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# A New Fluorescent Chemosensor for Selective and Sensitive Detection of $Mn^{2+}$ in Acidic Medium

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## Abstract

Recently, fluorescent sensors have attracted considerable attention in their sensitive and selective determination of heavy metal ions in the aqueous acidic medium due to their advantages such as low cost and easy handling. In this study, the bathocuproine (BCP) compound was used as a fluorescent chemosensor. The selectivity and sensitivity of BCP have been investigated against some metal ions of biological and environmental importance. The results obtained from the ultraviolet-visible region (UV-vis.) and the fluorescence spectroscopy experiments revealed that the BCP sensor showed selectivity and sensitivity only to Manganese (II) ions in the experimental conditions studied. In addition, the binding stoichiometry of BCP and $Mn^{2+}$ was determined to be 1:1 by the Benesi-Hildebrand method.

## Keywords

Fluorescent Chemosensor, $Mn^{2+}$, Fluorescence Quenching, Selectivity

## 1. Introduction

Thanks to rapid developments in modern industry and agriculture, pollution from heavy metals and transition metals has become very important. Therefore, these heavy metals [1] and transition metals [2] must be traced and determined. Manganese is an element that is abundant in our environment and in foods. The average amount of manganese our body should take daily is 5 mg/kg [3] [4] [5]. It is included as a structural component in a variety of enzymes and in photosynthetic devices [6] [7]. High levels of manganese cause disorders in the central nervous system [8]. Therefore, there is a need to develop methods that can selectively separate manganese from other metals. Although it has different oxidation

numbers in nature, the $Mn^{2+}$ structure is very stable in environmental samples. Therefore, although there are manganese ions with different oxidation numbers, it is even more important to develop a high precision and accuracy method, especially for the determination of $Mn^{2+}$ ions [9].

Many techniques have been used in the determination of different heavy metals until today. Unfortunately, these techniques involve very time-consuming, expensive, and complicated sample preparation processes. As an alternative to these techniques, a variety of studies involving chemosensors have been reported [10]-[15]. Fluorescence chemosensors have been widely used for the determination of metals due to their many advantages, such as high sensitivity, rapid response, and easy preparation [16] [17]. Despite those advantages, chemosensors for manganese detections are very rare [18] [19] [20]. Therefore, it is still a great challenge to develop a highly selective and sensitive sensor for the recognition of $Mn^{2+}$ ions.

In this study, bathocuproine (BCP) was used as a chemosensor. For the first time in the literature, the BCP compound was used as a chemosensor for Mn determination. By using its UV-vis. absorption and fluorescence spectroscopy, selectivity, and sensitivity studies of some of the selected metal ions of the biological, chemical, and environmental importance of the sensor in question were conducted. According to the results obtained from these studies, this sensor was found to show fast response, high sensitivity, and selectivity to Manganese (II). The work was conducted with acetate buffer at pH 3. In addition, the binding stoichiometry between the molecule and Manganese (II) was investigated and it was shown to be 1:1 ($Mn^{2+}$/BCP). The obtained results showed that BCP can be used for the selective determination of Manganese (II) ions in an aqueous acidic medium.

## 2. Experimental

### 2.1. Chemicals and Solutions

Solvents and reagents used in this study were purchased from commercial companies and used as-is without any purification. Bi-distilled pure water was used throughout all experiments. Metal salts, in $Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Ca^{2+}$, and $Mn^{2+}$ chlorides were obtained from Merck along with BCP and dimethyl sulfoxide (DMSO) solvent. Acetate buffer was obtained from Sigma Aldrich.

### 2.2. General Instrumentations

PG Instrument T70+ model spectrophotometer (UV-vis.) was used for the measurement of absorption spectra. Fluorescence measurements were made using the Varian Agilent Cary Eclipse instrument which was performed in quartz cells of $1 \times 1$ $cm^2$ size. Experimental measurements and studies were carried out at room temperature. pH measurements were made with an "a pocket pH meter" (Hanna Instruments Mauritius), calibrated with standard acetate buffer solution.

