

Sensing Capability of Fluorescent Sodium Salt of Amoxicillin

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Abstract The capability of already available antibiotic drug ‘amoxicillin’ based on its fluorescent property has been explored. The fluorescent sodium salt of amoxicillin was used for the detection of heavy metals in aqueous solutions. It was found that Copper and Silver has a quenching effect on the fluorescence of amoxicillin. Cu^{2+} ions were detected in aqueous solution up to 1×10^{-7} M and Ag^{1+} ions up to 1×10^{-6} M. Hg^{2+} ions were also detected in aqueous samples but in high concentration.

Keywords: sodium salt of amoxicillin, fluorescence, metallic sensing

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1. Introduction

Heavy metal ions play a vital role in a number of biological and environmental pathways [1,2]. Mostly Depends upon the biotic and abiotic environment and/or the microbes of interests, the biological, environmental and toxicological role of these ions are usually strongly structure dependent, i.e. they depend on the types and species [3,4]. The natural effectiveness of a single species, for example if it acts as a trace element or as an acute toxin, is critically determined by its concentration in the respective medium and the up take paths of an organism [5].

But at higher amount/ concentration, deposition of the heavy metal ions in an organism can result to unhealthy interactions in biochemical processes and can inhibit enzyme activity or nephrotoxicity [6]. Some of the heavy and transition metal ions are carcinogenic or mutagenic as well and a number of these ions affect the toxicity of organic molecules through interaction with metabolic results of enzymes or at the protein formation [6].

Metal nanoparticles have gained a great attention in the past era because of their distinctive electronic properties and optical-sensing applications [6,7]. Gold nanoparticles (AuNPs) have been prepared recently, emitting stronger fluorescence signals. These fluorescent gold nanoparticles are also called gold nano dots because of their exceptional fluorescence properties. AuNPs that are stabilized by poly-amidoamine dendrimer or poly-ethylenimine show stable fluorescence properties and high Quantum Yields [8,9]. The fluorescence occurrences of gold nanoparticles have been known for some time but their applications to chemical sensing are very limited, because of problems related with their chemical and fluorescence instability.

The Fluorescent behavior of nanoparticles is highly size dependent but the synthesis of gold nanoparticles with a small size distribution is very difficult [10,11]. Lot of work has been done for sensing heavy metal (i.e. copper ions detection). For example l-Cysteine capped ZnS quantum dots was prepared for sensing Cu^{2+} ions in water samples [12] and fast calorimetric detection of Cu^{2+} ion in aqueous samples using L-Cysteine functionalized gold nanoparticles [13]. Chitosan capped gold nanoparticles have been used for the detection of Cu ions [14]. A DNzyme Catalytic Beacon Sensor has been used for sensing of Paramagnetic Cu^{2+} ions in aqueous solution with high sensitivity and selectivity [15]. Silver nanoclusters have been used as fluorescent probes for sensing Cu ion [16]. Fluorescent film have been developed for sensing divalent copper ions [17]. Amoxicillin stabilized gold nanoparticles have been developed and used for the detection of copper ions in aqueous samples [18]. Consequently more precious and costly methods have been developed for sensing copper metal in water samples, but here we report a very simple method for sensing Cu^{2+} and Ag^{1+} ions in water samples. Industrially produced bulk material, amoxicillin has the ability to sense heavy metals like copper and silver in water samples.

2. Objectives of the Present Work

The main objectives of this work was to explore the sensing capabilities of already available chemicals which can be used as sensors for chemicals and heavy metals instead of synthesizing new compounds using precious metals like gold and silver etc in the form of nanoparticles. The synthesis of such new compounds needs time, scientists and capital. Therefore the screening of already

available chemicals for sensing capabilities will be more appreciable.

3. Methods

3.1. Materials and Measurements

Amoxicillin was provided by local company of pure analytical grade. Na_2CO_3 purchased from Merck. Doubly distilled water was used throughout the process. Photoluminescence spectra were taken on Perkin-Elmer Fluorescence photometer. Metal salts (FeSO_4 , CuSO_4 , CoCl_2 , ZnCl_2 , AgNO_3 etc.) used were all analytical grade (%).

