Green Synthesis of Silver Nanoparticles using Vitex Negundo Extracts and their Application in the Effluent Treatment of Cracker Industries

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Abstract. Silver nanoparticles were prepared by green synthesis, which is an eco-friendly and inexpensive method. The synthesis was carried out using Vitex Negundo leaf extract at room temperature. The nanoparticles were encapsulated with Poly Vinyl Alcohol (PVA) matrix to avoid agglomeration. The formation of silver nanoparticles was confirmed by X-ray Diffraction (XRD). The morphology of the nanoparticles was investigated by scanning electron microscope (SEM). Energy Dispersive X-ray Spectrum (EDX) confirmed the presence of elemental Ag. Adsorption experiments confirmed the removal of toxic cadmium and chromium present in the industrial effluents as analysed by atomic absorption spectroscopy. The silver nanoparticles showed maximum adsorption efficiency for chromium compared to cadmium.

1. Introduction
Nanoparticles are considered recently for environmental remediation in solving various problems such as waste water treatment [1], pollution monitoring [2], soil treatment [3]. For example, metal nanoparticles are used in the decontamination of aquifers and other soils and removing organic contaminants, pesticides, heavy metals, pharmaceutical and personal care related wastes [4]. The use of nanoparticles or nano metals is also promising for the adsorption of polluted ions present in the industrial effluents [5]. The large surface area, super paramagnetic property and low diffusion resistance of nanoparticles make them attractive for the purification of contaminants in the effluents. The effluents from cracker industries contain chemicals such as acids, alkaloids and heavy metals. Some of the key toxic heavy metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Zinc (Zn), Lead (Pb) etc., are present in the effluents of cracker industries [6]. These heavy metals are discharged into nearby water sources and highly contaminating them. This poses a big threat to the environment and its species. In the present work, water samples were collected from Sivakasi, Tamil Nadu, India which is a famous place for firecracker industries. Cadmium (II) and Chromium (VI) present in the effluent were removed through adsorption experiments using Silver (Ag) nanoparticles.

2. Experimental Methods
2.1. Preparation of Vitex Negundo leaf extract
Fresh leaves of Vitex Negundo, generally known as Chinese Chaste Tree was collected in the border of Western Ghats from Tamil Nadu, India. The leaves were repeatedly washed with double distilled
water to remove dirt and other soluble contaminants. Then, they are dried in sunlight and powdered using mortar and pestle. The powder was boiled with double distilled water at 100°C in an Erlenmeyer flask for 15 min to collect the extract. The leaf extract was filtered through filter paper (Whatman No.1.) and collected for further experiment.

2.2. Green synthesis of Silver nanoparticles

20ml of leaf extract was mixed with 100mL of 1×10^{-3}M aqueous silver nitrate and stirred vigorously for 1 h in a magnetic stirrer. It was observed that the color of the mixture changed from light green to dark brown indicating the formation of silver nanoparticles. To this solution, 10ml of PVA is added to avoid agglomeration. The dark brown precipitate was filtered and investigated to know their characteristics.

2.3. Characterization of Ag nanoparticles

Ag nanoparticles were characterized by powder X-ray diffraction (XRD) to confirm their formation and crystallinity. A Bruker D8 advance model powder X-ray diffractometer working at 40 kV was used. The spectrum was recorded using Cu Ka radiation (λ = 1.5418 Å) for the diffraction angles from 10° to 80° at 0.02° step and a count time of 0.2 s. Morphological features were observed by BRUKER, (VEGA3, TESCAN, Germany) scanning electron microscope (SEM) equipped with Energy Dispersive X-ray spectroscope (EDX). Atomic Absorption Spectroscopy (AA-6300, Shimadzu) was used to estimate the heavy metal concentration in the effluent before and after the adsorption experiment.

2.4. Adsorption Experiment

Industrial effluent was collected from Sivakasi, Tamil Nadu, India for the adsorption studies. Charcoal was used to remove color from the collected water sample. The colourless water sample was subjected to adsorption studies. 0.5gm of synthesized nano silver particle was added to 50ml industrial waste water which was taken in an adsorption bottle. The bottles were placed in a mechanical shaker and shaken at a speed of 135± 5 rpm for an hour at 28°C. A constant contact time of 60 min, pH in the range of 5-6 and temperature of 28 ± 1°C were maintained throughout the adsorption experiments. The solutions were filter through Whatman No. 1 filter paper after the equilibration and collected for the measurement of metal ion concentration using Atomic Absorption Spectroscopy as per standard procedure.

3. Results and Discussion

Figure 1 depicts the pictorial representation of the synthesis steps. Figure 2 represents powder X-ray diffraction pattern of Ag nanoparticle samples with PVA and without PVA (Sample A and B respectively). The fundamental crystalline silver peaks were observed at 38.33° (111), 44.51° (200), 64.67° (220) and 77.58 (311) [7]. The indices are correlating to face centered cubic structure of Ag nanoparticles. The other unidentified peaks are probably due to crystalline organic compounds present in the extract [8]. The organic compounds are helpful for the formation of Ag nanoparticles and their stabilization. We do not find any peaks related to PVA in the XRD spectrum. The average size of the nanoparticle was calculated using Debye-Scherrer equation.

