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کمپلکس کنگوقرمز-مس به عنوان یک حسگر شیمیایی انتخابی به کمک حلال با روش فلورسانی و رنگ سنجی برای تعیین چندین آنالیت با چشم غیر مسلح در مقیاس نانومولار: یک سوئیچ برگشت پذیر فلورسانی CN^{-}/CO_3^{2-} به عنوان قفل صفحه کلید

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Copper Coordinated Congo-Red as a Solvent Assisted Selective Fluorometric and Colorimetric Chemosensor for Determination and Naked-Eye Detection of Multiple Analytes in Nanomolar Scale: A Reversible Fluorescent CN^{-}/CO_3^{2-} Switch that Works as Keypad Lock

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چکیده

در این تحقیق به معرفی کنگوقرمز، شناساگر رنگزای در دسترس و ساده، به عنوان میزبان شیمیایی گزینش‌پذیر جدید، برای شناسایی کاتیون مس و آنیون‌های سیانید و کربنات در محیط آبی که قادر است به صورت گزینشی شناسایی و اندازه‌گیری چندین آنالیت را انجام دهد، پرداخته شد. افزایش مقدار ۵ درصد حجمی/حجمی اتانول باعث افزایش چشمگیر در گزینش سیانید از طریق اثر مهاری بر مزاحمت آنیون سولفیت ایجاد کرد. ویژگی‌های حسگری کنگوقرمز در مخلوط حلالی آب- اتانول (۹۵:۵) مورد بررسی قرار گرفت و گزینش‌پذیری بسیار بالایی در مقابل آنیون سیانید حاصل شد. مکانیسم شناسایی منطقی این روش به وسیله تکنیک‌های اسپکتروفتومتری فرابنفش-مرئی، اسپکتروسکوپی FTIR و فلورسانی مورد تائید قرار گرفت. حد تشخیص برای این کاوشگر جدید ۹۰ و ۲۰ ($nmol\ L^{-1}$) به ترتیب به روش رنگ سنجی و فلورسانی اندازه‌گیری شد، که بسیار کمتر از ماکزیمم حد مجاز سازمان سلامت جهانی (WHO) ۹/۱($\mu mol\ L^{-1}$) و حد تشخیص گزارش شده توسط بسیاری از حسگرهای شیمیایی برای تشخیص سیانید می‌باشد. از طرفی کمپلکس سیانید با کنگوقرمز-مس توانایی تشخیص ۱۵ ($nmol\ L^{-1}$) از آنیون کربنات را با پاسخ‌دهی در زمان کوتاه (کمتر از ۳۰ ثانیه) و تشخیص با روش فلورسانی در حضور سایر آنیون-ها نشان داد. بسته به ترتیب افزایش یون‌های مس، سیانید و کربنات، محلول کنگوقرمز به عنوان یک قفل صفحه کلید با ورودهای مس، سیانید و کربنات عمل کرد. ورودهای یونی به رنگزا جدید مشابه قفل و کلید مولکولی الکترونیکی عمل می‌کنند. نتایج به صورت موفقیت‌آمیزی با داده‌های حاصل از روش مرجع اسپکتروفتومتری برای یون‌های سیانید مقایسه شد. این روش را برای تشخیص و تخمین کمّی یون‌های سیانید و کربنات در نمونه‌های حقیقی متنوع، ممکن می‌سازد از مزایای تجزیه‌ای این روش، شناسایی یون سیانید در پساب‌های آبکاری فلز(EPWW)، سرم خون انسان، نمونه‌های آب معدنی و آب آشامیدنی است که نتایج با شیوه‌های استاندارد معمول، مقایسه شده است.

واژه‌های کلیدی

حسگرشیمیایی رنگ‌سنجی؛ حسگر فلورسانی؛ حلال کمکی؛ تشخیص سیانید؛ ا تشخیص کربنات؛ قفل صفحه کلید.

Abstract

A new diazo based, Congo-Red-Cu , was developed to act as an ‘Off–On’ reversible fluorescent probe for CN^{-} detection. The changes in solvent composition has been shown greatly effective on selectivity of anion sensing through eliminate of sulfite interference. Increasing the amount of ethanol up to 5% (v/v) cause a dramatic development in selectivity of CN^{-} via inhibitory effect on sulfite interferent. The chemosensing behavior of the CR-Cu has been demonstrated through fluorescence, absorption, visual color changes and FT-IR studies. This chemosensor (CR-Cu) has been shown a significant visible color change and displays a remarkable fluorescent switch on in the presence of CN^{-} ions. The ‘in situ’ prepared CN^{-} complexes of CR-Cu shows high “Turn-Off” selectivity toward CO_3^{2-} over the other anions. The detection limits for CN^{-} were 90 and 20 nM for colorimetric and fluorometric methods respectively, that is far lower than the WHO guideline of 1.9 µM. The complex of CN^{-} with CR-Cu also displayed ability to detect up to 15 nM CO_3^{2-} among other competing anions through a fast response time of less than 30 s which is much lower than most recently reported chemosensor probes. It has been possible to build an INHIBIT logic gate for two binary inputs viz., CN^{-} and CO_3^{2-} by monitoring the fluorescence emission band at 446 nm as output. The development of fluorometric an ‘‘Off–On’’ reversible switch for three chemical inputs Cu^{2+}, CN^{-} and CO_3^{2-} ions and mimics a molecular level keypad lock.

Keywords

Colorimetric Chemosensor; Fluorescent Modulation; Solvent Assisted; Cyanide Recognition; Carbonate Recognition; Keypad Lock.

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1. INTRODUCTION

Anions are ubiquitous in nature and are involved in biological processes, in industrial and agricultural pollutions [1-2]. Hence, development of systems that can be able to detect anions selectively and selectively and easily, has received considerable attention in recent decades [3]. Among the various anions, cyanide is one of the primary concerns, because it is known as one of the most rapidly acting and powerful poisons. The maximum permissive level of cyanide in drinking water is therefore set at as low as 1.9 µM by the World Health Organization (WHO) [4], which is caused by the inhibition of cellular respiration in living creatures via its binding to a heme unit in the active site of cytochrome c when it is absorbed through the gastrointestinal track, skin or lungs [5]. As a result, any accidental release of cyanide salts from industries involved in gold mining, electroplating, metallurgy and the synthesis of nylon and other synthetic fibers and resins can cause serious environmental disasters [6]. Consequently, sensing the presence of toxic CN^- anion has been attracted much attention. Various analytical methods, such as chromatographic [7-10], have been developed for determination of CN^- ions. Among the various chemosensors, colorimetric and fluorometric types present many advantages, including high sensitivity, low cost, easy detection, and suitability as diagnostic tool for biological concerns. Therefore, development of colorimetric selective receptors or fluorescent sensors for the CN^- ions has attracted much attention in supramolecular chemistry [11].