3.2. Experimental

1mM solution of amoxicillin was prepared in distilled water and Na_2CO_3 were added to the solution in equal molar ratio. Solution was kept overnight to ensure the formation of sodium salt of amoxicillin (Na-Amox). 0.1 mM solution of metal (Fe, Co, Ni, Cu, Ag etc.) salts were prepared in distilled water and stored. For measuring data on fluorescent photometer 2mL of (Na-Amox) solution was taken and fluorescence was recorded. Then 40 μL of metal solution was added from the stock solution and fluorescence was recorded. Similarly upto 10 or more readings were recorded by adding 40, 80, 120, 160, 200, 240, 280, 320, 360, 400 μL of metal solution. Comparative graph was drawn and the effect was studied. Same process was repeated for each metal.

4. Results and Discussion

The sodium salt of amoxicillin is fluorescent and thus it was used in the experiments (Figure 1). Amoxicillin gives blue emission in the range of 440nm. The absorption spectrum of amoxicillin [19] consists of one intense peak of $\pi\text{-}\pi^*$ transition at 291 nm with a shoulder peak at 325 nm. The fluorescence is because of weaker $n\text{-}\pi^*$ transition [20]. The Fluorescence spectra of Na-amox had an emission peak at 437nm. This peak is because of the weaker $n\text{-}\pi^*$ transition. The excitation peak of this transition occurs at 325nm. Emission spectrum is given in the Figure 1. Na-amox solution was observed under UV lamp. A blue emission in the solution was observed and is shown in the Figure 2.

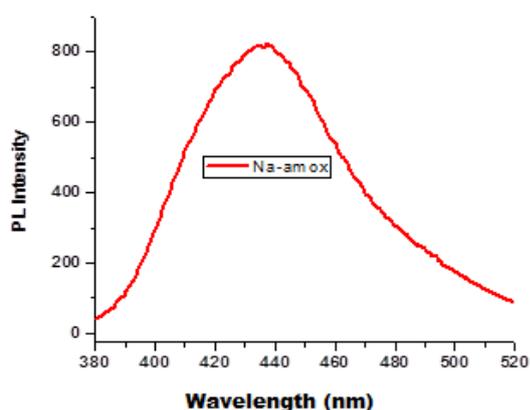


Figure 1. Photoluminescence spectrum of Na-amox

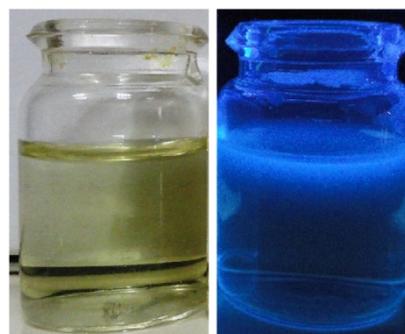


Figure 2. Na-Amox under UV lamp (right) and normal light (left)

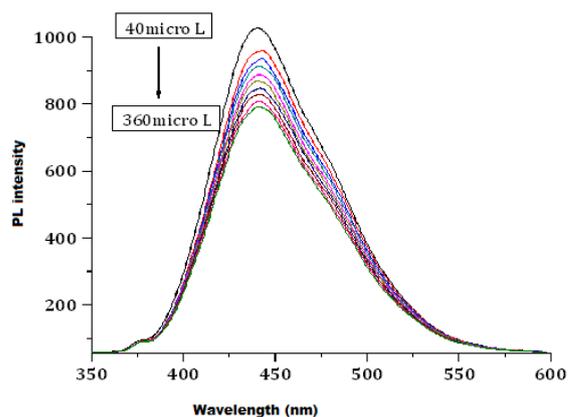


Figure 3. PL Spectra for detection of Cu^{2+} Conditions: $1 \times 10^{-7} \text{M}$ Cu^{2+}

