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Turmeric, naturally available colorimetric receptor for quantitative detection of fluoride and iron

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HIGHLIGHTS

- Turmeric, a natural material is used for the first time for the F^- and iron ions detection.
- Simple, reusable, cheap device is developed for the colorimetric detection of F^-.
- The detection is based on the intramolecular charge transfer mechanism.

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ABSTRACT

Turmeric (*Curcuma longa*) an important food ingredient has been used from ancient times for various biological applications, but to date it has not been considered for the colorimetric detection of anions and cations. In this work, the application of turmeric solution for the colorimetric detection of F^- and iron ions was demonstrated. Results showed a significant colour change from yellow to blue and yellow to orange upon addition of F^- and iron ions respectively. The detection mechanism was investigated using curcumin, a major component of turmeric powder. The change in colour and fluorescence quenching was attributed to the formation of receptor complex with F^- and iron ions which resulted in intramolecular charge transfer transition. The mechanism of binding has been confirmed by UV–vis, ^{1}H NMR and fluorescence titrations. The present detection concept was further explored to develop a low cost, reusable F^- detection kit, which showed its ability to detect F^- ions in both aqueous and organic medium at a very low concentration such as 1 ppm.

1. Introduction

The selective detection and quantitative analysis of anions and metal ions in real time using synthetic organic receptors is an emerging and attractive research area across several disciplines including chemistry, biology and environmental science [1]. Considering the role of anions and metal ions in human life, it is critical to design low-cost, simple, efficient and selective receptors for their detection for quantitative analysis. Fluoride (F^-) ion is one of the important anion with numerous medical applications, such as in the treatment of osteoporosis [2] and dental care [3]. However, excess of fluoride in drinking water may cause many diseases including dental and skeletal fluorosis [4], osteosarcoma, urolithiasis and nephrotoxic changes in human body [5,6]. Thus, the fluoride appeared to have advantageous and disadvantageous implications on human body depending on its concentrations. Due to its dual nature, it is crucial for selective quantitative detection of fluoride. Similarly, among cations, iron has been widely used as a catalyst in industries for the synthesis of fertilizers, also oxides of iron in paint and dye industries for pigmentation [7]. In addition, iron is an essential metal ion with several applications like physiological and metabolic functioning in humans as well as plant body. It plays vital role in the cell growth and proliferation, DNA and RNA synthesis, oxygen carrying, enzymatic reactions, hemoglobin synthesis [8–9]. Thus, iron deficiency causes many diseases such as anemia, methemoglobinemia. However, excess of iron will result in disorders like hemochromatosis, endocrine problems, arthritis, diabetes, and liver diseases [10–11]. Therefore, excess iron present in the

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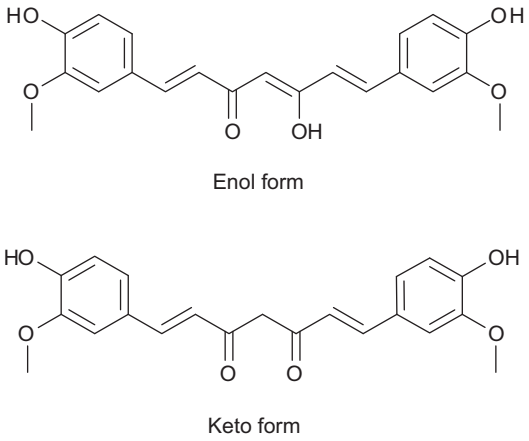
body could be harmful, however it is useful to the human body if present at required level. The permissible limit of the iron in drinking water as per WHO is 2 ppm [12]. Thus, considering the role of iron in biological and industrial activities, selective detection of iron in trace amount by real time attains significance.

In the past decades, several methods such as ion selective electrodes [13], ion chromatography [14] and ion monitoring probes [15] have been developed for the determination of fluoride ions from different fluoride sources. Similarly, various analytical techniques are available such as flame atomic absorption spectrometry (FAAS), atomic absorption spectrometry (AAS) [16], inductively coupled plasma optical emission spectrometry (ICP-OES) [17] for the quantitative detection of metal ions. However, most of the mentioned techniques are expensive, not portable, time consuming and require sophisticated instrumentations which need skilled labour to operate. The colorimetric detection of anions and metal ions on the other hand is specifically attractive, offering low cost, highly selective, sensitive, safe and easy to use. Several reports have been published on the detection of F^- ions, but majority of them are limited only for the detection of organic fluoride source such as tetrabutylammonium fluoride (TBAF) [18–19]. However, selective detection of inorganic fluoride source such as sodium fluoride (NaF) has not been widely explored to the extent of TBAF. Thus, it is important to explore the new receptors for the detection of inorganic fluoride. Also, it would be beneficial if the same receptor could be used for the detection of cations. Another important aspect is to find receptors based on natural materials are in particular advantageous for eco friendly approaches. The most currently used synthetic receptors are usually synthesized through hazardous chemical protocols. So the need of less harmful receptors for the detection of ions is highly desirable due to the environmental concern.

