Novel Metallochromic Hydrazone-Based Chemosensor Toward Colorimetric Paper Strip For Selective Detection Cu²⁺

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Abstract

A solid-state sensor was developed for the determination of copper ions (Cu^{2+}) in aqueous media using tricyanofuranhydrazone as a spectroscopic probe and a paper sheet as the hosting strip. A new tricyanofuranhydrazone-based colorimetric chemosensor (TCFH) was synthesized for selective detection of Cu^{2+} in aqueous environments. The synthesis strategy of TCFH involved an azo-coupling process between the diazonium salt of 8-aminoquinoline and an active methyl-bearing tricyanofuran (TCF) heterocyclic moiety. The molecular structure of the prepared TCFH chemical sensor was verified with FT-IR, ^1H and ^{13}C NMR, as well as elemental analysis. Due to intramolecular charge transfer, TCFH chromophore demonstrated pronounced solvatochromism depending on the solvent polarity. Changes in both color and UV-vis absorption spectra demonstrated by the developed chemosensor proved that TCFH can be utilized to detect Cu^{2+} in the presence of other competing metallic cations and anions. The synthesized TCFH probe, which contains a hydrazone recognition moiety, demonstrates dramatic solvatochromic activity and high selectivity at the microlevel of copper ions with a color shift from yellow to purple. Mechanisms accounting for both metallochromic and solvatochromic activities were explored. Moreover, test strips of TCFH were successfully developed and applied for the detection of copper ions at different concentrations in aqueous media. The colorimetric properties of the prepared TCFH-immobilized paper strips were investigated by CIE Lab chromogenic parameters, colorimetric strength (K/S) and UV-Vis absorbance spectra. The metallochromic paper strip exhibited a detection limit at the ppm range. The best detection of Cu^{2+} was achieved in the pH range of 6.6-7.4 demonstrating an immediate color switch from yellow to purple relying on the total content of Cu^{2+} . Scanning electron microscopy (SEM) was applied to characterize the deposition of tricyanofuranhydrazone onto the surface of the paper strip.

1. Introduction

Detection of different chemical species, such as heavy metal cations, has been necessary for various applications. Thus, numerous detection techniques have been developed. The conventional detection techniques are usually uncertain, unselective, time-consuming and costly, which restricts their usage to laboratory settings [1–3]. Hence, the development of an appropriate analytical device for the detection of a trace analyte in a real sample has been vital. Chemical sensors have been recognized as a promising approach with a low-cost and convenient procedure for the detection of metal ions [4]. Optical chemosensors have been particularly considered as a significant and efficient analytical method due to their simple operation, immediate responsiveness, as well as high sensitivity and selectivity. There has been a broad range of organic chemical sensors that have been utilized as colorimetric sensors to monitor a variety of analytes, such as metal cations. Organic chemical sensors with proper functional substituents can be employed as ligands to interact efficiently with metal cations and generate considerable colorimetric changes [5, 6]. In recent years, tricyanofuranhydrazone-based chemosensors have been considered as optically active chromophores for a variety of colorimetric and fluorescent sensing applications, such as the detection of heat, toxic gases, biological entities, pH and solvent polarity. This can be attributed to their simple and tunable chemical structure containing a hydrazone

sensing moiety [7]. Tricyanofuranhydrazones demonstrated antimicrobial activity and a very low cytotoxicity. Additionally, they have displayed the generation of various colors. Thus, tricyanofuranhydrazones-based materials can be applied as colorimetric probes for the efficient detection of metal cations, particularly copper ions in both aqueous and semi-aqueous solutions [8].