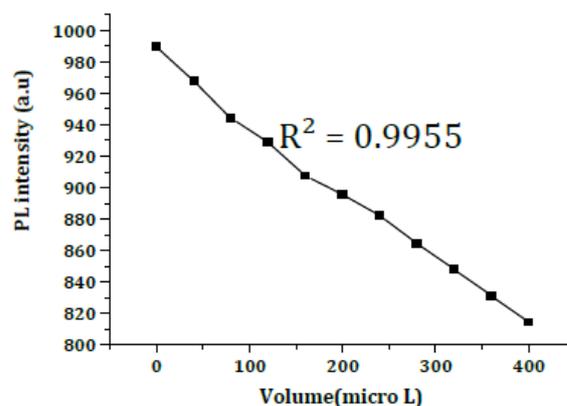


Figure 4. Detection of Cu^{2+} with a co-efficient of detection of 0.9955

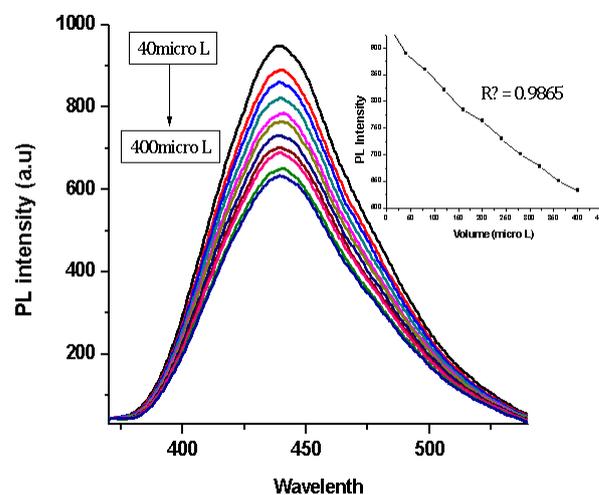


Figure 5. PL Spectra for detection of Ag^{+} Conditions: $1 \times 10^{-6} \text{M}$ Ag^{+}

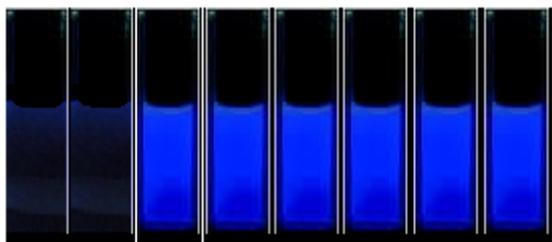


Figure 6. Fluorescence of amoxicillin under UV illumination after adding metal salts (samples 1 and 2 are with quenched fluorescence because of Ag¹⁺ and Cu²⁺ ions)

The fluorescent properties of amoxicillin were utilized for sensing heavy and toxic metals like Cu, Fe, Ag, Hg and Pb etc. The effect of each metal was checked on the fluorescence of Na-amox. It was found that amoxicillin can easily sense Cu²⁺ and Ag¹⁺ up to very small concentration by quenching its fluorescence as shown in Figure 3 and Figure 5. Toxic metal Hg was also detected Hg ions in water samples but only at higher concentration of about 1mM (Figure 7). Na-amox can detect Cu²⁺ ions in water samples to a concentration as low as 1x10⁻⁷M with coefficient of detection (R²) of 0.9955 (Figure 4) and Ag¹⁺ ions up to 1x10⁻⁶M with R² value of 0.9865. The fluorescent properties of amoxicillin for the detection of Cu²⁺ ions in aqueous solution were compared with already published amoxicillin stabilized AuNPs [13]. Amoxicillin can detect 100nM of Cu²⁺ ions in water samples. After adding Ag, Cu and other metal salts, their images under

UV light where quenching of fluorescence can easily be seen (Figure 6).

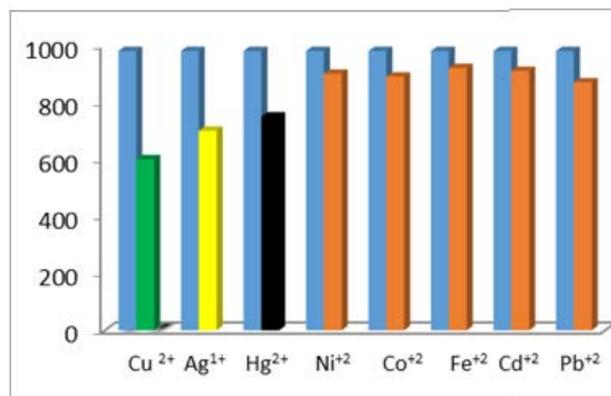


Figure 7. Comparative sensing of different metals using Na-amox Conditions; Cu²⁺(1x10⁻⁷M), Ag¹⁺(1x10⁻⁶M), Hg²⁺(1x10⁻³M) and rest of metals (1x10⁻³M)

4.1. FT-IR Spectra

FT-IR spectra suggest that C=O group of carboxylate group of amoxicillin in the region of 1600 to 1700cm⁻¹ has been disturbed with the attachment of Ag and Cu ions. Thus this group is probably involve in the quenching of fluorescence. The attachment of Ag¹⁺ or Cu²⁺ ions to the oxygen of this group hindered the excitation of n-π* (Figure 8).