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

Where \(D\) - average size of the crystallite, \(\lambda\) - wavelength of X-radiation, \(\beta\) - Full Width at Half Maximum (FWHM), \(\theta\) - Bragg’s diffraction angle. The average size of nanoparticle was calculated as 22 nm. Scanning electron microscopic picture in figure 3a shows the morphological features of vitex negundo as we already observed additional crystalline peaks of extracts in the powder XRD spectrum. SEM picture in Figure 3b shows the presence of very small size nanoparticles. Figure 4a shows slightly bigger size nanoparticles. Although the peak corresponding to PVA is not shown in XRD
spectrum, the size of the nanoparticles in Figure 3b is very small and well separated. On the other hand, sample B in figure 4a represents increase in size of the nanoparticles possibly due to agglomeration in the absence of PVA.

![Figure 1. Synthesis steps of Ag nanoparticles using Vitex Negundo](image)

XRD results also confirm that FWHM value is slightly larger for PVA coated nanoparticles compared to that of uncoated sample as PVA coating restricted the growth of nanoparticles in sample A. Green synthesis of nanoparticles using Vitex Negundo leaf extracts proved that the nanoparticles are spherical in shape and uniform in size as we observe from SEM pictures. The corresponding EDX shows the presence of Ag (Figure 4b). The Ag peak at 3 keV range confirms that Vitex Negundo leaf extract is highly useful in the reduction of AgNO₃ resulting in the formation of Ag nanoparticles. The concentration of heavy metals (Cadmium and Chromium) before and after the adsorption experiment was estimated using Atomic Absorption Spectroscopy (AAS). The results are represented in Table1. The concentration of heavy metals is found to be high in the effluents compared to the values permitted by world health organization (WHO).

![Figure 2. Powder X-ray diffraction pattern of Ag nanoparticles with PVA coating (Sample A) and without PVA coating (Sample B)](image)
The percentage of adsorption is calculated using the formula

\[ \% \text{Adsorption} = \frac{C_i - C_f}{C_i} \times 100 \]

Where \( C_i \) – initial concentration of heavy metals in the effluent and \( C_f \) – final concentration of heavy metals in the effluent [9]. From the results recorded in Table 1, we infer that nano silver was found to be effective in the removal of chromium compared to cadmium. As results suggest, chromium concentration is more in the effluent and it is effectively removed. In general, adsorption experiments confirmed that the adsorption increases with increase in initial concentration of heavy metals present in the solution [10]. Moreover the ionic radius of Cr (VI) is 58 pm and that of Cd (II) is 92 pm. It has been reported that the adsorption capacity depends on the ionic radius [11]. The elements with higher ionic radius rapidly saturate the adsorption sites because of the possible steric hindrance.

Figure 3. Scanning Electron Microscopic picture (a) Morphology of Extract (b) Ag nanoparticles (Sample A)

Figure 4. (a) SEM image of Ag nanoparticles (Sample B) (b) EDX spectrum
Table 1: Concentration of heavy metals in the collected water sample

| Heavy metals | Concentration of heavy metals before treatment (ppm) | Concentration of heavy metals after treatment (ppm) | Permissible limits (WHO) | Percentage Removal |
|--------------|----------------------------------------------------|--------------------------------------------------|-------------------------|--------------------|
| Cadmium (Cd) | 0.0347                                              | 0.0256                                           | 0.003                   | 26.2%              |
| Chromium (Cr)| 0.2053                                              | 0.0269                                           | 0.05                    | 86.9%              |

It might be the reason why chromium is adsorbed more compared to cadmium. As earlier reports suggest that the contact time of 60 min was also sufficient for an effective adsorption [12]. However, the concentration of chromium is well below permissible limit after adsorption, whereas the concentration of cadmium was reduced but not below the permissible limit. It again confirms that the competition between chromium and cadmium results in higher chromium adsorption. Higher initial concentration of chromium increases the driving force required for an effective adsorption at the interface until the adsorption sites of the adsorbent were saturated [10].

4. Conclusions
Green synthesis of silver nanoparticles with PVA matrix using Vitex Negundo was carried out by reduction method at room temperature. The average particle size was calculated to be around 22 nm. The advantages of green synthesis are simple, efficient and having good control over particle size. The XRD studies revealed the presence of crystalline silver nanoparticles and organic substances in the dispersion. SEM images confirmed the presence of spherical silver nanoparticles which were present over the crystalline phases of extracts. The adsorption studies confirmed the removal of cadmium and chromium by silver nanoparticles. 86.9% of chromium is removed by Ag nanoparticles due to its smaller ionic radius of 58 pm and 26.2% of cadmium which is having slightly bigger ionic radius of 92 pm. The study confirmed that the element with smaller ionic radius is preferentially adsorbed over the bigger one. The synthesis of Ag nanoparticles using Vitex Negundo extract is proved to be one of the efficient and cost effective pathways for effluent treatment. Green synthesized Ag nanoparticles are highly useful to protect our environment from the point sources of water pollution in the current situation.

5. References

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