Turmeric (*Curcuma longa*) is generally used as both spice and colouring agent [20]. Especially in Indian subcontinent, which has been used from centuries as a house hold remedy. Turmeric was widely studied for various biological activities such as anti-inflammatory, anticancer, Alzheimer's disease, antibacterial, antioxidant, and so on. However, turmeric has not been studied for analytical applications such as anion and cation receptor. The major component of turmeric, curcumin (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene- 3,5-dione; Scheme 1) [21] has been studied extensively from decades for various biological activities such as anticancer, anti-inflammatory, antioxidant, antitumor, chemoprevention, Alzheimer's disease, antimicrobial, antibacterial, antimalarial, rheumatoid arthritis, inhibition of human immune deficiency virus (HIV) replication, wound healing and many more [22–27].



Scheme 1. Enol and keto forms of curcumin.

In the present work, turmeric was used as a natural receptor for the effective colorimetric detection of F^- and iron ions. Our idea is motivated to use low cost receptors based on natural and green materials over existing organic receptors used for fluoride ion and iron detection. Turmeric is considered as 'generally recognized as safe' (GRAS) substance by Food and Drug Administration (FDA) [28]. In addition, turmeric is abundant in nature, requires no organic synthesis with toxic ingredients offers a greener way of detecting F^- and iron ions. By keeping this as a focal point, in this manuscript both naturally occurring turmeric and its major component curcumin have been studied for the detection of F^- and iron ions. To prove the concept, we have explored the sensitivity of detection method using different concentrations of both ions. We have developed a simple paper based colorimetric method and cost effective reusable F^- detecting kit that can be applied for real time usage. The presented work can be described as significantly useful to the regions like India, China, and Africa where the ground water fluoridation is a major threat.

2. Experimental section

All chemicals were purchased from Spectrochem/Central Drug House, India and used without further purification. All solvents were bought from Rankem, India with HPLC grade and used without further purification.

The ^{1}H NMR spectra were recorded on a Bruker (500 MHz) instrument using TMS as an internal reference and DMSO-d_6 as the solvent. UV–vis spectroscopy was carried out with Shimadzu 1700 PC UV–visible spectrophotometer using standard 10 mm cuvette. Fluorescence experiments were accomplished on Shimadzu RF 5301 PC spectrofluorometer. Liquid chromatography–mass spectrometry (LC–MS) analysis of turmeric powder was carried out with SYNAPT G2 HDMS instrument.

Locally grown turmeric root was taken, dried and ground into powder using mixer grinder. Further, turmeric powder was dissolved in organic solvent (dichloromethane) and filtered in order to separate undissolved fibers, carbohydrates etc. It was found that 97% of crude sample was containing carbohydrates, proteins, fibers and remaining 3% was the mixture of curcuminoids along with other volatile oils. Thus, extracted sample was concentrated and analysed using LC–MS to quantify the percentage of each curcuminoids present in it (Supporting information, Fig. SI. 1). From the analysis it was found that the turmeric has three major curcuminoids present in different percentages, where curcumin was major component with 52.1% followed by demethoxycurcumin and bisdemethoxycurcumin with 22.75% and 7.97% respectively (Supporting information, Table SI. 1).

The selective studies with turmeric were carried out using 1:1 (1% turmeric in DMSO:H_2O) organo-aqueous mixture for the detection of 1, 10, 100 ppm of inorganic fluoride such as NaF in aqueous media. Further, 9:1 (0.1% turmeric in DMSO:H_2O) organo-aqueous solution mixture was used for detection of F^- ions in organic media. Also, 0.1% turmeric solution in DMSO was used for F^- ion detection in organic media. 0.01% turmeric solution in DMSO was prepared and used for the detection of iron ions in aqueous medium. All selective experiments are carried out in series of glass vials with 2 mL of receptor solutions followed by the addition of 50 μL of 0.1 M solution of anion/cation solutions.

Curcumin powder was first dissolved in acetonitrile (ACN) (and DMSO) to get concentration of 2.5×10^{-5} M solution. All anion and cation solutions of 0.1 M concentrations are prepared using tetrabutylammonium (TBA) salts in ACN and nitrate salts (except Fe^{2+} ion which is in chloride form) in water respectively. All selective

studies using curcumin were carried out using 2 mL of 2.5×10^{-5} M receptor solution with the addition of 2 equiv. of 0.1 M anion and cation solutions in each vial. UV and fluorescence titrations are carried out using 2.5×10^{-5} M curcumin solution with the addition of 0.1 equiv. of 0.1 M fluoride ions and iron ions solution each time.

The ^{1}H NMR spectrum of curcumin was taken in DMSO-d_6 (Supporting information, Fig. SI. 2) in a similar way to match with earlier reports [29]. ^{1}H NMR analysis of curcumin (500 MHz, DMSO-d_6): δ 9.672 (s, 1H, –OH), δ 7.570 (d, 1H, –CH, J = 15.5 Hz), δ 7.328 (s, 1H, ArH), δ 7.167 (d, 1H, ArH, J = 8 Hz), δ 6.841 (d, 1H, ArH, J = 8.5 Hz), δ 6.776 (d, 1H, –CH, J = 16 Hz), δ 6.068 (s, 1H, –CH), δ 3.85 (s, 1H, –OCH_3).