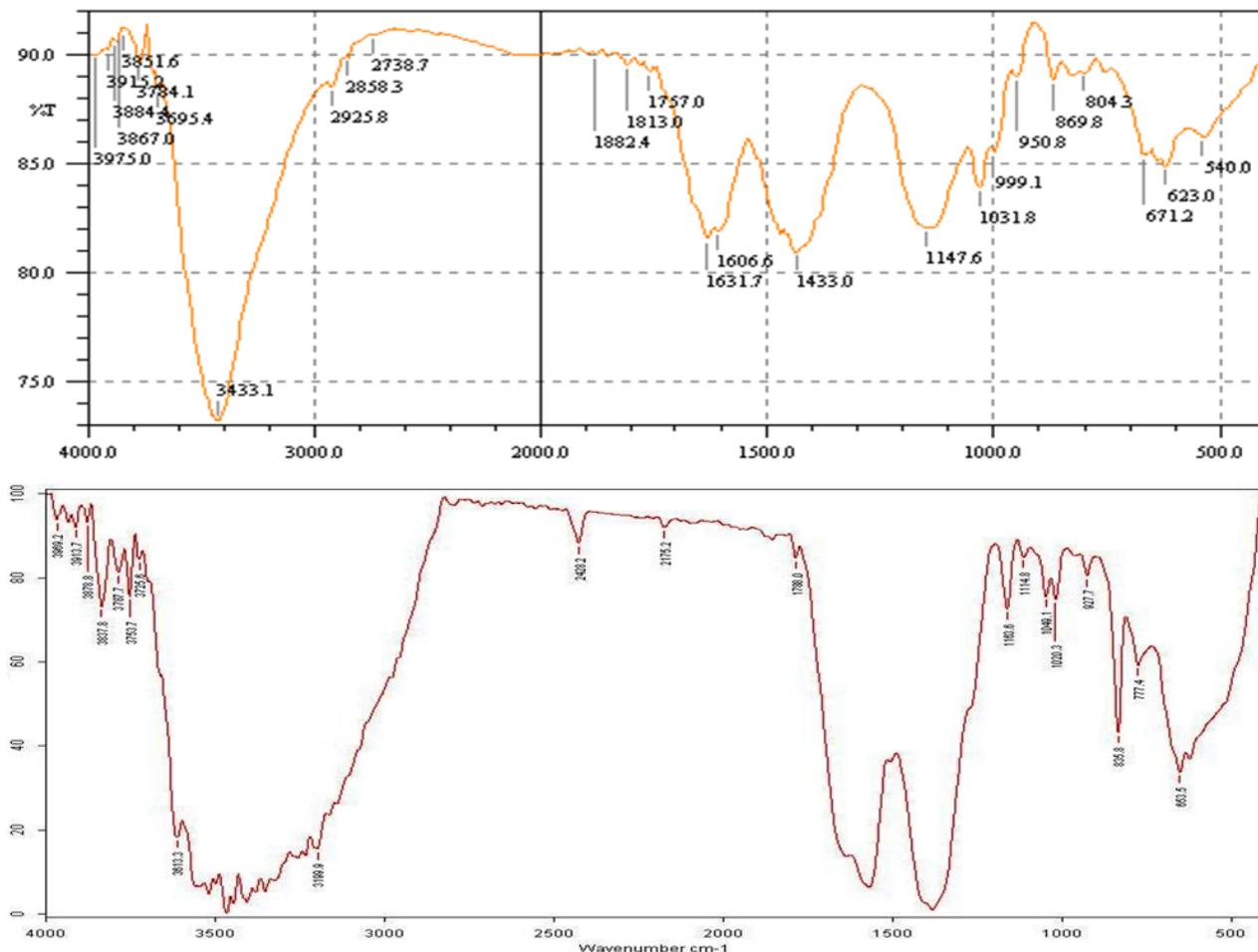


Figure 8. FTIR spectra of Na-salt of Amoxicillin (above) and after the attachment of heavy metal (below)

5. Conclusion

It was concluded that if already available chemicals were searched for sensing heavy metals and chemicals. Chemo-sensors and metallic sensors can be produced with quite good efficiency. For example the sensing capabilities of amoxicillin were explored and it was found that heavy metals like Cu^{2+} and Ag^{1+} ions were detected in aqueous samples up to nanomolar concentration. Hg^{2+} was also detected up to 1mM concentration.

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