Carbonate compounds were used extensively in the manufacturing of glass, paper, rayon, soaps, detergents and for dying processes in textile industries [12]. In view of its widespread occurrence in physiological, industrial and environmental samples, the accurate and rapid determination of carbonate is important. Thus, a number of methods have been developed for the quantification of carbonate [13-14]. However, maintenance and operational cost of these techniques are high and require adequate expertise.

On the other hand, the fluorescent optical sensing of a specific analyte and its integration into molecular level devices such as logic gates and molecular switches is an active area of research in supramolecular chemistry [15]. Numerous chemical systems have been developed which mimic various electronic devices performing digital operations [16-18]. Recently, a molecular keypad lock, which is an important electronic logic device, has been mimicked at the molecular level [19]. This device was used for numerous applications that in it access to a device is restricted to a particular person having the exact password to open the keypad lock. Such molecular devices, capable of authorizing password entries, has of high significance for information protection at the molecular scale [20]. Molecular machines stimulated by different chemical inputs would be of considerable interest for molecular computing [21].

Recently some workers started a new strategic methodology of anion detection by using receptor–metal ion ensemble as a recognition site. Such a type of receptor–metal ensemble can equip unsaturated coordination sites at the metal centers and furnish some geometrical preference for anions of a particular shape and size in aqueous medium [22]. Generally anions can modulate the optical properties of metal-based receptors via three ways: (i) by providing an extra coordination site to metal centers; (ii) by displacement of metal ion from the receptor center and; (iii) binding of anionic analytes to the receptor center through hydrogen bonding [23].

According to our knowledge, the previous receptors that reported above were organic based synthetic compounds. These are rather difficult to synthesize or required expensive instruments for detection. Taking this dilemma into consideration, we have undertaken an extensive research to explore easily available dyes that were demonstrated as high chromogenic and/or fluorescent receptors for cations and anions [24–31]. Our previous experience to sense CN^- using CR-Cu was not successful due to great disturbance caused by SO_3^- as major interference [32]. Herein, our efforts to overcome this problem revealed that increasing little amounts of a secondary solvent such as ethanol has greatly enhanced the selectivity through inhibition of sulfite. Based on the above facts we also investigated the anion recognition ability of CR-Cu as a receptor ensemble. Interestingly, CR-Cu gave selective Turn-On response for CN^- in H_2O/EtOH (95:5 v/v) medium with detection limits of 90 and 20 nM for the colorimetric and fluorometric methods, respectively. The complex of CN^- with CR-Cu displayed ability of detect up to 15 nM CO_3^{2-} over a large number of other anions. The detailed experimental and theoretical studies clearly established that, the present probe should be applicable as a practical system for monitoring of cyanide concentrations in aqueous samples. Thus our present strategy to exploit a simple receptor has its own worth for Cu^{2+}, $CN^-$and CO_3^{2-} detection due to its simplicity and robust nature having high sensitivity, low detection limit and ability to mimic INHIBIT logic function and a molecular level keypad lock with lucrative mechanism.

2. EXPERIMENTAL

2.1. Reagents

Reagents with analytical grades and demineralized water were used for preparing the solutions. CR dye (Congo-Red: disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl) diazenylphenyl] phenyl] diazenyl-naphthalene-1-sulfonate) was purchased from Merck, and used without further purification. Stock solutions (1.0×10^{-1} M) of Na^+, K^+, Ca^{2+}, Ba^{2+}, Mn^{2+}, Cr^{3+}, Co^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+} and Ni^{2+} were prepared by direct dissolution of proper amounts of nitrate salts in deionized water. Stock solutions (1.0×10^{-1} M) of anions were prepared by direct dissolution of proper amounts of potassium salts of anions (F^-, Cl^-, Br^-, I^-, $(COO)_2^{2-}$, $C_6H_5O_7^{3-}$ (Cit^{3-}), CH_3COO^- (AcO^-), SCN^-, NO_3^-, $H_2PO_4^-$, $C_6H_5COO^-$ (BzO^-), CN^-, CO_3^{2-}, HSO_3^- and HSO_4^-). Working standards were prepared daily by serial dilutions from the 1.0×10^{-1} M concentrated solution. All spectroscopic measurements were performed in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0).

2.2. Apparatus

A Shimadzu 1601 PC UV-Vis spectrophotometer with a quartz cuvette (path length=1cm) was used for recording all spectra and absorbance measurements in the wavelength range of 200-700 nm. H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0) without any indicator was used in the reference cell. All measurements were made in the absorbance mode. A Perkin-Elmer LS50 luminescence spectrophotometer with excitation and emission slits 10.0 nm was used for fluorescence measurements. FT-IR spectra were recorded on a Bruker Vector 22 Fourier Transmission Infrared spectrometer with wave numbers in the range of 400–4000 cm^{-1}. A Jenway 3510 pH-meter calibrated with two standard buffer solutions at pH 4.0 and 10.0 was used to measure the pH of the solutions. A Hamilton syringe (10 µL) was used to deliver small volumes of reagent into the cell.

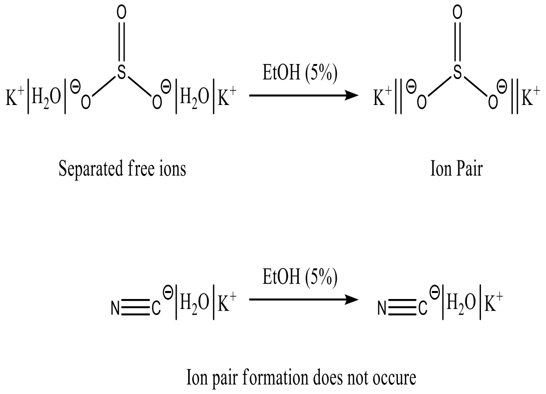
2.3. Sample preparation

Water samples were collected from two main sources in December 2015. All the water samples were prepared according to our previous publications [27]. Electroplating wastewater (EPWW) was used after metals recovery and 15 times dilutions. The serum sample was prepared from hospital (Namazi, Shiraz). A 0.5 mL of EPWW and serum samples were spiked with three CN^- levels, namely 25, 50 and 100 µg L^{-1} of standard stock solution of potassium cyanide and analyzed by the proposed method.