3. Result and discussion

3.1. Colorimetric detection of fluoride ions using turmeric

The real time applicability of turmeric was colorimetrically evaluated by treating with inorganic fluoride such as sodium fluoride (NaF) in 1:1 (1% turmeric solution in DMSO:H_2O) organo-aqueous mixture. Fig. 1 shows series of colorimetric tests for the detection of F^- ions from 1 ppm to 100 ppm concentrations. Results showed notable colour change from yellow to brownish yellow upon the addition of 1 ppm of NaF. Further, with the addition of 10 and 100 ppm of NaF showed more intense colour such as orange and brown respectively. Thus, turmeric showed sensing ability towards F^- ions even at low concentrations such as 1 ppm. It is worth to note here that the permissible limit of F^- in potable water is up to 1 ppm [30].

The selectivity of turmeric powder towards F^- ions over other anions was tested by treating 0.1% turmeric solution in DMSO with other anions such as chloride, bromide, iodide, hydrogensulphate, dihydrogenphosphate and acetate in the form of tetrabutylammonium (TBA) salts. An instantaneous colour change from yellow to blue was observed only in case of F^- ions. Further, to ensure the selectivity towards F^- ions, 9:1 (0.1% turmeric solution in DMSO:H_2O) organo-aqueous mixture was treated with 0.1 M TBAF, which showed colour change such as yellow to brown (Fig. 2).

To evaluate the practical applicability, turmeric coated paper strip was prepared. The strip was initially treated with different anions in the form of TBA salts. The strip showed significant colour change from yellow to dark brown with the addition of F^- ions and yellow to pale brown with AcO^- ion (Fig. 3). This colour change proves the strong binding capability of turmeric towards F^- ions over other mentioned anions (in TBA form). However, the strip did not work as expected in aqueous media for the detection of inorganic fluoride.

In order to overcome this issue, a novel reusable fluoride detecting kit was developed. As turmeric showed less colour intensity, its main component curcumin was used for F^- ions detection in aqueous media. The kit was made up of a glass tube (3 mm diameter and 7 in. height), one end of which was permanently sealed and the other end was closed with a removable cap. The glass tube was filled with 1 mL of curcumin solution and was clamped to a white solid platform as illustrated schematically in Fig. 4. Device contains standard colour references printed on it for different fluoride concentrations. Upon addition of 50 μL of test sample into the glass tube, the curcumin solution instantaneously changed its colour depending upon the concentration of F^- ions present. This change in colour was compared with the reference colours printed on the device. So that one can easily match the change in colour to determine the concentration of F^- ions present in the sample. The kit can easily be used for the detection of both organic and inorganic F^- ions qualitatively in laboratory as well as in field for real time detection studies.

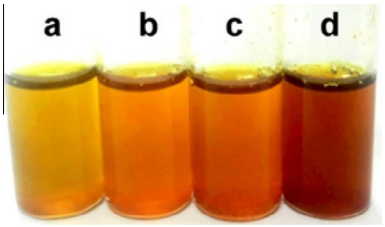


Fig. 1. Colour change in 1% turmeric solution after addition of F^- ions in DMSO (a) 1% turmeric solution, (b) 1 ppm, (c) 10 ppm, (d) 100 ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The reusable fluoride detection kit was examined in real time for the detection of inorganic F^- such as NaF. When the sample containing F^- ions was added into the tube, there is an instantaneous change in colour depending upon the amount of F^- ions present in the sample. The device displayed positive results for sample with as low amount as 1 ppm. Further, it was tested for 10, 50 and 100 ppm of F^- ions. As the amount of F^- ions increased in the sample, the change in colour intensity of curcumin solution has also increased (Fig. 5). Thus, the kit was not only detected inorganic F^- ions but also was able to distinguish the amount of F^- ions present in the aqueous media.

In order to investigate the mechanism of colour change, curcumin solution (2.5×10^{-5} M) was treated with various anions such as fluoride, chloride, bromide, iodide, hydrogensulphate, dihydrogenphosphate and acetate ions in the form of tetrabutylammonium (TBA) salts to ensure the selective colorimetric detection of F^- ions over other mentioned anions in acetonitrile (ACN) solvent. The curcumin solution spontaneously showed a significant colour change from yellow to blue and yellow to pale brown upon the addition of F^- and AcO^- ions respectively. The curcumin exhibited more change in colour intensity towards F^- ions. This indicated the strong binding of F^- ions, whereas with AcO^- ions showed weaker interaction resulted in less change in colour intensity (Supporting information, Fig. SI. 3). Further, selectivity of curcumin with F^- and AcO^- ions was confirmed with UV–vis spectroscopy. Upon addition of F^- and AcO^- ions, a significant shift in the absorption band has been observed. The absorption band which has been generated after the addition of F^- ions was much more intense than that of AcO^- ions. Therefore, it is clear that F^- ions bind significantly stronger to curcumin over AcO^- ions. At the same time other anions did not perturb with any changes in absorbance of curcumin which showed that there was no interaction between curcumin and other anions (Supporting information, Fig. SI. 4).