### 2.3. General Procedure for Spectral Experiments

Stock solutions of $Mn^{2+}$ and other metal salts were prepared in distilled pure water. The stock solution of the chemosensor BCP was prepared at 1 mM concentration in dimethyl sulfoxide (DMSO) medium and then diluted to μM concentrations using DMSO/$H_2O$ (v/v, 2:1) and 10 mM acetate buffer at pH 3. 1 mM stock solutions were prepared in deionized water using $Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Ca^{2+}$, and $Mn^{2+}$ chloride salts. Solutions of DMSO/$H_2O$ (2:1, v/v) and 10 mM acetate buffer at pH 3 at 25˚C were prepared for measurement of the ultraviolet-visible region and fluorescence spectra at μM level. Fluorescence spectra were recorded at the excitation wavelength of 298 nm.

## 3. Results and Discussion

### 3.1. Effects of pH Values

The effect of pH values on the chemosensor BCP sensitive to $Mn^{2+}$ was studied by measuring the absorption sensitivity of the chemosensor BCP in the presence of $Mn^{2+}$ ions. As seen in Figure 1, when pH values are lower than 4, the absorbance value of BCP/$Mn^{2+}$ is high at 298 nm, and if the pH range is between 4 and 10, the absorbance value of BCP is almost unchanged. Therefore, in this study, 3 were chosen as the optimum pH.

### 3.2. Response Time

Response time is an important reference for the sensitivity of BCP to $Mn^{2+}$. The changes in absorption values of BCP at 298 nm in the presence of $Mn^{2+}$ in a wide time interval ranging from 0 to 60 minutes were examined. As seen in Figure 2, it was observed that the absorption values did not change in this time interval. Under these experimental conditions, BCP appears to give a rapid reaction to $Mn^{2+}$. A schematic representation of the resulting complex is shown in Figure 3.

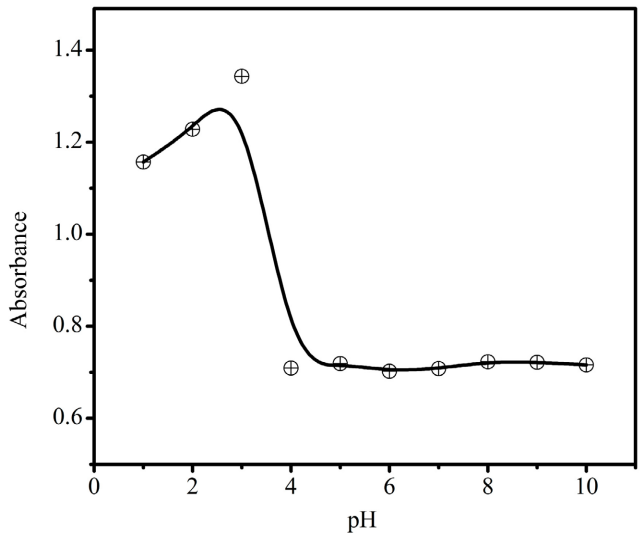


Figure 1. Absorbance values recorded for BCP at varying pH values in the presence of $Mn^{2+}$ ions.

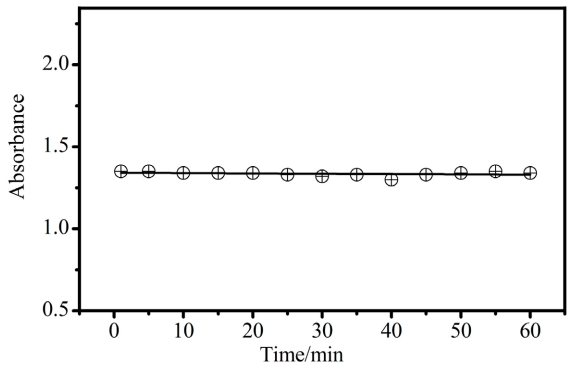


**Figure 2.** Time profile of BCP in the presence of $Mn^{2+}$ ions (pH = 3, acetate buffer at 298 nm).

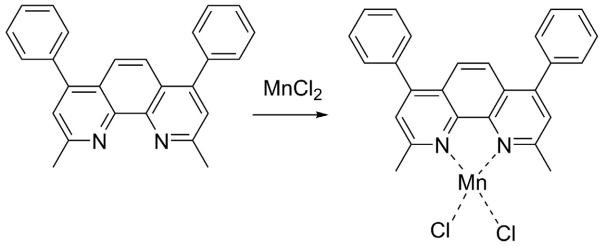


**Figure 3.** Schematic representation of (BCP) $MnCl_2$.

### 3.3. UV-Vis. Absorption and Fluorescence Spectral Response

The sensitivity and selectivity properties of chemosensor BCP for some biologically and environmentally important metal ions have been investigated in acetate buffered medium (DMSO/$H_2O$, v/v, 2:1, at pH 3). Firstly, absorption spectra were measured between 250 - 400 nm wavelengths using UV-vis. absorption spectrophotometer (**Figure 4**).