3. RESULT AND DISCUSSION

3.1. Solvent assisted selectivity

As it is mentioned by increasing the amount of ethanol, the anion sensing selectivity was shifted from SO_3^{2-} toward CN^-. As it is clear, addition of ethanol decreases the solvation of ions and therefore a tendency is emerged toward formation of ion pairs in the case of both KCN and K_2SO_3. Therefore it is obvious that sulfite ion carrying two minus charges possess greater tendency for ion pair formation however it does not occur for cyanide with one minus charge. So it can be easily understood that CN^- is a more powerful nucleophile than sulfite due to its freeness and activity (Scheme 1).



Scheme 1. Solvent assisted selectivity.

3.2. Metal binding studies

The metal binding ability of CR was initially evaluated by UV-Vis spectral analysis. The UV-Vis titrations were carried out in 25 µM aqueous solution of CR. Free receptor displayed split absorption bands around 344 and 498 nm ($\varepsilon_{498\ nm}=2.17\times10^4\ M^{-1}cm^{-1}$) in a H_2O/EtOH (95:5v/v) (10 mM HEPES buffer solution, pH 8.0) solvent system. Upon addition increasing concentrations of Cu^{2+} ions (1.0×10^{-9}–1.4×10^{-4} M) two bands around 344 and 498 nm were decreased. During the course of titration a beautiful UV-Visible spectral pattern was observed with a clear isosbestic point at 584 nm that indicates chemical interaction of Cu^{2+} with CR (Fig. 1). At this stage the color of solution became red from orange (left inset Fig. 1).

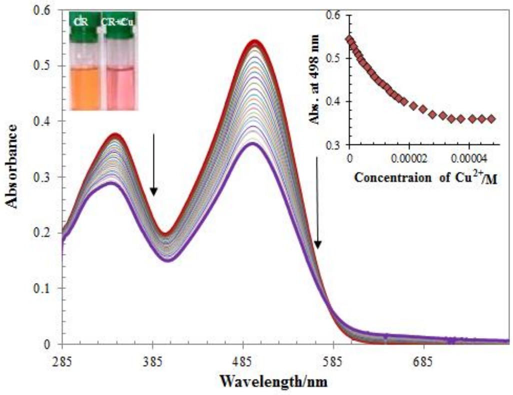


Fig. 1. UV–Vis spectra of CR (25.0 µM) upon addition of Cu^{2+} (1.0×10^{-9}–1.4×10^{-4} M), left inset: corresponding color change of CR and CR with Cu^{2+}(left to right), rigth inset: the plot of absorbance at 498 nm vs. concentration of Cu^{2+} in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0).

The absorption spectrum of CR was also perturbed by the separate additions of a number of metal ions (Na^+, K^+, Ca^{2+}, Ba^{2+}, Mn^{2+}, Cr^{3+}, Co^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, $Mg^{2+}$and Ni^{2+}) in non-similar fashion as it was observed in the case of Cu^{2+} (see ESI; Fig. S1†). Thus the colorimetric detection of Cu^{2+} solution of CR contained high selectivity.

The stoichiometry binding between CR and Cu^{2+} was conformed through mole ratio plot (see ESI; Fig. S2†) which clearly shows a 2:1 stoichiometry between guest (Cu^{2+}) and host (CR). The binding constant for the complex between CR and Cu^{2+} was determined by Benesi-Hildebrand analysis [33] (see ESI; Fig. S3†) of the corresponding absorption e titration data in 2:1 binding equation as $(1.78\pm0.51)\times10^{10}$ M^{-2} with satisfactory correlation coefficient value ($R^2=0.9977$) (Table 1). To check the practical applicability of CR as selective colorimetric chemosensor for Cu^{2+}; a competitive experiment was performed for the estimation of Cu^{2+} (400µM) in the presence of any of Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, (400µM). No significant difference in the absorbance was observed by comparing the absorbance with and without other metal ions (see ESI; Fig. S4†). The distinctive binding of Cu^{2+}, which suggested an interesting panorama to develop CR as a chemosensor for Cu^{2+} even in the presence of other metal ions.

3.3. Anion binding studies

3.3.1. CR-(Cu)$_2$ as a receptor

The generation of new complex observed only by adding CN^- to the solution containing [CR-(Cu)$_2$], whereas the other anions did not show any significant spectral change (Fig. 2). The behavior of fluorescence switch "On" of the [CR-(Cu)$_2$] complex was remarkably selective and only in presence of cyanide anions was observable. Addition of about 300 µM of cyanide anions increases the fluorescence intensity. On the other hand, nearly, there are no differences in the presence of other anions. Thus, the observed results strongly proved the selectivity of [CR-(Cu)$_2$] for detection of CN^-.

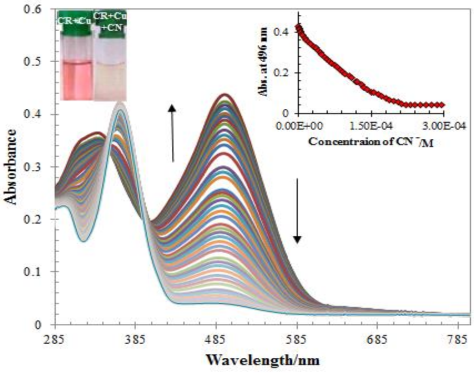


Fig. 2. UV–Vis spectra of CR (25.0 µM), with combination of Cu^{2+} (50.0 µM) and upon addition of CN^- (1.0×10^{-9}–3.0×10^{-4} M), of CR-Cu and CR-Cu with CN^- (left to right), rigth inset: the plot of absorbance at 496 nm vs. concentration of CN^- in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0).