Copper ions have been a significant entity in both biological systems and industrial processes. Copper has been used for a variety of applications, such as electric wires, industrial machinery systems, electronics, paints, plumbing and roofing, as well as nutritional supplements and fungicides in agriculture [9]. Copper can get into drinking water streams from industrial plants or even the household plumbing network. The human body requires some copper to continue healthy; however, too much is dangerous. It has been an essential trace mineral required for survival as it can be found in all body tissues. It must be supplied on a daily basis as a nutrition material from food and water [10]. Copper has a significant role in the production of red blood cells. It is vital for the normal functioning of the brain, immune system and nervous system. It also assists the human body in producing energy and collagen, as well as absorption of iron. Nonetheless, the abnormal absorption of excessive copper ions results in health defects, such as Wilson's disease, damages to the kidney and liver, diabetes, Menkes disease, gastrointestinal defects, Alzheimer's disease, and even death [11]. World Health Organization illustrated that the normal dose of copper in drinking water should be 20 μM . Long-term exposure to copper usually results in irritations to the eyes, mouth and nose. In addition, it may cause diarrhea, headache, dizziness, stomach cramps and vomiting. Thus, the development of practical methods for monitoring the total content of copper ions in water and soil has been really essential [12].

The detection of copper ions, particularly at the ppm range, utilizing a highly sensitive solid-state surface has been an attractive target. This could be attributed to the possible accumulation of the detected analyte via adsorption onto this surface to result in an improved sensitivity supported by increasing both surface area and porosity [13, 14]. Paper strips with high porosity and large surface area would be an attractive hosting surface for the development of sensor materials with rapid responsiveness and higher sensitivity. The large surface area of the paper strip results in fast diffusion throughout the mesh and high adsorption on the paper surface of spectroscopic sites and detected analytes [15, 16]. Thus, colorimetric sensors containing a hosting paper dipstick and active detection sites are promising as they apply less labor, lower cost and simple operation procedures. Recently, colorimetric sensors have been significant and efficient tools for naked-eye detection of a diversity of hazardous materials [17].

Herein, we report on the development of novel tricyanofuranhydrazone (TCFH) colorimetric sensor bearing quinoline-substituted hydrazone moiety for highly selective detection of Cu^{2+} ions in aqueous environments. The synthesis, characterization, optical properties, solvatochromism and metalochromism of this chromophore chemical sensor containing both hydrazone and quinoline moieties were investigated. The quinoline moiety can function as a ligand comprising a complexation ability with metal ions, while the hydrazone moiety has the ability to change the intramolecular charge transfer leading to color change in response to metal ions. The chemical structure of TCFH was fully investigated by infrared, elemental analysis and $^1\text{H}/^{13}\text{C}$ NMR. The complex formation between the

tricyanofuranhydrazone ligand containing quinoline-substituted hydrazone and copper ions was studied with UV-vis absorption spectra. Moreover, the detection mechanism was explored. Test strips immobilized with TCFH were successfully developed and applied for naked-eye real-time detection of copper ions. The colorimetric properties of the TCFH-immobilized paper strips were studied by CIE Lab parameters, color strength (K/S) and UV-vis absorbance spectra. Both SEM and EDXA were employed to characterize the deposition of tricyanofuranhydrazone onto the paper surface.

2. Experimental

2.1. Materials

All aqueous solutions of metal ions were prepared by dissolving the corresponding metal salts, CoCl_3 , AlCl_3 , BaCl_2 , FeCl_3 , CrCl_3 , NaCl , MgCl_2 , LiCl , SnCl_4 , HgCl_2 , and CuCl_2 ; (Sigma-Aldrich) in distilled water (5.0×10^{-2} M). A standard solution of tricyanofuranhydrazone (TCFH) bearing quinoline-substituted hydrazone was prepared in acetonitrile (1.0×10^{-3} M). Solvents utilized in the current study were purchased from Aldrich and Fluka. 8-Aminoquinoline, 3-hydroxy-3-methyl-2-butanone, and malononitrile were purchased from Sigma-Aldrich. TCF was synthesized according to the previous procedure [18]. All reactions were observed using Merck aluminium thin layer chromatography plates (PF_{254}) coated with silica gel, and were applied to visually monitor the progress of reactions for the synthesis of TCF and TCFH under UV lamp (254 and 365 nm).