As seen in **Figure 4**, a sharp peak of BCP appears at 298 nm. On the other hand, when $Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Ca^{2+}$, and $Mn^{2+}$metal ions (1.0 Equiv.) were added to the chemosensor BCP (50 μM) solution and the absorption spectra were taken, no significant change was observed for the first six ions. An increase in absorption spectrum was observed only when the $Mn^{2+}$ (1.0 Equiv.) ion was added to the solution medium where the sensor is located. According to these experimental results, the chemosensor BCP has been found to show significant optical behavior change in terms of absorption only against $Mn^{2+}$ ions.

Fluorescence spectroscopy measurements in the study were also conducted within the same physical conditions. The excitation wavelength was selected to be ($\lambda_{exc}$ = 298 nm) when taking the fluorescent spectrum. Emission peaks were recorded between 350 nm and 500 nm.

As shown in **Figure 5**, the chemosensor BCP gave a fluorescence emission band while it is in free form. Fluorescence intensity doubled when the $Mn^{2+}$ metal ion was added to the chemosensor BCP solution. In contrast, no significant change in emissions was observed when other metal ions were added separately to the BCP solution and fluorescence spectra were taken. Considering the

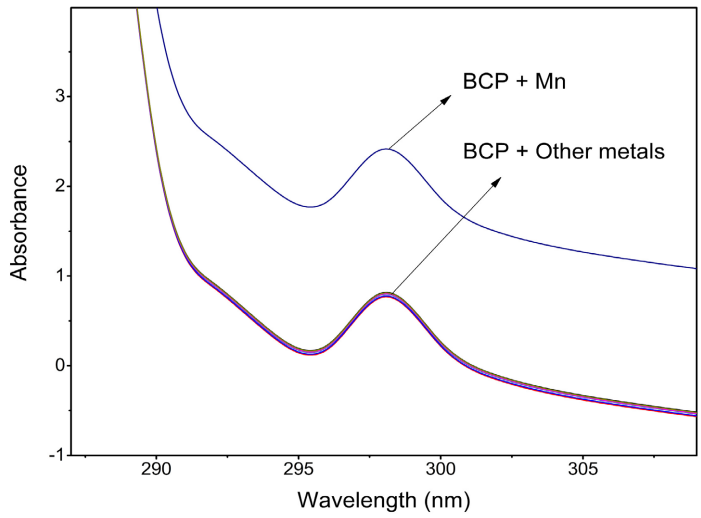


**Figure 4.** The UV-vis. absorption spectra are given by the chemosensor BCP in free form and after the addition of metal ions.

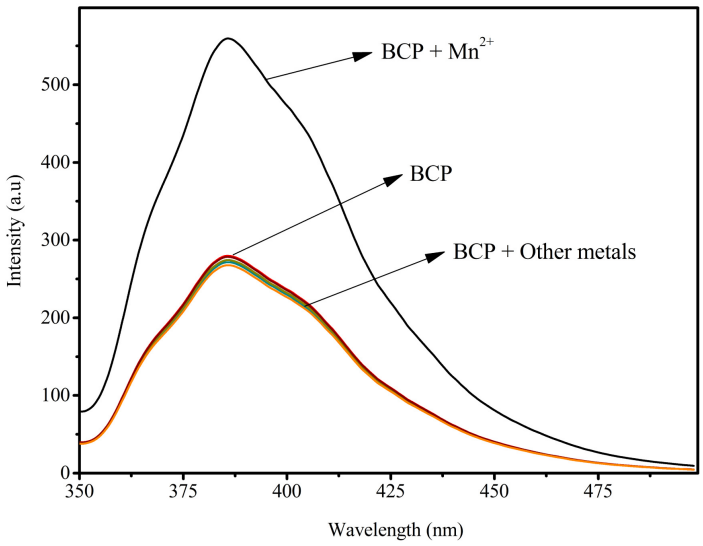


**Figure 5.** Fluorescence spectra given by chemosensor BCP in free form and after adding metal ions ($\lambda_{exc}$ = 298 nm).

results of fluorescence spectroscopy, the chemosensor BCP was found to show a significant signal increase only against $Mn^{2+}$ ions among the tested metal ions.