To verify the generation of new complex from CN^- and [CR-(Cu)$_2$], we performed a UV–Vis and fluorescence experiment. The [CR-(Cu)$_2$] complex was titrated in presence of cyanide anions. When 50 µM of Cu^{2+} were added to CR, the chemosensor [CR-(Cu)$_2$] for cyanide detection was prepared in situ. Ability of [CR-(Cu)$_2$] for sensing CN^- in aqueous solution at room temperature was explored with UV–Vis absorption spectroscopy.

Table 1. Detection values of Cu^{2+} with CR, apparent detection values of receptor CR-Cu ensemble towards CN^- and receptor CR-Cu-CN toward CO_3^{2-}.

Receptor	Analyte	Spectroscopic Method	Stoichiometry	Association constants (M^{-2})	linear range (µM)	LOD (nM)
CR	Cu^{2+}	Colorimetry	1:2	$(1.78\pm0.51)\times10^{10}$	0.53-19.6	60.0
CR-Cu	CN^-	Colorimetry	1:2	$(1.15\pm0.22)\times10^{8}$	0.69-50.3	90.0
		Fluorimetry	1:2	$(1.67\pm0.18)\times10^{9}$	0.11-93.0	20.0
CR-Cu-CN	CO_3^{2-}	Fluorimetry	1:2	$(2.00\pm0.17)\times10^{8}$	0.13-90.3	15.0

Gradual addition of CN^{-} to $[CR\text{-}(Cu)_2]$ complex leads to a decrease in the absorbance bands near 498 and 344 nm that was also accompanied by a red shift (about 24 nm), from 344 to 368 nm (Fig. 2). More importantly, the CN^{-} sensing and the concomitant changes of absorption were clearly visible by "naked eye", as shown left inset in Fig. 2, which the red solution of $[CR\text{-}(Cu)_2]$ became colorless upon addition of cyanide.

The above mentioned facts also supported the results obtained from our fluorescence studies, i.e. new complex generated from the $[CR\text{-}(Cu)_2]$ in presence of cyanide (Fig. 3). To further understand the fluorescence switch "Off–On" property of the chemosensor, we have performed fluorescence titration experiments. The fluorescence intensity of the $[CR\text{-}(Cu)_2]$ was almost Off, the $[CR\text{-}(Cu)_2]$ solution was titrated by the addition of various amounts of cyanide ions. Fig. 3 shows that the intensity of the fluorescence emission increases with by growing up concentration of the cyanide anions to about 50 µM of CN^{-}, so the fluorescence intensity along with the maximum emission peak were almost 870 a.u. and color of the solution changed from a non-fluorescent color to fluorescent white color under UV light (right inset Fig. 3).

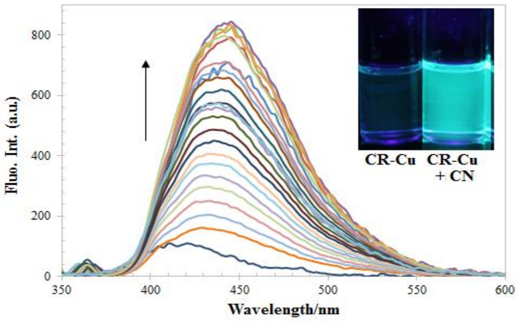


Fig.3. Fluorescence spectra (λ_{ex}=297 nm) of CR (25.0 µM), with various combinations of Cu^{2+} (50.0 µM) and upon addition of CN^{-} (1.0×10^{-9}–3.0×10^{-4} M), in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0) (λ_{ex} = 297 nm), Inset: photograph taken under illumination of a handheld UV lamp at 365 nm.

As the fluorescence intensity and absorbance spectrum is recorded within 30 s after cyanide addition, and these does not change by spending time, so the monitoring system is a real-time and stable (see ESI; Fig. S5† and S6†). The results of the spectroscopic studies also indicate that $[CR\text{-}(Cu)_2]$ chemosensor forms a new complex during the addition of cyanide anions. The formation of new complex from $[CR\text{-}(Cu)_2]$ in the presence of cyanide is also monitored by quantum yield calculation [34]. Fluorescence quantum yield (λ_{em}=446 nm) of $[CR\text{-}(Cu)_2]$ was found at 0.052 and addition of cyanide anion to $[CR\text{-}(Cu)_2]$ complex increased the quantum yield to 0.68. The changes in absorbance spectra and fluorescence intensity upon addition of CN^{-} are completely distinguishable, as shown in Fig. 2 and 3. Under these conditions, CN^{-} could be determined by UV–Vis and fluorescence spectroscopy.

As a highly selective probe for the target analyte, the good capacity of resisting disturbance was required. Hence, the competition experiments in the presence of potentially competitive anions were performed by UV-Vis absorption and fluorescence spectra for each individual anion. Except for CN^{-}, addition of other anions (300.0 µM) to $[CR\text{-}(Cu)_2]$ do not produce significant absorbance and fluorescence intensity changes (see ESI; Fig. S7† and S8†). Increasing emission intensity at 446 nm was observed only upon addition of CN^{-}.

For all practical purposes the interactions between $[CR\text{-}(Cu)_2]$ ensemble and cyanide have been considered. Hence we could only determine the apparent binding constants of cyanide and $[CR\text{-}(Cu)_2]$ ensemble by considering 2:1 stoichiometry binding, respectively. The Benesi-Hildebrand analysis (see ESI; Fig. S9† and S10†) of fluorescence UV-Vis titration data yielded the value of binding constants as $(1.67\pm0.18)\times10^{9}$ M^{-2} (R^2=0.9967) and $(1.15\pm0.22)\times10^{8}$ M^{-2} (R^2=0.9956), respectively (Table 1.).

The practical applicability of $[CR\text{-}(Cu)_2]$ as a selective colorimetric and fluorescent chemosensor for CN^{-} has been demonstrated by performing the competitive anion interference experiments. For that, tested anions (300.0 µM) were added to a solution of probable complex, $[CR\text{-}(Cu)_2]$ and reversibly by the CN^{-}ion was added to a solution of $[CR\text{-}(Cu)_2]$ containing excess of other anions (Fig.4 & Fig.5). No significant variation in absorbance and emission were observed in comparison to emission spectra of $[CR\text{-}(Cu)_2]$ in either condition. These results demonstrated that the CN^{-} recognition by $[CR\text{-}(Cu)_2]$ is barely interfered by other coexisting anions.

