Mercury is considered as one of the most dangerous metal detected in the atmosphere, therefore, its exclusion from wastewater sooner than these being released into the environment is essential [1]. The major pathway for mercury enters into the water resources is through wastes from industrial processes like metal plating, mining, acid battery, chloralkali, paper and pulp, oil refinery, paint and pharmaceutical [2]. Contrast organic pollutants, which are prostrate to biological degradation, mercury is non-biodegradable and builds up beside the food chain in living organisms, which causes a severe danger to human health. As a result of its high toxicity and the extensive applications, new and effective methods for mercury removal from the aqueous solution are constantly being formulated, such as chemical precipitation, adsorption, ion-exchange, membrane filtration, reverse osmosis, and electrochemical treatment. Adsorption is one of the efficient methods that have been successfully employed for mercury removal from wastewater [3]. Various traditional adsorbents have been developed and used to remove metal ions from wastewater such as granulated activated Carbon [4], fly ash [5], peat [6], recycled alum sludge [7], peanut hulls [8], resins [9], kaolinite [10], manganese oxides [11], zeolite [12], and biomaterials [13]. Though, the adsorption capacities of these traditional adsorbents were low as compared to nano sorbents due to great exterior surface area, high density of reactive surface sites, great intrinsic reactivity of surface sites and small internal diffusion resistance [14]. Nowadays, zero valent nanoparticles are successively employed for the removal of heavy metals from aqueous medium and industrial effluent [15-17]. Recently, zero valent AgNPs were exploited for the wastewater treatment [18]. From the literature survey, it was found that
the application of CRGE capped AgNPs (zero-valent metal) for adsorbing heavy metals has not been reported yet. Hence in the present study, we have synthesized these CRGE capped AgNPs and applied these AgNPs for adsorbing heavy metals from aqueous solution. Silver nanoparticles have been synthesized using various plant extracts such as Hibiscus rosa sinensis [19], Svensonia hyderabadensis [20] etc. So far, the AgNPs has not been synthesized using CRGE. Hence, we report an inexpensive and reproducible method for the large-scale synthesis of silver nanoparticles using CRGE. Here CRGE acts as reducing, encapsulating and stabilizing agent. In this study, we explored the potential of the CRGE capped AgNPs for removal of mercury from aqueous medium in the absence and presence of competing ions Ca\(^{2+}\), Mg\(^{2+}\) and Na\(^{+}\) at much greater levels than the target heavy metal.

6.2. Materials and Methods

6.2.1. Materials

The raw plant material used in the present study was C. rotundus. This is a plant material freely available in Tamil Nadu, India (Fig.1). AR grade SD fine silver nitrate (AgNO\(_3\)) was purchased and its 0.1 M solution was prepared in stock and diluted to 1 mM solution. The other chemicals and reagents were of chemically pure grade (AnalaR) procured from SD Fine Chemicals, India.

6.2.2. Methods

6.2.2.1. Preparation of CRGE

Fresh C. rotundus grass were collected and washed with sterile distilled water and dried. After drying cut into small pieces. The extract was prepared by taking 20 g of
thoroughly washed finely cut C. rotundus grass in a 250-mL Erlenmeyer flask with 100 mL of deionized water, and then boiling the mixture at 60 °C for 5 min. After boiling, the solution was decanted and filtered through nylon mesh (spectrum). The filtrate is used as reducing agent and stabilizer, stored at 4°C for further nanoparticles synthesis process.

6.2.2.2. Green synthesis of AgNPs

For synthesis process, the 2 mL of CRGE was added to 25 mL of 1 mM AgNO₃ aqueous solution and the resulting solution became brown in color. Then the mixture was stirred for 30 min to obtain the AgNPs. Here the formation of
Fig. 2 (a) Silver nitrate mixture before (b) grass extracts and (c) After the synthesis of AgNPs

AgNPs was identified by change in the color of the stock solution to brown within 20 min (Fig. 2). These biologically-reduced aqueous solutions of Ag nanoparticles were used for further characterizations. This process carried out at room temperature.