Depending on the $Mn^{2+}$ concentration, the change in absorption and emission spectra was also examined. As seen in **Figure 6(a)**, absorption spectra gradually increased when $Mn^{2+}$ ion (0 - 1.0 Equiv.) was added to the chemosensor BCP (50 μM), at different concentrations. Fluorescence spectra were taken concomitantly, and they are shown in **Figure 6(b)**. The findings showed that the chemosensor BCP showed a proportional change depending on the $Mn^{2+}$ ion concentration.

On the other hand, $1/I - I_0$ versus $1/[Mn^{2+}]$ plot was drawn and the plot in **Figure 7(a)** was obtained using the Benesi-Hildebrand Equation (1).

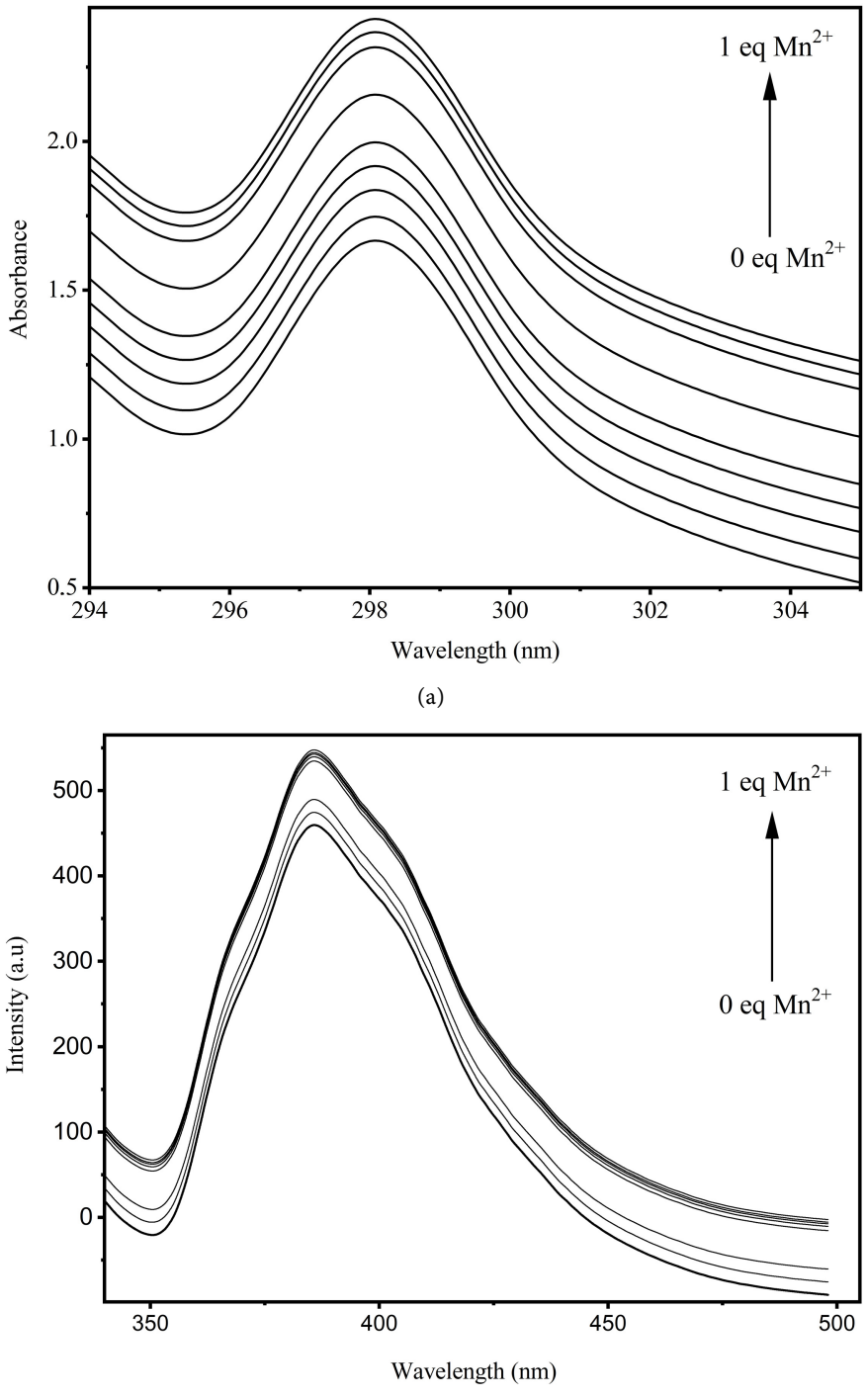


**Figure 6.** (a) Absorption spectra of the chemosensor BCP after adding $Mn^{2+}$ ion at several concentrations, (b) Fluorescence spectra of the chemosensor BCP after adding $Mn^{2+}$ ion in different concentrations ($\lambda_{exc}$ = 298 nm).