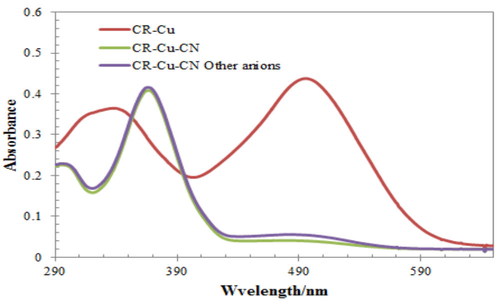


Fig. 4. UV-Vis spectra of $[CR\text{-}(Cu)_2]$, $[CR\text{-}(Cu)_2]$ +50.0 µM of CN^{-} ion, and $[CR\text{-}(Cu)_2]$+anions (300 µM of F^{-}, Cl^{-}, Br^{-}, I^{-}, $(COO)_2^{2-}$, Cit^{3-}, AcO^{-}, SCN^{-}, NO_3^{-}, $H_2PO_4^{-}$, BzO^{-}, HSO_3^{-} and HSO_4^{-}+50.0µM of CN^{-} in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0).

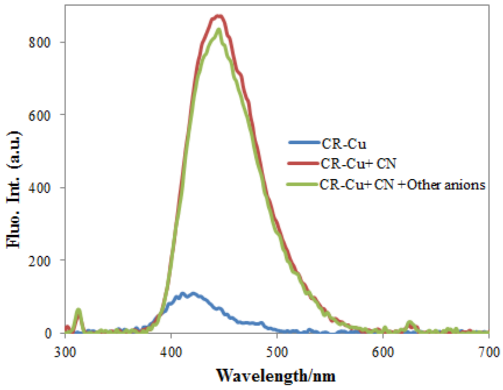


Fig. 5. Fluorescence spectra of [CR-$(Cu)_2$], [CR-$(Cu)_2$]+50.0 µM of CN^-, and [CR-$(Cu)_2$]+anions (300 µM of F^-, Cl^-, Br^-, I^-, $(COO)_2^{2-}$, Cit^{3-}, AcO^-, SCN^-, NO_3^-, $H_2PO_4^-$, BzO^-, CO_3^{2-}, HSO_3^- and HSO_4^-+50.0 µM of CN^- in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0) (λ_{ex} = 297 nm).

3.3.2. [CR-$(Cu)_2$]$(CN^-)_2$ as a receptor

The receptor [CR-$(Cu)_2$]$(CN^-)_2$ was not changed in its fluorescent spectrum for the presence of different anions such as F^-, Cl^-, Br^-, I^-, $(COO)_2^{2-}$, Cit^{3-}, AcO^-, SCN^-, NO_3^-, $H_2PO_4^-$, BzO^-, CN^-, HSO_3^-, CO_3^{2-} and HSO_4^- (see ESI; Fig. S11†). However, the fluorescence of [CR-$(Cu)_2$]$(CN^-)_2$ ensemble was almost quenched in presence of carbonate ions (Fig.6). Other chosen anionic analytes were unabled to produce any quenching effect to [CR-$(Cu)_2$]$(CN^-)_2$ ensemble (Fig.7). The 25 µM aqueous solution of CR having 50 µM of Cu^{2+} and 50 µM of $CN^-$was treated separately with gradual additions of carbonate ions. The emissive nature of [CR-$(Cu)_2$]$(CN^-)_2$ ensemble was almost completely quenched upon addition of 150 µM of carbonate ions (right inset Fig. 6). Upon increasing concentration of CO_3^{2-} (0.001–150.0 µM) to a solution of [CR-$(Cu)_2$]$(CN^-)_2$, relative fluorescence intensity decreased significantly at 446 nm along with the Stern-Volmer quenching constant $(1.62 \pm 0.12) \times 10^4$ L mol^{-1} (R^2=0.9950) whereas, the intensity of emission band 446 nm decreased (see ESI; Fig. S12†) and the quantum yield of the emission band were obtained 0.052. Color of solution appeared as non-fluorescent under UV light (right inset Fig.6).

For all practical purposes the interactions between [CR-$(Cu)_2$]$(CN^-)_2$ ensemble and carbonate anion have been considered. Hence we could only determine the apparent binding constants of CO_3^{2-} and [CR-$(Cu)_2$]$(CN^-)_2$ ensemble by considering 2:1 binding stoichiometry. The Benesi-Hildebrand analysis (see ESI; Fig. S13†) of fluorescence titration data yielded the value of binding constants as $(2.00 \pm 0.17) \times 10^8$ M^{-2} (R^2=0.9975) (Table 1.).

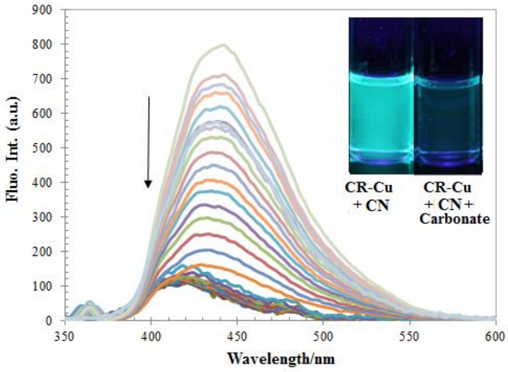


Fig. 6. Fluorescence spectra (λ_{ex}=297 nm), of [CR-$(Cu)_2$]$(CN^-)_2$ upon addition of CO_3^{2-} (1.0×10^{-9}–1.5×10^{-5} M) in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0), Inset: photograph of [CR-$(Cu)_2$]$(CN^-)_2$ and [CR-$(Cu)_2$]$(CN^-)_2$ with carbonate (left to right) taken under illumination of a handheld UV lamp at 365 nm.

