

# Unmodified Silver Nanoparticles synthesized by solvent reduction method as tool for detection of Cr (VI) colorimetrically in solution

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## Abstract

A Colorimetric recognition technique of Cr (VI) in watery environment with the help of combined silver nanoparticles (Ag NPs) is devised. The technique includes reducing of Cr (VI) to Cr (III) by the overabundance of a reducing agent present in the synthesised AgNPs dispersion. This reduction leads to the accumulation of silver NPs by Cr (III), prompting red-move of the resonance peak. The UV-vis retention spectra in the wavelength range of 200-800 nm is used to affirm the collection of the Ag NPs. Cr (VI) upto a concentration of 0.01 M was detected which was further diluted to detect the lower concentrations using the silver nanoparticles probe. The detection was colorimetric as the solution of silver nanoparticles pale yellow in colour changed its colour to purple when Cr (VI) was added to it. Even the method was found out to be extremely selective. Thus a rapid and a simple partially green technique are developed to detect Cr (VI) which was also selective in nature when tested over other heavy metal ions.

## Keywords

Silver nanoparticles, Cr (VI), colorimetric, Waste water, green

## 1. Introduction

Due to various anthropogenic activities like pigment production, chrome plating, and leather tanning an increase in the amount of chromium has been witnessed [1, 2, and 3]. Chromium is also among the main contagion in hazardous waste areas [4]. Both Cr

(III) and Cr (VI) are poisonous but only compounds containing Cr (VI) leach easily into water [5]. Studies have shown that Cr (VI) is around 100-1000 times more dangerous than Cr (III) [6]. It is considered as a serious ecological toxin, because of its profoundly cancer-causing properties [3]. The environmental agency in USA (US EPA) mentioned that chromium was the most dangerous to people [3]. A lot of studies have been carried out on the toxicity of chromium and chromium proves to be a lethal contaminant [7, 8, 9,10].

Due to the above mentioned reasons a lot of efforts have been put on the detection of Cr (VI). Techniques like atomic absorption spectroscopy [11], inductive coupled plasma mass spectrometry [12], chromatography [13] and spectrofluorimetry [14] were devised for the detection of Cr (VI). All these techniques are extremely accurate and sensitive but the only problem with these is that they are expensive, time consuming and complex (thus requiring skilled man force). Recently Cr (III) was detected using chemical sensors [15, 16].

Not only this, but various methods based on nanoparticles have also been developed to detect Cr (VI). These take advantage of the property of fluorescence [17, 18] and surface Plasmon resonance [19, 20] for the detection. These methods though effective, use costly nanoparticles like gold or are not handy enough to be used directly on sight. Recently Elavarasi and colleagues developed a colorimetric based approach to detect chromium in nanomolar range [21]. They used the Creighton method for preparing the silver nanoparticles. They used tri-

Sodium citrate as the reducing agent and the cause of the the colour change as well reducing of Cr (VI) to Cr (III) was used [21]. We modified the method by using Ascorbic acid as reducing agent and SDS as stabilizing agent the process used for the synthesis was solvent reduction method as it is much simple and does not involve multiple stages like the Creighton method [22]. They method devised is simple, is less costly, is less hazardous and also it is has a detection limit of  $10^{-12}M$ , which is much greater than that reported by Elavarasi and group [21]. Also the method devised is partially green as it utilises ascorbic acid which is another form of Vitamin C.

## 2. Materials and methods

### 2.1 Materials

Millipore water was used for the experiments. Sodium Dodecyl sulphate (SDS), ascorbic acid and silver nitrate were provided by the institute. Potassium dichromate ( $K_2Cr_2O_7$ ) was the compound providing the Cr (VI) ions and was also provided to us by the institute.

### 2.2 Synthesis of silver nanoparticles

All the glass wares utilized were completely washed with deionised water and aqua regia and afterwards rewashed with distilled water and air dried. The silver nanoparticles were prepared using a modified solvent reduction method. In the method, to 60 mL of ascorbic acid (0.02M), 1 mL of SDS is added. The solution is chilled for 20 minutes. After this 0.01M  $AgNO_3$  is added drop wise to the solution. The colour of the solution changes to pale yellow. The prepared AgNPs are characterized using UV-Visible spectroscopy.

### 2.3 Detection of Cr (VI) colorimetrically

For detection of Cr (VI), 1mL of different concentration solutions of potassium dichromate were prepared and these solutions were added to 10mL of prepared AgNPs. The colour changes were recorded and these solutions were analyzed by UV-Visible spectroscopy.