6.2.2.3. Spectral analysis

The synthesized AgNPs were characterized by UV–Vis Schimadzu 1800 spectrophotometer. The colour change was monitored and the surface Plasmon resonance band in 300–700 nm range. FT-IR spectral data of the AgNPs, free and Hg$^{2+}$ loaded AgNPs were recorded with a SHIMADZU MODEL FT-IR spectrometer by using KBr pellets at the wave number ranging from 400 to 4000 cm$^{-1}$.

6.2.2.4. Morphological analysis

Morphological analysis of the free and Hg$^{2+}$ loaded AgNPs were studied using Vega3 Tescan Scanning electron microscope (SEM) and Bruker energy-dispersive
microanalysis (EDX) machine. Thin film of the samples were prepared on a carbon coated copper grid by just dropping a very small amount of the grid, extra solution was detached using a blotting paper and afterward the film on the SEM grid were permitted to dry by putting it underneath mercury lamp for 5 min.

6.2.2.5. Structural analysis

The synthesized AgNPs were checked using X’Pert Pro Materials Research diffractometer system. The X-ray diffraction (XRD) pattern was calculated by drop coated films of AgNO$_3$ on glass plate and worked with characteristic radiation in the range of $20^0$ to $90^0$ at a scan rate of 0.05$^0$/min with the time constant of 2 s, CuK$_\alpha$ radiation and amplitude wave $\lambda = 1.5418$ Å working with a 40 kV voltage and 30 mA current. The full–width at half–maximum (FWHM) from three different peaks were used in Scherrer’s equation to find out the average crystallite size of the nanoparticles.

6.2.2.6. AFM analysis

A minute quantity of sample was spread on a well cleaned glass cover slip surface mounted on the AFM stub, and dried with nitrogen flow at room temperature. Images were obtained in tapping mode using a silicon probe cantilever and resonance frequency 209-286 KHz, spring constant. The scan rate used was 1 HKz. A least of five images for every sample were obtained with AFM and analyzed to ensure reproducible results.

6.2.2.7. Thermal analysis

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) were used to the find out the thermal degradation of the samples like free and Hg$^{2+}$ loaded AgNPs using a SII MODEL 6000 thermal analyzer.
6.2.2.8. Batch adsorption studies:

The adsorption studies were carried out by 0.25g of AgNPs was introduced onto 40 mL solution having known Hg(II) concentration and the preferred contents of competing cations such as Na(I), Mg(II), and Ca(II) were introduced into solution as needed by dissolving their corresponding nitrates with high concentration than the target toxic metal at 30°C. The final solution volume was measured as 100mL. The solution were then transferred to a 250ml glass bottles and shaken at 200 rpm stirring speed onto the Remi rotator water bath shaker for 30 min to find out the percentage of adsorption. The adsorption studies were also done for removal of mercury from aqueous solution in the absence of competing ions like Na (I), Mg (II), and Ca (II). The all metal ions concentration in the supernatants after the adsorption onto the adsorbents was determined by using standard titration techniques as per the literature [21]. The percentage of adsorption was estimated with the help of following equation:

\[
\text{% of adsorption} = \frac{(C_o - C_e)}{C_o} \times 100 \text{%} \quad (1)
\]

Where \( C_o \) is the initial mercury (II) concentration (mg/L) and \( C_e \) is the concentration of metal ion (mg L\(^{-1}\)) at equilibrium.

6.3. Results and discussion

6.3.1 Spectral characterization

6.3.1.1. UV–Vis spectra
Fig. 3. UV-Visible Spectra of the synthesized AgNPs

Earlier reports revealed that the spherical silver nanoparticles produce absorption bands around 400–440 nm in the UV-Visible spectrophotometer [22]. These bands were understood to expose the association of silver nanoparticles. UV–Visible spectra showed that the broad surface plasmon resonance at 425 nm (Fig.3). The broad spectra indicate the presence of particles with a broad size distribution.