Curcumin was further studied in DMSO solvent to ensure the selectivity. The curcumin displayed instantaneous change in colour from yellow to blue upon adding F^- ions and yellow to pale green with AcO^- ions. As expected the binding of F^- ions showed much stronger interaction which resulted in intense colour change compared to AcO^- ions. This change in colour intensity was attributed to weak binding of AcO^- ions to curcumin compared to that of F^- ions (Supporting information, Fig. SI. 5). On the other hand, the addition of other anions were not resulted in any colour change. The strong selectivity of F^- ions over AcO^- ions was confirmed by UV–visible spectroscopy. The above mentioned anions are treated with curcumin in DMSO solution, which resulted in the generation of new absorption band for F^- and AcO^- ions. The absorption band generated for F^- ions was much more intense compared to the absorption band of AcO^- ions. This provided the evidence that F^- ions binds to curcumin intensely compared to AcO^- ions (Supporting information, Fig. SI. 6).

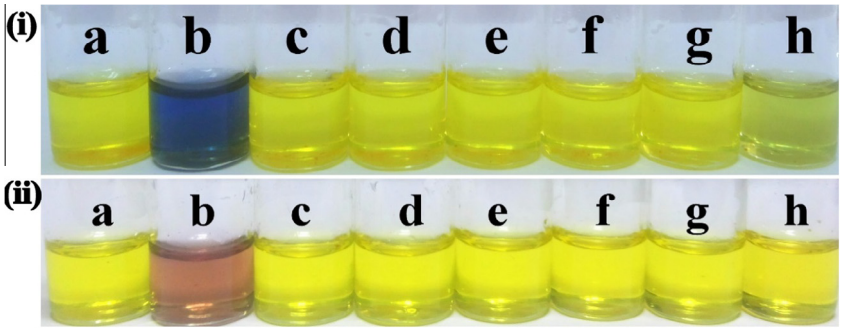


Fig. 2. (i) Change in colour of 0.1% solution of turmeric in DMSO solvent and (ii) Change in colour of 9:1 (0.1% solution of turmeric in DMSO:H_2O) organo-aqueous mixture after the addition of 50 μL of anion solution, (a) 0.1% turmeric solution, (b) F^-, (c) Cl^-, (d) Br^-, (e) I^-, (f) HSO_4^-, (g) $H_2PO_4^-$ and (h) AcO^- ions in TBA form. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

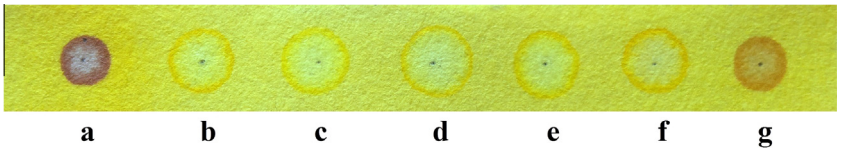


Fig. 3. Turmeric strip showing colour change for different anions, (a) F^-, (b) Cl^-, (c) Br^-, (d) I^-, (e) HSO_4^-, (f) $H2PO_4^-$ and (g) AcO^- ions (in TBA form). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

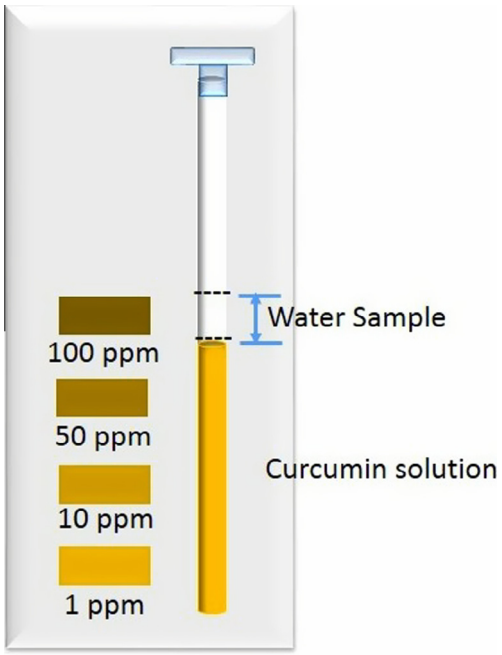


Fig. 4. Graphical image of reusable fluoride detecting kit showing reference colours for various concentrations of F^- ions in water. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Further, to evaluate the sensitivity of curcumin UV–vis titration was carried out by varying the concentration of F^- ions (in the form of TBA salts) in ACN solvent. The curcumin was sensitive enough to detect the F^- ions even at 2.5 μM concentration using UV–vis spectroscopy. The change in absorption with the increasing concentration of F^- ions is presented in Fig. 6. The curcumin in ACN displayed absorption band at 417 nm which corresponds to –OH functionality. The incremental addition of F^- ions to ACN solution of curcumin (2.5×10^{-5} M) resulted in gradual decrease in the absorption band at 417 nm. This gradual decrease in absorption band attributed to the involvement of –OH groups in detection process. Simultaneously, a new absorption band at 565 nm with an isosbestic point at 456 nm was appeared. This new absorption band at 565 nm with a bathochromic shift of 148 nm attributed to the intramolecular charge transfer (ICT) [31] transition between the curcumin:F^- ion complex. The stoichiometry of F^- ion complexation with curcumin was determined by Benesi–Hildebrand plot method [32] in ACN (inset of Fig. 6). This clearly confirmed the formation of 1:2 stable stoichiometric complex between curcumin and F^- ions.