2.2. Methods and equipment

The UV-visible spectra of tricyanofuranhydrazone probe in different organic solvents were measured by JASCO V-630 and Ocean Optics USB-4000 spectrophotometer. Cyclic voltammetry study of tricyanofuranhydrazone probe was performed on potentiostat CHI600. Traditional three electrodes were assembled under N_2 atmosphere to report the cyclic voltammograms. Ag/AgNO_3 (Ag/Ag^+) functioned as reference electrode, platinum wire was employed counter electrode, and ITO-coated glass electrode acted as working electrode. Elemental analysis of the tricyanofuranhydrazone probe was studied using Perkin Elmer 2400 (Norwalk, USA). Infrared spectra (FTIR) were applied to explore the functional groups on the prepared TCFH chemical sensor using Shimadzu FT-IR 8400 spectrophotometer. $^1\text{H}/^{13}\text{C}$ NMR spectra of tricyanofuranhydrazone were investigated under ambient conditions using Bruker 400 MHz. The chemical shifting is denoted with δ (ppm) employing TMS as an internal standard. Both morphology and chemical compositions of the TCFH-coated paper strips were studied by Quanta FEG 250 SEM (Czech Republic) coupled with TEAM-EDX.

2.3. Synthesis of TCF intermediate

In a water bath, sodium metal (150 mg, 6.5 mmol) was dispersed in ethyl alcohol (10 mL) under ambient conditions. 3-Hydroxy-3-methyl-2-butanone (4.5 g, 44 mmol) and malononitrile (6 g, 90.5 mmol) were added to the previously prepared sodium ethoxide solution. The mixture was stirred for an hour, and then extra amount of absolute ethanol (35 mL) was added. The solution was refluxed for an additional hour,

cooled in a fridge, filtered off, washed with minimal quantity of cold absolute ethanol, and finally air-dried to give the first crop of off-white crystals (10.93 g). Concentrating the filtrate afforded a second crop (1.14 g) to introduce a total yield of 68%; m.p. 200-202°C; ^1H NMR (400 MHz, CDCl_3): 2.37 (s, 3H), 1.65 (s, 6H).

2.4. Synthesis of hydrazone chemosensor

8-Aminoquinoline (1.44 g, 10 mmol) was dispersed in an admixture of distilled water (6 mL) and hydrochloric acid (4 mL); and then subjected to cooling at 0-5°C using an ice bath. $\text{NaNO}_{2(\text{aq})}$ (0.69 g, 10 mmol) in distilled water was added slowly. The generated diazonium salt was added slowly to a cold solution of TCF (2 g, 10 mmol) and CH_3COONa (5 g) in acetonitrile (5 mL). The crude product was filtered off, washed with distilled water (3 x 5 mL), recrystallized from ethanol, and finally air-dried to afford a red solid (yield 81%); m.p. 225-227°C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 13.04 (s, 1H), 12.02 (s, 1H), 8.97 (d, 1H), 8.45 (d, 2H), 7.77 (t, 2H), 7.68 (t, 1H), 1.91 (s, 3H), 1.84 (s, 3H); Elemental analysis: calculated for $\text{C}_{20}\text{H}_{14}\text{N}_6\text{O}$ (354.36): C 67.79, H 3.98, N 23.72; Found: C 67.57, H 3.85, N 23.39.

2.5. Preparation of colorimetric test stripes

TCFH can be reported as a dispersed dye due to its small molecular size and poor solubility in aqueous media. To prepare colorimetric test strips, an off-white Whatman cellulose filter paper (2.0 x 7.5 cm; Sigma-Aldrich) with a thickness of 180 μm , 240 mm diameter qualitative filters, pore size of 11 μm , and basis weight of 87 g/m^2 was subjected to immersion into a solution of TCFH in acetonitrile (10 mM) and then air-dried. The produced test strips immobilized with TCFH were then soaked in aqueous solutions of Cu^{2+} at different concentrations in the range of 50-300 ppm M for about 1-2 minutes and then air-dried.

2.6. Quantitative detection of Cu(II)

Aqueous solutions of copper chloride in distilled water were fabricated at different concentrations (50 to 300 ppm). The paper strip was soaked for 1-3 s in the above aqueous solutions to show different colorimetric shades starting from yellow to orange, reddish, violet and purplish, depending on the total content of copper ions. Moreover, different aqueous solutions of some selected metal salts, including Cr(III), Fe(III), Li(I), Hg(II), Sn(IV), Na(I), Al(III), Mg(II), Ba(II), Cu(II), and Co(III) were prepared at the same concentration (~300 ppm) were prepared and tested by the hydrazone-loaded paper strip under the same conditions. Photographs of the hydrazone-loaded paper strip before and after immersion in an aqueous solution of Cu(II) at different concentrations were taken by Canon A710 IS camera. The above aqueous solutions of copper chloride and other tested metal salts were prepared and adjusted at a pH value of ~7.00 using a buffer solution.