## 2.4 Selectivity test experiment

To see to it that the prepared AgNPs only detect Cr (VI), solutions of different metal ions like Zn, Fe, Cu, Hg and Pb were prepared and added to the prepared silver nanoparticles. Metal chlorides were used as source of ions. And the concentration of each of them was fixed at  $10^{-4} M$ .

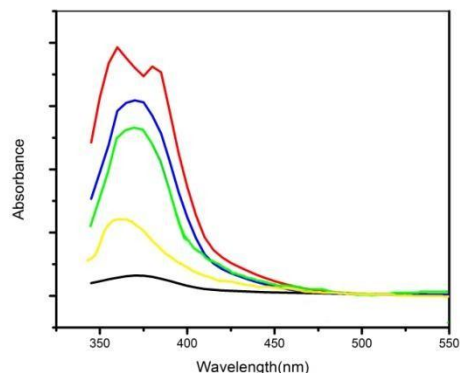
## 3. Results and discussion

### 3.1 Detection of Cr (VI)

The synthesised silver nanoparticles we synthesised had two major peaks as can be seen in figure 2. The two peaks probably correspond to the different size of silver nanoparticles produced. The maximum absorbance was seen at around 375nm. Upon addition of Cr (VI), the colour change in the solution was from pale yellow to violet and then faded slowly with decrease in concentration of Cr (VI). The most probable reason for this was that the silver nanoparticles aggregated upon addition of Cr (VI). The excess aggregation of AgNPs was stabilized by the presence of negatively charged ascorbate ions [23]. The Absorbance also decreased with addition of Cr (VI) as can be seen in the graph.



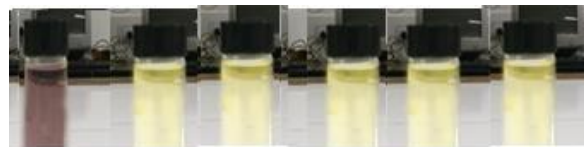
Figure 1. Colour of solutions (from left to right): AgNPs, AgNPs+ $10^{-2}M$  Cr (VI), AgNPs+ $10^{-4}M$  Cr(VI), AgNPs+ $10^{-6}M$  Cr(VI), AgNPs+ $10^{-9}M$  Cr(VI), AgNPs+ $10^{-12}M$  Cr(VI)



**Figure 2. UV-Visible spectra: Red-AgNPs, Blue-AgNPs+ $10^{-2}$ M Cr(VI), Green- AgNPs+ $10^{-6}$ M Cr(VI), Yellow- AgNPs+ $10^{-9}$ M Cr(VI), Black- AgNPs+  $10^{-12}$ M Cr(VI)**

### 3.2 Selectivity test

After this experiment selectivity tests were carried out and the result was that the colour of the solution only changed for Cr (VI) as can be seen in figure 3. The rest of the solutions retained their colour. Thus the method devised was selective to the chromium metal ions.

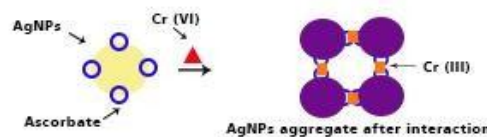


**Figure 3. Selectivity test for  $10^{-4}$  M (from left to right): AgNPs + Cr (VI), AgNPs +  $Zn^{2+}$ , AgNPs +  $Fe^{3+}$ , AgNPs +  $Pb^{2+}$ , AgNPs +  $Cu^{2+}$ , AgNPs +  $Hg^{2+}$**

### 3.3 Possible mechanism

As mentioned by Elvasari and group [17], the reduction of Cr (VI) to Cr (III) lead to the colour change and thus the excess reductant and its interaction with the AgNPs was responsible for the detection. Thus the ascorbic acid which acted as a reducing was mostly responsible for the colour change. We propose that just like the citrate ions in [17], the ascorbate caps the silver nanoparticles. The interaction of Cr (VI) with these capped silver nanoparticles lead to the reduction and chelation of

the Cr (VI) and lead to colour and absorbance change observed.



**Figure 4. Possible mechanism of detection**

## 4. Conclusion

Thus a partially green method for detection of Cr (VI) on-site and selectively was developed. The detection limit was around  $10^{-12}$  M, which is well beyond the risk concentration as proposed by (reference). Also the method is simple and colorimetric, thus can be easily used to detect chromium ions. The reported limit of  $10^{-12}$  M is the best limit reported so far. Also the method devised is selective.

## 5. Acknowledgements

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