The UV–vis titration was further extended to curcumin solution (2.5×10^{-5} M) in DMSO with incremental addition of TBAF. The titration profile showed similar changes as that of curcumin solution in ACN (Supporting information, Fig. SI. 7). Upon gradual increase in F^- ions, absorption band at 434 nm corresponds to –OH functionality, decreased gradually due to its involvement in the detection process. A new absorption band at 575 nm was developed with an isosbestic point at 480 nm. This bathochromic shift of 141 nm was accounted for the ICT transitions between curcumin:F^- ions complex.

The fluorescence change of curcumin was studied with above mentioned anions. Upon addition of F^- ions curcumin showed significant quenching in the fluorescence. However, other anions did not induce any changes (Supporting information, Fig. SI. 8). This selective quenching of curcumin (2.5×10^{-5} M) in ACN with F^- ions was confirmed with fluorescence studies. Upon addition of F^- ions, a significant quenching in fluorescence was observed and other anions did not perturb any fluorescence changes which showed that there was no interaction between curcumin and other anions (Supporting information, Fig. SI. 9). The quenching of fluorescence emission has been evaluated using fluorescence titration of curcumin with F^- ions. The curcumin solution was excited at 417 nm to record the emission at 507 nm. The incremental addition of F^- ions to ACN solution of curcumin (2.5×10^{-5} M) resulted in regular quenching of fluorescence emission at 507 nm (Supporting information, Fig. SI. 10). This constant quenching in emission is attributed to initial hydrogen bonded curcumin:F^- ion complex formation followed by deprotonation of hydroxyl group at higher concentration of F^- ions. Similar studies carried out in DMSO showed comparable results (Supporting information, Fig. SI. 11).

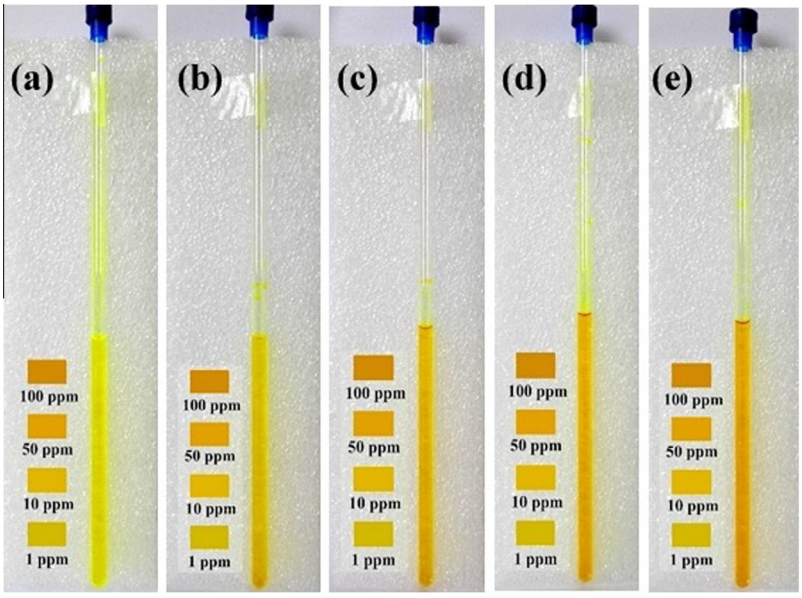


Fig. 5. The real reusable fluoride ions detection kit showing different colour for different concentrations of F^- ions present in the aqueous media. (a) curcumin solution, (b) addition of 1 ppm, (c) 10 ppm, (d) 50 ppm and (e) 100 ppm of F^- ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

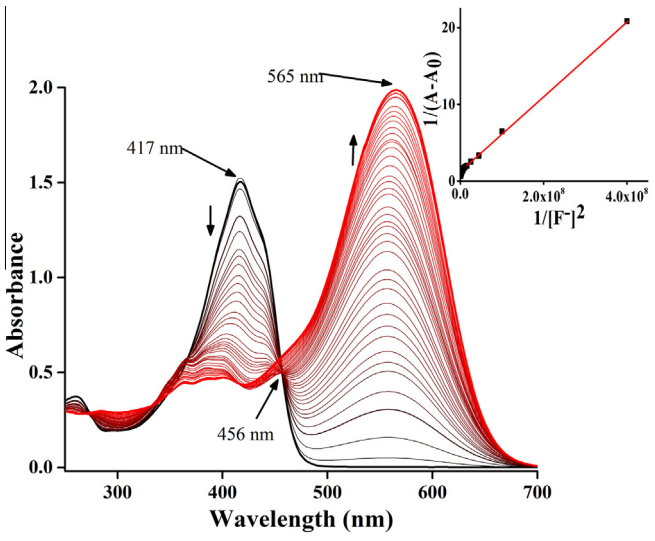


Fig. 6. UV–vis titration of curcumin (2.5×10^{-5} M) with tetrabutylammonium fluoride (TBAF) in ACN. Inset: Benesi–Hildebrand plot of curcumin binding with F^- ions associated with absorbance change at 565 nm in ACN.

With above evidence the reaction mechanism of curcumin with F^- ions was predicted in Scheme 2. Both profiles (curcumin in ACN as well as in DMSO) showed the involvement of –OH functionality in the detection process. Upon the addition of F^- ions, hydrogen bond was formed between phenolic –OH of curcumin and F^- ions, resulted in 1:1 curcumin:F^- ion complexation. However, at higher concentration of F^- ions, deprotonation of –OH group was observed which resulted in charge transfer transition within the molecule to attain stability to form 1:2 curcumin:F^- ion complex.