2.7. Effect of pH

With the purpose of exploring the optimum pH value for the detection process, aqueous solutions of copper chloride (~29 ppm) was prepared and adjusted at different pH values (2.6 and 9.2) using a buffer system. The pH value was determined by BECKMAN COULTER pH340.

2.8. Coloration properties

The colorimetric studies of the prepared TCFH-immobilized paper strips were carried out by testing CIE Lab chromogenic parameters, tinctorial strength (K/S) and UV-visible spectral profiles employing Ultra Scan Pro spectrophotometer (Hunter Lab, USA); where, L^* indicates lightness from white (100) to black (0), a^* is color ratios of red (+) to green (-), and b^* is color ratios of yellow (+) to blue (-).

3. Results And Discussion

3.1. Chemistry of TCFH sensor

In this work, a new optically active colorimetric chemosensor based on tricyanofuranhydrazone (TCFH) was developed using a simple and efficient synthetic method as shown in Scheme 1. The synthesized chemical sensor comprising a suitable functional quinoline moiety displayed excellent selectivity for copper ions at microlevel together with an obvious color change. It has been known that simple chemical sensors bearing functional substituents can present high detection performance for ionic species. The molecular structure of the synthesized colorimetric TCFH probe was proved by FT-IR, $^1\text{H}/^{13}\text{C}$ NMR, and elemental analysis. TCFH was produced by an azo-coupling between the diazonium salt of 8-aminoquinoline with TCF heterocyclic compound. This azo-coupling process is formal due to the presence of an active methyl group on the TCF heterocyclic compound. The hydrazone formation was verified with the singlet NH peak at 12.02 ppm in ^1H NMR spectrum of TCFH. ^1H NMR spectrum also demonstrated another peak at 8.97 ppm due to the proton on the hydrazone =C-H group. The downfield shifting of this singlet signal (=C-H) was attributed to the strongly electron-withdrawing effect arising from the cyano groups on TCF. Additionally, the FT-IR spectrum of TCFH displayed a characteristic absorption band at 3348 cm^{-1} attributed to the hydrazone NH, while the absorption band at 2219 cm^{-1} was ascribed to stretch vibration of hydrazone C=N group. Knoevenagel reaction has been important in the synthesis of electronically deficient compounds such as TCF heterocycle, which was provided in a relatively good yield of 68% via Knoevenagel reaction between malononitrile and 3-hydroxy-3-methyl-2-butanone in the presence of sodium ethoxide as a strong catalytic base [19]. During the azo-coupling reaction, the strong electron-withdrawing cyano groups on TCF facilitates the stabilization of the generated TCF carbanion provided by removing a proton from the active methyl substituent using sodium acetate as a weak base. Treating TCF with the diazonium chloride of 8-aminoquinoline generate an unstable azo-form product which transforms directly to the more stable hydrazone-form [20].

3.2. Solvatochromic properties

The maximum UV-Vis absorption wavelengths of TCFH were monitored in the range of 530-565 nm in different solvents. The colors of TCFH chromophore in different pure solvents ranged from yellow, orange, red to blue. The UV-Vis absorbance spectra of TCFH in different organic solvents are shown in Figure 1 and Table 1. As anticipated, a distinctive solvatochromic performance was monitored in both protic and non-protic solvents. Protic solvents function as H-bond donor to partially protonate the nitrogen atom on the quinoline moiety of the tricyanofuranhydrazone dye [21]. This partial protonation of nitrogen atom on quinoline moiety results in charge reduction leading to hypsochromic shift. In a non-

protic solvent; however, this H-bond donor effect should be negligible. Thus, we should turn our attention to other contributions to solvation, such as solvent dipolarity. The solvatochromism of TCFH arises from changes in the contribution level from the lone pair of electrons on hydrazone NH as shown in Scheme 2. This lone pair of electrons can partially function as a bridge between the quinoline-substituted hydrazone moiety and the highly electron-withdrawing TCF moiety in a partial donor-acceptor molecular system. This results in an interesting positive solvatochromic activity as a result of the higher extended conjugation [22]. Thus, the polarizability of the quinoline moiety certainly plays an important role in inducing solvatochromism.