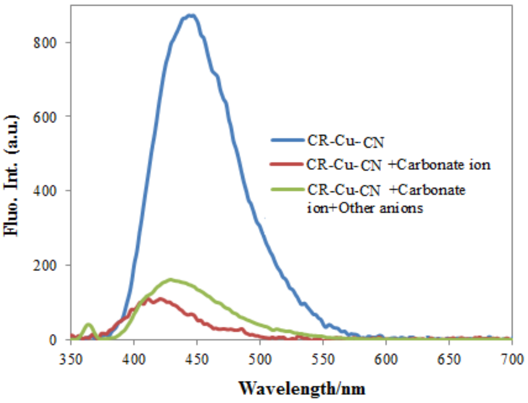


Fig. 7. Fluorescence spectra of [CR-$(Cu)_2$]$(CN^-)_2$, [CR-$(Cu)_2$]$(CN^-)_2$+50.0 µM of CO_3^{2-}, and [CR-$(Cu)_2$]$(CN^-)_2$+anions (300 µM of F^-, Cl^-, Br^-, I^-, $(COO)_2^{2-}$, Cit^{3-}, AcO^-, SCN^-, NO_3^-, $H_2PO_4^-$, BzO^-, CN^-, HSO_3^- and HSO_4^-+50.0 µM of CO_3^{2-} ion in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0) (λ_{ex}=297 nm).

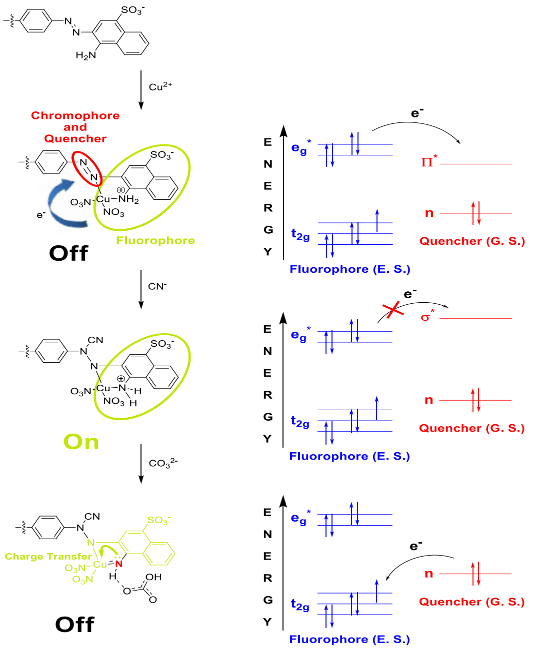
3.4. Effect of pH

To investigate the influence of the different buffer solutions on the spectra of receptors, some experiments were performed to find a suitable pH span, which receptors can selectively and efficiently detect cations and anions (Cu^{2+}, CN^- and CO_3^{2-}). The receptors solution was mixed with Cu^{2+}, CN^- and CO_3^{2-} in H_2O/EtOH (95:5v/v) (10 mM buffer solution). The buffers were: pH 3.0–4.0, CH_3COOH/NaOH; pH 4.5–7.0, MES/NaOH; pH 7.0–10.0, HEPES; pH 10.0–11.4, CABS. As shown in ESI Fig. S14, the addition of Cu^{2+} and CN^- have greatest impact on the absorbance spectra over a comparatively wide pH range (7.0–9.0). ESI Fig. S15, the addition of CO_3^{2-} has greatest impact on the emission spectra over a comparatively wide pH range (7.0–9.5).

Consequently, the present chemosensors may be used to detect Cu^{2+}, CN^{-} and CO_3^{2-}in approximately pH ranges 7.5–9.0. Therefore, further UV-Vis and fluorescent studies were carried out in HEPES buffer solution (pH= 8.0).

3.5. Discussion of the reaction mechanism of anions with Congo-Red based receptors

To investigate the details of photochemical On-Off or Off-On switching related to each step we have proposed a reasonable mechanism based on current evidences obtained in the experiments, data in literature and FT-IR studies. Olivucci *et. al*. [35] reported that the azo moiety in azo dyes acts as an efficient quencher for fluorophores through charge or hydrogen atom transfer. Therefore, it is clear that both CR and its copper complex (CR-Cu_2) could not be fluorescent due to presence of N=N moiety in their structures. Addition of CN^{-} into the N=N annihilates the azo quencher upon conversion into N-N-CN which is not further a quencher. Subsequently, the fluorescence of CR-Cu-CN adduct switches off upon addition of CO_3^{2-} which seems to be due to proton abstraction and simultaneous binding of hydrogen carbonate via hydrogen bonding into the amine center, subsequent, electron transfer from amine lone pair into the copper renders the amine nitrogen as a quencher (Scheme 2).



Scheme 2. The molecular structure of Congo-Red: (disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl) diazenylphenyl] phenyl] diazenyl-naphthalene-1-sulfonate), CR and the proposed host-guest binding mode of CR in the presence of Cu^{2+}, cyanide and carbonate ions in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0).

To further confirm the mode of interaction between receptor and anions a characterization was performed by FT-IR using pure Congo-Red as reference which is shown in Fig. 8. As it was cleared in Fig. 8 there are some changes between the receptor CR-Cu spectra and subsequent, complexes with anions. The N=N absorption peak centered at 1600 was disappeared due to pi-bond dissociation upon addition of cyanide anion into N=N. In addition, new absorption peaks were emerged in 2080-2250 cm^{-1} when CN^{-} was added into CR-Cu. New absorption peak at 3530 cm^{-1} in the vicinity of amine NH group were appeared after addition of carbonate shows the formation of hydroxyl group of hydrogen carbonate moiety. Multiple absorption peaks appeared in vicinity of N=N absorption peak from 1620-1680 were related to hydrogen carbonate C=O groups. As it can be seen in Scheme 2, carbonate binding site locates on amine NH's which is the fluorophore and so carbonate does not affect the chromophore therefore no color change was took place after addition of carbonate.

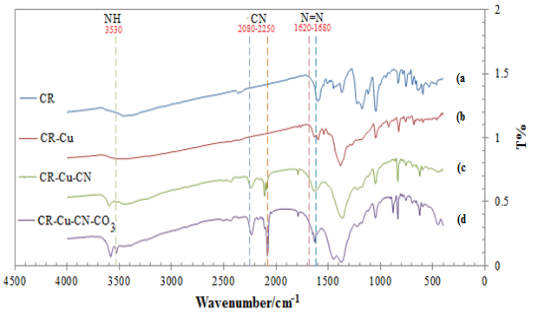


Fig. 8. Standard FT-IR spectras of **(**a) CR; (b) CR-Cu (c) CR-Cu+CN^{-} and (d) CR-Cu-CN+CO_3^{2-}.