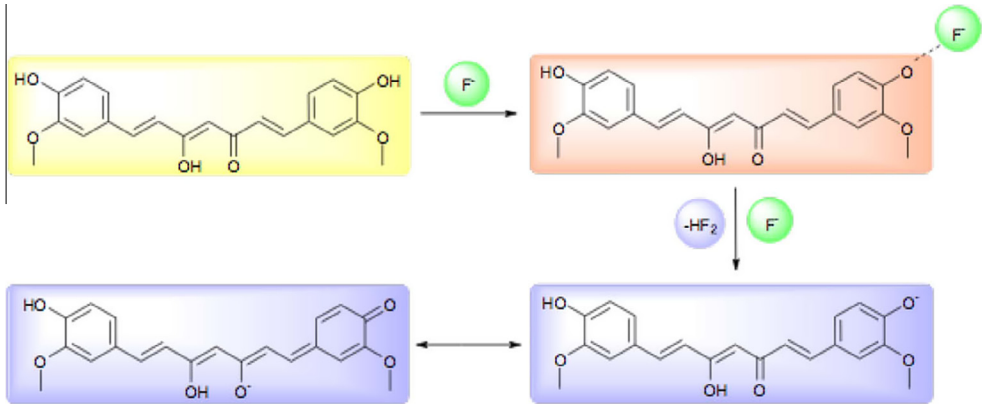
Further, in order to justify the proposed mechanism ^{1}H NMR titration with F^- ions was carried out in DMSO-d_6 (Fig. 7). The peak at δ 9.7 corresponds to –OH functional group which was completely disappeared after the addition of 0.5 equiv. of F^- ions. This disappearance was attributed to fast proton exchange. However, there was no significant change in the aromatic region. Upon addition of 1 equiv. of F^- ions, a slight upfield shift in the aromatic protons were observed. Simultaneously splitting in the aromatic peaks was disappeared. This upfield shift and disappearance of splitting was perhaps due to the charge transfer transition in curcumin. As F^- ions concentration increased to 10 equiv., a significant merging in aromatic region was observed. In addition, a broad triplet peak at δ 16.1 corresponding to HF_2 was appeared [33]. This generation of peak corresponding to HF_2 clearly indicated the deprotonation process in the curcumin.

3.2. Colorimetric detection of iron ions using turmeric

Further, turmeric powder was evaluated for the colorimetric detection of cations. Different cations such as Ca^{2+}, Cr^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{2+}, Cd^{2+}, Sn^{2+}, Hg^{2+} and Pb^{2+} ions were prepared in H_2O and treated with 0.1% turmeric solution in DMSO. Turmeric showed astonishing colour change from yellow to orange for Fe^{2+} and Fe^{3+} ions, whereas remaining cations did not show any colour change (Fig. 8).

Later, turmeric solution (0.01%) prepared in DMSO was investigated for the real time application by treating with different concentrations of Fe^{2+} and Fe^{3+} ions such as 1, 10 and 100 ppm (Fig. 9). Though turmeric could sense 100 ppm Fe^{2+} ions, there was no remarkable colour change between 0 and 10 ppm of Fe^{2+} ions. On the other hand, upon the addition of 1 ppm Fe^{3+} ion solution, colour of turmeric was slightly intensified. Thus, turmeric showed its ability to detect Fe^{3+} ions as low as 1 ppm. Later, colour was changed from pale yellow to orange yellow and brownish yellow with the addition of 10 and 100 ppm of Fe^{3+} ions respectively.

To prove turmeric as an effective natural colorimetric detector, it was further investigated using curcumin which is a main ingredient of turmeric. The colorimetric experiment was conducted to evaluate the selectivity of curcumin towards Fe^{2+} and Fe^{3+} ions over other cations such Ca^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{2+}, Cd^{2+}, Sn^{2+}, Hg^{2+} and Pb^{2+} ions. The selective binding of curcumin with Fe^{2+} and Fe^{3+} ions which resulted in the colour change from yellow to brown (Supporting information, Fig. SI. 12). On other hand, other cations either became colourless or did not show any colour change. The change in colour indicated the strong binding



Scheme 2. Proposed mechanism for the fluoride ion binding to the curcumin.