Table 1
Changes of maximum absorption wavelength of TCFH in different solvents.

Solvent	λ_{max} (nm)
Acetone	541
Acetonitrile	480
Ethyl acetate	477
Toluene	477
1,4-Dioxane	476
Methylene chloride	498
Chloroform	497
Methanol	500
Ethanol	503
Tetrahydrofuran	481
Dimethylformamide	509

3.3. Solution-based detection of Cu²⁺ ions

The performance of TCFH was assessed by naked-eye and spectrophotometric methods for the detection of copper ions at different concentrations in acetonitrile as a solvent (Figure 2 and Table 2). The intended chemosensor (TCFH), as a colorimetric probe, can be utilized to visually monitor copper ions in water. To verify that water itself has no effect on TCFH, UV-Vis absorption intensity at 530 nm monitored in sensing copper ions remained unchanged with increasing the ratio of distilled water. Hence, TCFH can be applied as a novel optical chemosensor for the determination of copper ions in real water samples. In order to practically apply the current approach for possible commercialization, test strips immobilized with TCFH were fabricated and utilized to monitor different concentrations of copper ions (0-100 μM) in an aqueous medium. As shown in Figure 3, TCFH-immobilized solution displayed obvious colorimetric changes due

to copper ions in an aqueous medium. Nonetheless, the TCFH-immobilized solution had no noticeable color change at total contents lower than 10 μM . Thus, TCFH-immobilized solution can be considered as a simple and effective detection tool for sensing copper ions in real water samples.

Table 2
Absorption maxima of
TCFH in various
aqueous solutions of
different metallic salts.

Solvent	λ_{max} (nm)
CH ₃ CN	500
LiCl	507
BaCl ₂	501
SnCl ₂	501
HgCl ₂	500
CoCl ₃	560
AlCl ₃	526
FeCl ₃	500
NaCl	500
MgCl ₂	503
CrCl ₃	507
CuCl ₂	540

3.4. Electrochromic measurements

In view of the reversible electrochemical behaviors, the electrochromic of tricyanofuranhydrazone performance was investigated in acetonitrile solution. TCFH (5 mM) was dissolved in a solution of Bu₄NPF₆ (0.2 M) in acetonitrile. Both counting and working electrodes were platinum wire and glassy carbon, respectively. On the other side, Ag/AgCl was applied as a reference electrode [23, 24]. Figure 4 and Table 3 shows one electron irreversible reduction peak at -1.10 V and a stable reversible reduction peak at -1.50 V. Thus, TCFH shows two separated reduction peaks indicating that the second reduction peak is in need of higher energy than the first reduction. Therefore, that the tricyanofuranhydrazone ring is electronically well connected with 8-(12-azaneyl)quinolone [25, 26]. The height of the reduction signal specified a correspondence to one electron reduction process. The ferrocenium/ferrocene (Fc/Fc⁺) couple was used as reference (E° (Fc/Fc⁺) = 0.63 V NHE) to specified the peak position. The UV-Vis absorption

spectra was performed to investigate the electrochromic behavior of TCFH as illustrated in Figure 5 demonstrating a red color with an absorbance band at 550 nm.

