transfer for signalling purposes. Coord Chem Rev. 2000;205:41–57. https://doi.org/10.1016/S0010-8545(00)00238-1.

Fu Z, Chen R. Study of complexes of tannic acid with Fe(III) and Fe(II). J Anal Methods Chem. 2019;2019:1–6. https://doi.org/10.1155/2019/3894571.

Gao Q, Ji L, Wang Q, et al. Colorimetric sensor for highly sensitive and selective detection of copper ion. Anal Methods. 2017;9:5094–100. https://doi.org/10.1039/C7AY01335C.

Grover IS, Bala S. Antimutagenic activity of Terminalia chebula (myroblan) in Salmonella typhimurium. Indian J Exp Biol. 1992;30:339–41.

Gülay A, Çekiç Y, Musovic S, et al. Diversity of Iron oxidizers in groundwater-fed rapid sand filters: evidence of Fe(II)-dependent growth by *Curvibacter* and *Undibacterium spp*. Front Microbiol. 2018;9:2808. https://doi.org/10.3389/fmicb.2018.02808.

Hu Q. Simultaneous separation and quantification of iron and transition species using LC-ICP-MS. Am J Anal Chem. 2011;02:675–82. https://doi.org/10.4236/ajac.2011.26077.

Iron Poisoning: Symptoms and Treatments. https://www.healthline.com/health/iron-poisoning. Accessed 11 Nov 2021

Iron in Drinking Water. http://www.idph.state.il.us/envhealth/factsheets/ironFS.htm. Accessed 11 Nov 2021.

Iron—LiverTox—NCBI Bookshelf. https://www.ncbi.nlm.nih.gov/books/NBK548214/. Accessed 11 Nov 2021.

Jiang P, Guo Z. Fluorescent detection of zinc in biological systems: recent development on the design of chemosensors and biosensors. Coord Chem Rev. 2004;248:205–29. https://doi.org/10.1016/j.cct.2003.10.013.

Kang JH, Kim C. Colorimetric detection of iron and fluorescence detection of zinc and cadmium by a chemosensor containing a bio-friendly octopamine. Photochem Photobiol Sci. 2018;17:442–52. https://doi.org/10.1039/C7PP00468K.

Kumar M (2020) Phytochemical and Pharmacological Profile of Terminalia chebula. Int J Pharmacogn Chin Med. https://doi.org/10.23880/ipcm-16000208.

Madhu SV, Raj A, Gupta S, et al. Effect of iron deficiency anemia and iron supplementation on HbA1c levels - Implications for diagnosis of prediabetes and diabetes mellitus in Asian Indians. Clin Chim Acta. 2017;468:225–9. https://doi.org/10.1016/j.cca.2016.10.003.

Pinyou P, Kradtap Hartwell S, Jakmunee J, et al. Flow injection determination of iron ions with green tea extracts as a natural chromogenic reagent. Anal Sci. 2010;26:619–23. https://doi.org/10.2116/analsci.26.619.

Rajmohan N, Prathapar SA. Occurrence and extent of arsenic, fluoride and iron contamination in groundwater in selected districts in eastern Ganges basin-a review. 2016; https://www.indianjournals.com/ijor.aspx?target=ijor:jag&volume=18&issue=4&article=002. Accessed 28 Sep 2022.

Saithongdee A, Praphairaksit N, Imyim A. Electrospun curcumin-loaded zein membrane for iron(III) ions sensing. Sens Actuators B Chem. 2014;202:935–40. https://doi.org/10.1016/j.snb.2014.06.036.

Sarkar R, Hazra B, Mandal N. Reducing power and iron chelating property of *Terminalia chebula* (Retz.) alleviates iron induced liver toxicity in mice. BMC Complement Altern Med. 2012;12:144. https://doi.org/10.1186/1472-6882-12-144.

Sask $H_2O$. http://www.saskh2o.ca/. Accessed 11 Nov 2021.

Sheng Z, Zhao J, Muhammad I, Zhang Y. Optimization of total phenolic content from *Terminalia chebula* Retz. fruits using response surface methodology and evaluation of their antioxidant activities. PLoS ONE. 2018;13:e0202368. https://doi.org/10.1371/journal.pone.0202368.

South PK, Miller DD. Iron binding by tannic acid: effects of selected ligands. Food Chem. 1998;63:167–72. https://doi.org/10.1016/S0308-8146(98)00040-5.

Sun X, Zhang J, Wang X, et al. Colorimetric and fluorimetric dual mode detection of $Fe^{2+}$ in aqueous solution based on a carbon dots/phenanthroline system. Arab J Chem. 2020;13:5075–83. https://doi.org/10.1016/j.arabjc.2020.02.007.

Suresh P, Azath IA, Pitchumani K. Naked-eye detection of $Fe^{3+}$ and $Ru^{3+}$ in water: colorimetric and ratiometric sensor based on per-6-amino-β-cyclodextrin/p-nitrophenol. Sens Actuators B Chem. 2010;146:273–7. https://doi.org/10.1016/j.snb.2010.02.047.

Tkaczyszyn M, Comín-Colet J, Voors AA, et al. Iron deficiency and red cell indices in patients with heart failure: Iron deficiency and red cell indices in heart failure. Eur J Heart Fail. 2018;20:114–22. https://doi.org/10.1002/ejhf.820.

Tsui Y-K, Devaraj S, Yen Y-P. Azo dyes featuring with nitrobenzoxadiazole (NBD) unit: a new selective chromogenic and fluorogenic sensor for cyanide ion. Sens Actuators B Chem. 2012;161:510–9. https://doi.org/10.1016/j.snb.2011.10.069.

Upadhyay A, Agrahari P, Singh DK. A review on the pharmacological aspects of *Terminalia chebula*. Int J Pharmacol. 2014;10:289–98. https://doi.org/10.3923/ijp.2014.289.298.

Wei D, Sun Y, Yin J, et al. Design and application of $Fe^{3+}$ probe for "naked-eye" colorimetric detection in fully aqueous system. Sens Actuators B Chem. 2011;160:1316–21. https://doi.org/10.1016/j.snb.2011.09.068.

Welna M, Lasowska J, Zyrnicki W. Determination of some inorganic species of Fe, Mn and Cr by chemical vapor generation hyphenated with inductively coupled plasma atomic emission spectrometry. J Braz Chem Soc. 2011;22:1164–9. https://doi.org/10.1590/S0103-50532011000600023.

You GR, Park GJ, Lee SA, et al. Chelate-type Schiff base acting as a colorimetric sensor for iron in aqueous solution. Sens Actuators B Chem. 2015;215:188–95. https://doi.org/10.1016/j.snb.2015.03.064.

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