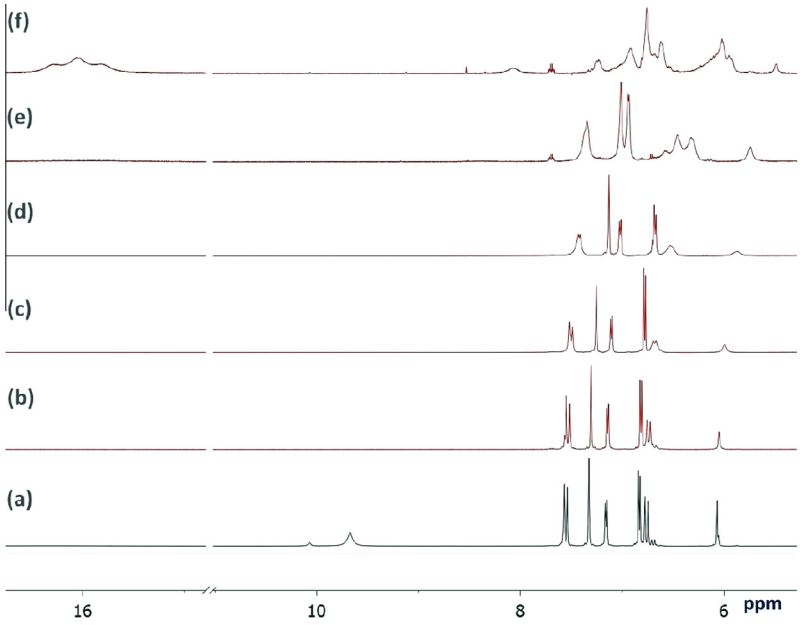


Fig. 7. Partial ^{1}H NMR titration spectra of curcumin with F^{-} ions at different concentrations in DMSO-d_6. (a) Curcumin, (b) 0.5 equiv., (c) 1 equiv., (d) 2 equiv., (e) 4 equiv., (f) 10 equiv. of F^{-} ions.

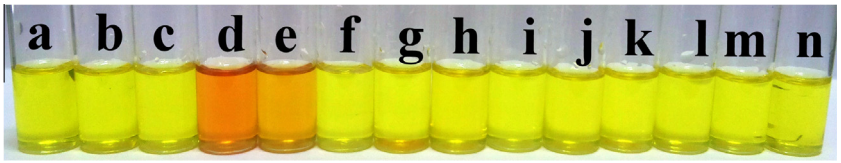
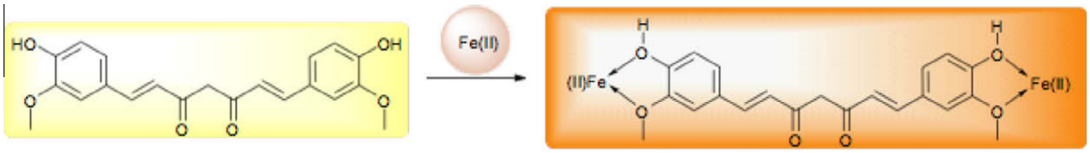


Fig. 8. Change in colour of 0.1% solution of turmeric in DMSO after adding different cations, (a) 0.1% turmeric solution, (b) Ca^{2+}, (c) Cr^{2+} (d) Fe^{2+}, (e) Fe^{3+}, (f) Co^{2+}, (g) Ni^{2+}, (h) Cu^{2+}, (i) Zn^{2+}, (j) Ag^{2+}, (k) Cd^{2+}, (l) Sn^{2+}, (m) Hg^{2+} and (n) Pb^{2+} ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of Fe^{2+} and Fe^{3+} ions with curcumin. In evidence, the selectivity of Fe^{2+} and Fe^{3+} ions was justified with the help of UV–visible experiments of curcumin. Upon the addition of Fe^{2+} and Fe^{3+} ions, a considerable shift in the absorption band was observed. Whereas other cations did not show such notable shifts in the absorption bands. This spectrum was evident for the binding of iron ions with the curcumin over other cations (Supporting information, Fig. SI. 13).

In order to evaluate the spectral changes observed upon addition of Fe^{2+} and Fe^{3+} ions, UV–visible titration was conducted. The UV–visible titration of curcumin (2.5×10^{-5} M) in ACN was carried out with incremental addition of Fe^{2+} ions (Fig. 10). The characteristic absorption peak at 417 nm corresponds to –OH functionality which decreases gradually with increase in the concentration of Fe^{2+} ions. This showed the involvement of phenolic –OH group in the detection process. The peak at 417 nm decreases gradually with the development of new absorption peak at 484 nm with isosbestic point at 453 nm due to the charge transfer (CT) [34] transition between curcumin and Fe^{2+} ions. The new absorption peak at 484 nm with bathochromic shift of 67 nm is due to



Scheme 3. Proposed mechanism for the Fe^{2+} ions binding to the curcumin molecule.

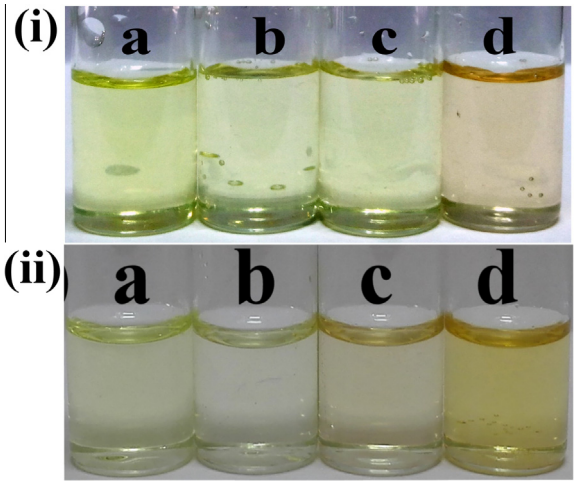


Fig. 9. Colour change in 0.01% turmeric solution after the addition of (i) Fe^{2+} and (ii) Fe^{3+} ions in DMSO (a) 0.01% turmeric solution, (b) 1 ppm, (c) 10 ppm, (d) 100 ppm of ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