Table 3
Redox potential and UV-visible absorbance maxima of TCFH in cyclic voltammetry.

compound	redox potential vs Ag/Ag ⁺ (V)	max abs (nm) Before	max abs (nm) After
TCFH	-1.10 irrev, -1.50 rev	500	550

3.5. Preparation of colorimetric paper strip

The tricyanofuranhydrazone probe can be described as a dispersed dyestuff due to its small molecular size and poor solubility in aqueous media. Thus, it can be embedded easily as dispersed particles between the cellulose fibers of the paper sheet. In order to prepare the colorimetric test strips, an off-white Whatman cellulose filter paper was immersed in an acetonitrile solution of tricyanofuranhydrazone and air-dried to show a yellow color. Solutions of copper chloride in distilled water were prepared at different concentrations in the range from 50 to 300 ppm. Photographic images of sensor strips before and after exposure to copper salt in aqueous media at various contents are illustrated in Figure 6. Cu(II) ions were detected by immersing the paper test strip for a few seconds in aqueous solutions of Cu(II) ions to generate different colors between yellow, orange, red, violet, light purple and dark purple due to increasing the concentration of copper in the range of 50-300 ppm. The paper dipstick did not display any colorimetric switch and maintained yellow in the absence of copper. The blank off-white filter paper which was uncoated with TCFH demonstrated no color change upon immersion in aqueous solutions of copper ions at different concentrations. The coordination bonding between Cu(II) ions and nitrogen atoms of quinoline and hydrazone moieties should form colored complexes, which were compatible with UV-vis absorption spectra (Figure 7).

A calibration curve for detecting aqueous solutions of copper ions at different concentrations (50 to 300 ppm) was assembled by recording the changes in the values of the maxima absorption intensity at 530 nm. The current paper dipstick was successfully employed to approximate an unknown concentration of copper ions dissolved in water. Figure 7 displayed a linear correlation for the copper concentrations in the range of 0 - 300 ppm. The absorbance intensity at 530 nm was found to bathochromically shift to 565 nm with increasing the concentration of copper ions. The colorimetric changes were observed with the increase of Cu(II) concentration due to the complex formation of nitrogen atoms of quinoline and hydrazone moieties with Cu(II) ions. The detection limit was also studied by monitoring the changes in the absorbance spectra as no more increments were detected in the absorbance intensity at 565 nm with increasing the concentration of copper ions higher than 300 ppm.

Both interference and selectivity are significant factors to assess the efficiency of a sensor device. The selectivity of the paper strip to copper ions was explored by inspecting different metal ions, including Cr(III), Fe(III), Li(I), Hg(II), Sn(IV), Na(I), Al(III), Mg(II), Ba(II), Cu(II), and Co(III). The paper strip showed an astonishing selectivity improvement of the absorption intensity to copper ions, whereas no major variations were observed for the other competing metallic ions excepting Co(II) and Al(III), which showed small increments in their absorbance intensities (Figure 8). These different sensitivities of metal ions could be ascribed to their different abilities to form complexes with the TCFH chromophore coated onto the paper strip. Thus, the current strategy provides an efficient sensor strip that can be applied conveniently for naked-eye selective detection of copper ions in the presence of other competitive free ions.

The interferences of the paper sensor were examined against different materials of varied properties, including toluene, benzene, aniline, dimethyl sulfoxide, tetrahydrofuran, ethyl acetate, ethylene diamine, dimethylformamide, *iso*-propanol, ethanol and acetonitrile. No colorimetric shifts were observed upon the immersion of the paper dipstick into solutions of those materials. In this context, we can apply the current test strips for simple, immediate and naked-eye detection of copper ions without interference with other materials. Thus, the current sensor strip introduces a very simple strategy for real-time and naked-eye detection ability providing qualitative and quantitative information on copper ions without the necessity for complicated or costly instrumental analysis.

3.6. Morphological studies of paper dipstick

Microfibrinous cellulose paper sheets generally exhibit large surface area making them potential toward the development of highly sensitive sensing tools. The morphology of the TCFH-coated paper strip was evaluated as illustrated in Figure 9. The immobilization of TCFH onto the paper strip was monitored as nanoparticles deposited onto the strip surface as illustrated by SEM micrographs. The thin TCFH film deposited onto the paper surface demonstrated high sensitivity to copper ions due to the large surface area of the microfibrinous cellulose paper sheet, which enable better diffusion of TCFH probe as the active spectroscopic sites and copper ions as the analyte.