3.6. Binding and interpretation of related logic gates and *keypad lock studies*

The ‘‘On-Off’’ switching behaviour of [CR-$(Cu)_2$] can be demonstrated with the help of binary logic. The output signals were measured as the fluorescence emissions at 446 nm of the [CR-$(Cu)_2$] being ‘‘1’’ when fluorescence emission is high and ‘‘0’’ when fluorescence emission is low. The two chemical inputs of CN^{-} and CO_3^{2-} are considered as ‘‘1’’ when they are present and ‘‘0’’ if they are absent (Fig. 9). When both the CN^{-} and CO_3^{2-} inputs were absent, they were read as ‘0’ and for their presence were ‘1’. On the other hand, CN^{-} ion enhanced the fluorescence significantly, and the output signal was read out as ‘1’ and the gate was ‘‘On’’. However, when both the inputs were presented together, then the output was ‘0’ and the gate was ‘‘Off’’. These studies clearly demonstrated a INHIBIT logic gate for these ions at 446 nm (Fig. 10).

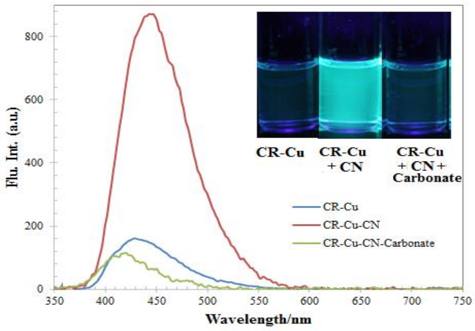
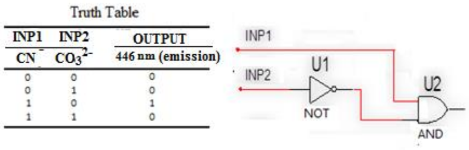


Fig. 9. Fluorescence of CR-Cu (5.0 µM), with CN^- and CR-Cu-CN with CO_3^{2-} (λ_{ex}=297 nm) and right inset photograph as mentioned taken under illumination of a handheld UV lamp at 365 nm in H_2O/EtOH (95:5 v/v) (10 mM HEPES buffer solution, pH 8.0).


Truth Table

INP1 CN^-	INP2 CO_3^{2-}	OUTPUT 446 nm (emission)
0	0	0
0	1	0
1	0	1
1	1	0

Fig. 10. The complementary INHIBIT logic gate and its truth table. INP_1 and INP_2 represent Input CN^- and Input CO_3^{2-}, respectively.

On the other hand, the results of our research on the chemical inputs (Cu^{2+}, CN^-, CO_3^{2-}), the CR can switch between different fluorescence emission cases ‘‘Off-On-Off’’. Research photophysical behavior of CR was performed by using various combinations of three chemical inputs (Cu^{2+}, CN^- and CO_3^{2-}, 25, 50 and 50 µM each respectively). The three chemical inputs Cu^{2+}, CN^- and CO_3^{2-}, were selected as ‘‘C’’, ‘‘N’’ and ‘‘A’’, respectively.

Of six maybe input combinations (CNA, ACN, NCA, NAC, CNA, CAN), only the CAN gave a vary fluorescence output signal (Fig. 11). For the CAN input, with the addition of 25 µM of Cu^{2+} ions, the fluorescence emission at 446 nm gets completely quenched ‘‘Off’’ and the compound remains in the ‘‘Off’’ with addition of 50 µM of CO_3^{2-} ions (Fig. 9). The addition of 50 µM of CN^- ion results in reviving of fluorescence emission at 446 nm ‘‘On’’ (Fig. 9). The selectivity and reversibility of CR helps us to develop the sequence dependent logic circuit capable of memory functions. The most important feature of the keypad lock system is the dependence of the output signal on the correct order of the input signals [36]. The CR operates as a keypad lock sequence of three chemical inputs (Cu^{2+}, $CN^-$and CO_3^{2-}). The three chemical inputs Cu^{2+} (25 µM), CO_3^{2-} (50 µM), and CN^- (50 µM) ions were defined as IN1, IN2 and IN3, respectively. The sequence of adding Cu^{2+}, CN^- and CO_3^{2-} ion leads to different input series that determine the value of the output signal at 446 nm (Table 2). Fig. 11 shows the fluorescence emission as output signals at 446 nm obtained from six possible input combinations.

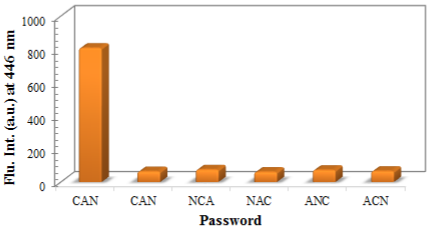


Fig. 11. Fluorescence emission output corresponding to six possible input combinations at 446 nm bar graph representation.

Table 2. Truth table for the molecular keypad lock system upon varying The sequence of the C, N and A input signals

Sequence	IN 1	IN 2	IN 3	Output
1	C	A	N	1
2	C	N	A	0
3	N	C	A	0
4	N	A	C	0
5	A	N	C	0
6	A	C	N	0

Fig. 12 develops a molecular keypad lock that ‘‘opens’’ by inserting the sequences of three input keys, C, A and N, respectively. The TRUE output signal‘‘1’’ can be used to ‘‘open’’ the molecular keypad lock while the FALSE signal‘‘0’’ failed to open the lock, which can result in the ‘‘alarm’’ signal indicating the wrong password. Thus, exact codes would be possible by assigning the correct order of input signals so that only one code would work. This concludes that a security code “CAN” is developed, which one can use to open fluorescent lock of CR at 446 nm.

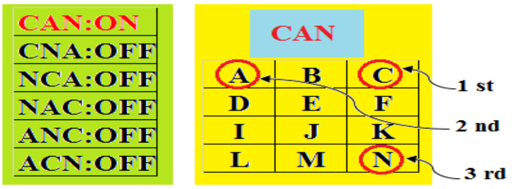


Fig. 12. Molecular keypad lock applicable for generating a strong emission at 446nm, only when a correct password (CAN) is entered. Keys C, A, and N hold the relevant Cu^{2+}, CN^- and CO_3^{2-} ion, respectively.