$$1/I - I_0 = 1/I - I_0 + 1/(I_1 - I_0)K\left[Mn^{2+}\right] \quad (1)$$

Using the Benesi-Hildebrand Equation (1), the binding constant, Kb, was obtained from **Figure 7(a)** to be $1.4 \times 10^4$ $M^{-1}$. The magnitude of this value indicates

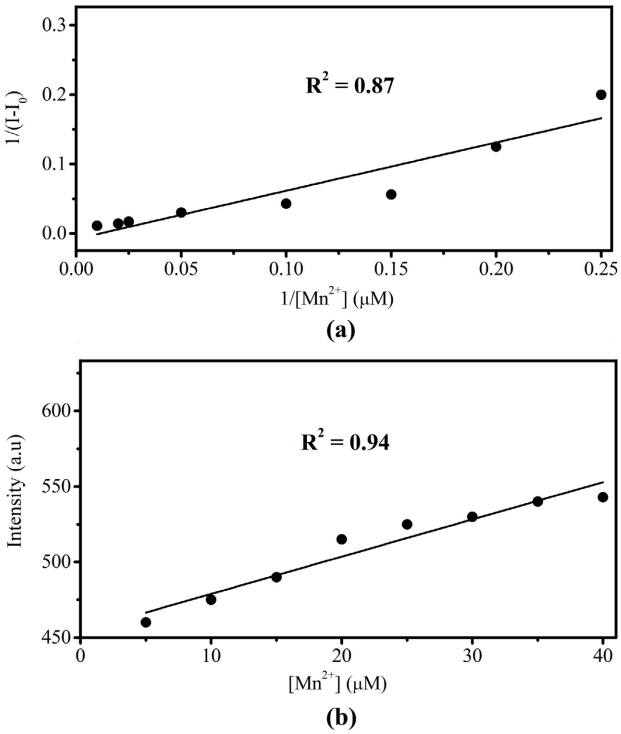


**Figure 7.** (a) The Benesi-Hildebrand plot ($1/(I - I_0)$ vs. $1/[Mn^{2+}]$), (b) Graphical representation of fluorescent emission intensities of BCP at 386 nm in response to added $Mn^{2+}$ concentrations (I vs. $[Mn^{2+}]$).

that the complex is solid. Using this value, Gibbs free energy was calculated as $\Delta G^{\circ} = -24$ kj/mol [21] [22] [23]. The negative value of this value indicates that the event developed spontaneously. Emission intensities at 386 nm are plotted against the added $Mn^{2+}$ ion concentration to calculate the lower limit of determination. As seen in **Figure 7(b)**, emission intensities increased linearly along with concentration.

$$\mathrm{LOD} = 3\sigma/m \tag{2}$$

where $\sigma$ is the standard deviation of the absorbance values of the blindly used solution while $m$ is the slope of the regression plot drawn by taking the emission intensity versus concentration. 0.22 μM is the lower determination limit calculated in the aqueous medium for $Mn^{2+}$ using the determination limit Equation (2) defined by IUPAC [24].

## 4. Conclusion

The results obtained in this study showed that chemosensor BCP responded significantly in terms of absorbance and fluorescence only against $Mn^{2+}$ ion among some biologically and environmentally important metals that were selected to test. The binding ratios between the chemosensor BCP and $Mn^{2+}$ ions are suggested to be 1:1. The lower detection limit for the $Mn^{2+}$ ion in the aqueous medium using the receptor BCP was found to be 0.22 μM and the binding constant

was found to be $1.4 \times 10^4$ $M^{-1}$. Thus, it has been shown that chemosensor BCP, being easy to use, responding quickly, offering low cost, and not requiring sophisticated equipment and expert personnel, can be used in detecting and determining the $Mn^{2+}$ ion in an aqueous acidic medium.

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## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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