3.7. Effect of pH on paper dipstick sensing

Both TCFH chromophores and copper ions have been known to be relatively sensitive to alkaline and acidic solutions. To study this fact, an aqueous solution of copper salt (300 ppm) was prepared. The pH of the prepared solution was adjusted at different values in the range between 2.6 and 9.2 by adding calculated quantities from HCl_(aq) (1 N) and NaOH_(aq) (1 N), respectively. The absorbance intensity was then measured for each solution. The absorbance intensity was plotted as a function of the pH value (Figure 10) to show negligible changes in the absorbance intensity of the generated complex for the pH values lower than 6.6 and higher than 7.4. This can be ascribed to the coagulation of copper chloride occurring efficiently in the very basic media, which prevent both absorption and diffusion of the coagulated copper chloride through the microfibrinous surface of the paper strip [27]. For the pH values lower than 6.6, TCFH chromophore exhibit a very low ability to lose a proton from the hydrazone-NH

making it difficult to form a complex with copper ions [21]. For the pH values between 6.6 and 7.0, the absorption intensity was found to improve suggesting a potential binding between TCFH and copper ions. This could be ascribed to the nitrogen atoms existing in the structure of TCFH with the ability to function as coordinative active sites as long as the pH is lower than the pKa magnitude of TCFH at pH = 7.0 [28]. Therefore, the paper sensor strip can be employed as a detection tool for copper ions in the near-neutral/alkaline pH (pH = 6.6 - 7.0).

3.8. Colorimetric study on paper dipstick

The current color assay was effectively applied for the quantitative and qualitative detection of copper in an aqueous sample. TCFH-paper test strips were employed to detect copper in particular aqueous solutions by generating a stable TCFH-Cu(II) complex by a chromogenic reaction (Figure 11). The color change from yellow to purple depended on the concentration of copper ions. The low concentrations of copper ions result in coordination with a partial amount of TCFH at the surface of the paper strip to result in a partial chromogenic reaction. This partial coordination was monitored to increase with the increase of Cu(II) concentration introducing a range of different colors.

Both of K/S and CIE Lab were employed to evaluate the sensor ability to monitor copper ions in aqueous media (Tables 4 and 5). The maximum absorbance wavelength of the sensor was determined before and after exposure to copper ions in aqueous solutions of different concentrations. The maximum absorbance wavelength varied between 530 nm for the low concentrations of Cu(II), and 565 nm for the high concentrations of Cu(II). Considerable increments were monitored in K/S upon increasing the concentration of the copper salt. The color of the TCFH-uncoated paper sheet exhibited an off-white color with high L^* (87.45), low a^* (-0.04) and low b^* (1.20). Upon increasing the concentration of the copper salt, the sensor strip showed considerable variations in CIE Lab values. L^* was highly decreased upon raising the total content of the copper ions to indicate the formation of darker color. a^* was increased and switched from negative to positive values representing a colorimetric change from green to red, whereas b^* decreased and switched from $+b^*$ to $-b^*$ to designate a colorimetric change from yellow to blue.

Table 4
Colorimetric parameters for the sensor paper strip at different concentrations of copper ions.

Cu(II) (ppm)	Color	L*	a*	b*	K/S	$\lambda_{\max}$ (nm)
Zero	Yellow	80.62	- 4.75	10.64	2.51	530
10	Yellow	80.11	- 2.83	9.76	2.83	532
50	Yellow	79.34	- 1.91	9.22	3.27	532
100	Orange	72.08	15.07	- 3.20	4.70	543
150	Red	69.00	15.21	- 4.28	4.91	546
200	Violet	65.54	13.73	- 5.05	6.02	555
250	Light Purple	60.29	13.10	- 5.81	6.88	557
275	Light Purple	54.10	10.36	- 6.53	7.25	557
300	Dark Purple	47.22	9.88	- 7.47	7.79	565
350	Dark Purple	45.96	8.57	- 8.01	8.10	565
400	Dark Purple	44.91	7.82	- 8.73	9.05	565
450	Dark Purple	44.64	7.31	- 9.55	9.76	565

Table 5
Colorimetric coordinates of the sensor dipstick for different heavy metals (300 ppm).