3.7. Linearity, sensitivity and precision for the proposed procedure

In order to obtain the linearity response, a 10-point (in triplicate) calibration curve, based on peak areas, was constructed using a least-square linear regression analysis of aqueous solutions. Concentration ranges of cyanide and carbonate, LODs, stoichiometry and association constants were summarized in Table 1. To evaluate the repeatability and the intermediate precision, aqueous cyanide samples (n=3) at three concentration levels 5.0×10^{-6}, 1.0×10^{-5} and 1.3×10^{-5}M were measured in one single day and 2 day per week during 1 month, for CN^- and CO_3^{2-} ions respectively. The repeatability, expressed as relative standard deviation, was in the range 2.2–3.7%. Intermediate precision, expressed as relative standard deviation, was in the range 3.6–4.3%. The accuracy of the proposed method for carbonate ions was checked by the following procedure: Different synthetic samples with different amounts of $CaCO_3$ were prepared. These samples were analyzed using the proposed method. Recoveries between 97.0 and 104.0% were obtained in all cases, as it can be seen in Table 3.

Table 3. Recoveries obtained for synthetic calcium carbonate samples by using the proposed method detection (mean±standard deviation, n=5).

Added (CO_3^{2-} μg mL^{-1})	Found (CO_3^{2-} μg mL^{-1})	Recovery (%)
0.5	0.51±0.03	102.0
1.0	0.99±0.05	99.0
2.0	2.08±0.04	104.0
4.0	3.88±0.02	97.0

3.8. *Analysis of CN^- in real samples*

The proposed method was applied for determination of cyanide in real samples. The experimental results are tabulated in Table 4 while each sample was analyzed in five times. The accuracy of the analytical procedure was therefore evaluated by recovery experiments after spiking the EPWW, human serum and tap water samples at three cyanide concentration levels, namely 25, 50 and 100 μg L^{-1}. The results are evaluated by reference method (EPA 9014-1 method). The first two levels are below or equal to the E.U. limit in drinking water [37], while the latter level is below the U.S. EPA limit [38]. Statistical treatment of data using F test [39] revealed that, no significant differences exist between the two variances of the developed and the EPA 9014-1methods. The calculated values of F are lesser than the tabulated F-value (6.39) for five replicate measurements. The Student's *t*-test [39] was also applied to the analytical data of the developed and EPA 9014-1methods. No significant difference was observed between the two methods. The tabulated t-value at 95% confidence limit was 2.541 and the calculated t value by applying Student's t-test to the results of EPWW sample was found lesser for five measurements.

4. CONCLUSIONS

In summary, we have demonstrated successfully 'Off-On-Off' switching of a diazo base by Cu^{2+}, CN^- and CO_3^{2-} ion. We believe that the simplicity and sensitivity of CR with high detection limit for Cu^{2+}, $CN^-$and CO_3^{2-} in aqueous medium, will definitely place CR on the upper shelf in the library of fluorescent receptors for ionic analytes. Moreover, application of CR as potential logic gate and molecular switches adds further luster to the same. Advantages offered by the proposed method, compared with those suggested previously (Table 5) indicates that they have lower detection limit [9, 27–29, 41–44, 46, 48] and wider working range of measurements.

ACKNOWLEDGEMENT

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Table 4. Analysis of CN^- (μg L^{-1}) in water sample by the developed Spectrofluorimetric (A) UV-Vis spectroscopy (B) and EPA9014-1 method (C) methods (mean±standard deviation, n =5).

	CN^- (Added)	CN^- (Found) A	CN^-(Found) B	CN^-(Found) C
Tap water	–	NDa	ND	ND
	25.0	24.9±1.1	25.5±2.3	25.7 ±1.3
	50.0	50.3 ±1.4	50.8±1.2	50.5 ±1.2
	100.0	98.9±2.2	99.4±2.9	99.6 ±2.1
EPWW b	–	151.2±2.1c	150.7±1.7c	150.9±3.2
	25.0	176.6±2.8	177.0 ±1.2	177.1±1.6
	50.0	202.6±2.6	202.9±3.6	202.5±2.5
	100.0	252.9±1.2	252.2±1.5	253.0 ±2.7
Human serum	–	ND	ND	ND
	25.0	25.5±2.7	25.4±2.1	25.3 ±1.8
	50.0	50.4±1.3	49.9±1.6	50.3 ±2.0
	100.0	99.3 ±1.6	98.8 ±3.2	99.5 ±2.7

[a] ND Not Detect; [b] Electroplating wastewater; [c] Value determined after 15 times dilution.

Table 5. Analytical features of the developed and some of the recently published methods for the cyanide determination**.**

Ref.	Application	LOD ($\mu g\ L^{-1}$)	Range ($\mu g\ L^{-1}$)	Recovery %	Analysis time (min)
[40]	Drinking water	1.9	5.2-52	–	–
[41]	Pond, ocean, river water	5.0	10–3000	94.6–102.0	>3.0
[9]	Tap, mineral water	2.5	7.5–200	94.2–103.6	7.5
[42]	–	130.0	–	–	–
[43]	–	39.0	520–2600	–	–
[44]	Tap, bottle &groundwater	16.0	50–2000	99.0–109.0	–
[45]	–	–	520	–	–
[46]	Industrial waste water	20.0	40–1200	97.6–99.2	0.33
[47]	Water & serum	6.3×10^4	$1.0–25\times10^5$	100.0–104.0	5.0
[48]	Mine effluent	50.0	10–80,000	88.1–96.4	15.0
[27]	Water & serum	11.2	86–1524	96.3 – 102.8	<0.5
[28]	EPWW[a], Water & serum	12.5	117–2174	96.8 – 102.4	<0.17
[29][b]	EPWW, Water & serum	7.8	52–462.8	96.4 – 101.4	<1.0
[29][c]	EPWW, Water & serum	1.04	3.4–605.8	98.8 – 102.5	<1.0
Present work[b]	EPWW, Water & serum	2.34	17.9–1307.8	96.4 – 101.4	<1.0
Present work[c]	EPWW, Water & serum	0.52	2.9–2418	98.8 – 102.5	<1.0

[a] Electroplating wastewater; [b] Colorimetric method; [c] Fluorimetric method

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