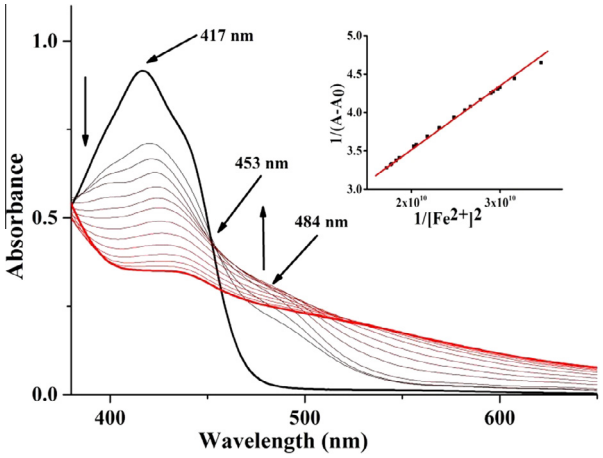


Fig. 10. UV–vis titration of curcumin (2.5×10^{-5} M) with Fe^{2+} in ACN. Inset: Benesi–Hildebrand plot of curcumin binding with Fe^{2+} ions associated with absorbance change at 484 nm in ACN.

curcumin:Fe^{2+} complex formation. The complexation of Fe^{2+} ions with curcumin was studied by Benesi–Hildebrand method [32] using UV–visible spectroscopy (inset of Fig. 8). From the plot it is clear that formation of 1:2 stable stoichiometric complex between curcumin and Fe^{2+} ion. Similar studies were carried out for Fe^{3+} ions which showed similar changes (Supporting information, Fig. SI. 14).

Later, fluorescence study of curcumin was carried out in different cations to study the fluorescence behaviour of iron ions. Upon the addition of Fe^{2+}, Fe^{3+}, Cu^{2+} and Hg^{2+} ions curcumin showed instant quenching of fluorescence. Whereas, other cations did not attribute any fluorescence change (Supporting information, Fig. SI. 15). This selectivity was justified using fluorescence experiments wherein upon the addition of Fe^{2+}, Fe^{3+}, Cu^{2+} and Hg^{2+} ions, a considerable quenching in fluorescence was observed in spectra. However, other cations did not show any changes in fluorescence (Supporting information, Fig. SI. 16). Fluorescence quenching upon the addition of iron ions was studied using fluorescence titration of curcumin (2.5×10^{-5} M) in ACN against Fe^{2+} ions. The curcumin solution was excited at 417 nm to analyze the emission at 507 nm. Upon the addition of Fe^{2+} ions into the curcumin solution, it showed gradual decrease in the fluorescence emission at 507 nm. As the Fe^{2+} ions concentration increases, fluorescence of curcumin was completely quenched (Supporting information, Fig. SI. 17). Similarly, curcumin showed fluorescence quenching upon the addition of Cu^{2+} and Hg^{2+} ions. This behaviour of Cu^{2+} and Hg^{2+} ions was due to diminished donor-acceptor interactions [35]. As a result there was no charge transfer (CT) between these ions and curcumin. This was clearly shown by UV–visible spectra of Cu^{2+} and Hg^{2+} ions with curcumin, where peak corresponds to –OH functionality at 417 nm was completely disappeared upon the addition of Cu^{2+} and Hg^{2+} ions. Similar studies were carried out for Fe^{3+} ions which showed similar changes (Supporting information, Fig. SI. 18).

From the above evidence, it is clear that –OH functionality is involved in the binding process. The binding mechanism of Fe^{2+} ions with curcumin was predicted in Scheme 3. Upon adding Fe^{2+} ions, resulted in establishment of CT complex between curcumin and Fe^{2+} ions. Thus, it lead to the formation of CT stabilized 1:2 curcumin:Fe^{2+} ion complex.

4. Conclusion

Turmeric, a naturally occurring Indian spice has been explored and demonstrated as a natural receptor for the selective quantitative detection of F^- and iron ions in organic as well as in organo-aqueous media. Upon the addition of F^- and iron ions showed colour change from yellow to blue and orange respectively. A reusable fluoride detecting kit was developed using curcumin and its performance was investigated to detect inorganic fluoride even at a very low concentration (1 ppm) in aqueous media. Further, curcumin (a major component of turmeric) was used for scientific investigation to study the complexation behaviour of turmeric with F^- and iron ions. Curcumin showed colour change from yellow to blue followed by fluorescence quenching with the addition of F^- ions. The detection process of F^- ions involves the formation of 1:2 curcumin:F^- ions complex followed by deprotonation which leads to intramolecular charge transfer transitions. Similarly, curcumin exhibit colour change from yellow to brown along with fluorescence quenching with the addition of iron ions, resulted in the formation of 1:2 curcumin:iron ions complex followed by charge transfer between curcumin and iron ions. Turmeric has ability to sense inorganic fluoride source such as NaF and Fe^{3+} ions at as low concentrations as 1 ppm helps in real time colorimetric detection of F^- and Fe^{3+} ions in organo-aqueous media. Thus, the development of low-cost, easy to use kit has a considerable potential to be used for simple fluoride detection in water in remote areas where it is currently not available.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.05.113.

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