Metal ion (300 ppm)	Strip color	L*	a*	b*	K/S	$\lambda_{\max}$ (nm)
Ba(II)	Yellow	78.65	- 1.92	9.43	2.73	530
Co(III)	Blue	77.00	- 2.40	11.04	3.06	588
Mg(II)	Yellow	78.78	- 2.28	10.28	2.58	530
Cr(III)	Yellow	76.92	- 3.93	9.57	2.66	530
Li(I)	Yellow	76.60	- 2.78	10.15	3.01	530
Hg(II)	Yellow	80.18	- 2.25	11.95	2.97	530
Na(I)	Yellow	77.19	- 2.62	10.56	3.15	530
Sn(IV)	Yellow	78.32	- 3.07	11.08	2.30	530
Cu(II)	Purple	47.22	9.88	- 7.47	7.79	565
Fe(III)	Yellow	76.34	- 1.96	9.32	2.85	530
Al(III)	Red	77.03	- 3.17	9.56	2.73	550

4. Conclusions

In conclusion, we have synthesized quinoline-substituted tricyanofuranhydrazone colorimetric chemical sensor (TCFH) for the detection of Cu^{2+} ions in aqueous solutions. TCFH was synthesized using simple and efficient method via azo-couple reaction of TCF heterocycle with the diazonium chloride of 8-aminoquinoline. The produced sensor displayed high selectivity and sensitivity at microlevel for copper ions together with a color change from yellow to purple. Effective characteristics on the sensing performance of Cu^{2+} were evaluated, such as reversibility, competition tests, stability, and utility for optical detection in aqueous solutions. The reversibility was also investigated to indicate a good ability of TCFH to detect copper ions in a reversible process without fatigue. TCFH was employed for the determination of copper ions in tap water. TCFH exhibited positive solvatochromism and metallochromism demonstrating different colors that varies from yellow, orange, red, wine to purple in response to organic solvents of different polarities and different metal ions. Thus, TCFH demonstrated potential for effective and highly reversible chemical sensors for detecting solvent polarity and metal ions. Moreover, paper test strips immobilized with TCFH were successfully prepared and applied for the detection of copper ions at different concentrations in the range of 10^{-3} - 10^{-7} M in aqueous media. The detection process depends on the formation of a colored TCFH-Cu(II) complex on the surface of the paper strip. In comparison to previously described detection methods that require electronic/electric components, the current strategy introduces a naked-eye colorimetric sensor distinguished with simplicity, portability, fast detection, high sensitivity, and selectivity, as well as easy to operate over other techniques without the need of complicated instruments and trained staff. Moreover, the current detection technique can be simply applied to drinking water or industrial samples to detect Cu(II).

Declarations

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Declaration of Interest

Authors declare no conflict of interest.

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Scheme

Schemes 1 and 2 are available in the Supplemental Files section.

Figures

Figure 1

UV-Vis absorbance spectra of TCFH in various organic solvents.

Figure 2

UV-Vis absorbance spectra of TCFH in various aqueous solutions of different metallic salts.

Figure 3

UV-Vis absorbance spectra at different concentrations of the copper salt.

Figure 4

Cyclic voltammograms of tricyanofuranhydrazone (TCFH) in acetonitrile solution Redox potential versus Ag/AgCl (reference electrode) reported in a traditional three electrodes cell employing platinum as the counter electrode, glassy carbon as working electrode, and tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆; 0.2 M) as supporting electrolyte in CH₃CN.

Figure 5

UV-Vis absorption spectra demonstrates the electrochromic behavior.

Figure 6

Photographic images of paper test strips demonstrating colorimetric changes in the presence of copper ions at different concentrations.

Figure 7

Changes in the absorbance intensity of the paper strip due to increasing the concentration of copper ions.

Figure 8

Absorption intensities of paper sensor for many metallic ions (300 ppm).

Figure 9

SEM micrographs of blank (*left*) and TCFH-coated (*right*) paper strips.

Figure 10

Changes in absorbance intensity of the paper strip at 565 nm resulting from immersion in an aqueous solution of copper ions (conc. 300 ppm) at different pH values.

Figure 11

A suggested mechanism for the generation of TCFH-Cu(III) complex.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
- [Scheme2.png](#)
- [Graphicalabstract.docx](#)