6.3.1.2. FT-IR spectra

The FT-IR spectrum of free and Hg$^{2+}$ loaded AgNPs are shown in Fig.4a and b. It is used to explore the organic compounds present in the surface of the AgNPs and the capping agents on the nanoparticles. The band at 3479 cm$^{-1}$
Fig. 4a and b. FT-IR Spectra of the free and Hg$^{2+}$ loaded AgNPs

corresponds to intermolecular O-H stretching vibrations. The peaks at 2854 and 2930 cm$^{-1}$ are belonging to C-H aromatic stretching frequencies. The medium absorption peak located at 1666 & 1743 cm$^{-1}$ is identified as the amide group. This amide band occurs due to carbonyl stretching and N–H deformation vibrations in the amide linkage of proteins present in it. The band observed at 1462 cm$^{-1}$ may be due to the C–O–H vibrations. The band at 1267 cm$^{-1}$ is assigned to polyphenols. The band at 2362 cm$^{-1}$ corresponds to C–N stretching vibrations of aliphatic amines. All these bands clearly confine the presence of polyphenols, proteins, tannins and flavonoids in CRGE which act as reducing agents for the synthesis of silver nanoparticles. Thus, the IR spectroscopic study confirmed that the CRGE has the capability to perform dual functions of reduction and stabilization of
AgNPs. Subsequently while comparing these two figures (fig.4a and b), it can be seen that these peaks moved away or moved out after the adsorption of Hg$^{2+}$ onto the adsorbents. This may be due to the bond of Hg$^{2+}$ and carboxyl groups, which distorted the novel power of the adsorbents [23].

6.3.1.3. SEM

The synthesized AgNPs structure morphology was scanned and confirmed by scanning electron microscope (SEM) was done by using Vega3 Tescan instrument. The AgNPs placed on the carbon coated copper grid, it reveals spherical in shape (Fig.5a and b). Then the all SEM images were indicating that the morphology of silver nanoparticles is almost spherical which is in good harmony with the shape of SPR band in the UV–Vis spectra. The size of the AgNPs range was around 1-100nm [24].

![Fig.5a and b. SEM images of AgNPs using CRGE leaf extract](image)

6.3.1.4. EDX

The SEM-EDX spectrum of free and Hg (II) loaded AgNPs are shown in Fig.6a and b. The EDX pattern obviously shows that the AgNPs are crystalline in nature by the reduction of Ag$^+$ by using grass broth. It depicts strong absorption signal in the silver
region and prove the formation of AgNPs. Metallic silver nano crystals usually demonstrate absorption peak around at 3 keV due to surface plasmon resonance [25]. Other elemental signals are recorded maybe due to elements from enzymes or proteins present within the grass extract. Then comparison of this SEM-EDX spectrum before and after Hg (II) sorption shows that the presence of Hg (II) peak in the spectrum confirms the adsorption of Hg (II) onto adsorbents [26].

![Fig.6a and b. EDX spectra of the free and Hg\(^{2+}\) loaded AgNPs](image)

### 6.3.1.5. XRD

The XRD pattern of the AgNPs is as exposed in Fig.7 and Table.1. The major diffraction peaks observed are (1 0 0), (1 0 1), (1 0 3), (0 0 6), (1 1 0) and (2 0 2) reflections of face centered cubic structure of metallic silver, correspondingly enlightening that the synthesized AgNPs are composed of pure crystalline silver (JCPDS file no. 87-0598). The average particle size of AgNPs can be calculated using Debye–
Scherrer equation: \( D = \frac{k\lambda}{\beta \cos \theta} \), where \( D \) is the thickness of the nanocrystal, \( k \) is a constant, \( \lambda \) is the wavelength of X-rays and \( \beta \) is the full width at half maxima of (111) reflection at Bragg’s angle \( 2\theta \) [27]. The average crystallite size calculated from the XRD patterns is 24.26 nm.

![Fig.7. X-ray diffraction pattern of AgNPs](image)

<table>
<thead>
<tr>
<th>Peak Pos. [°2Th.]</th>
<th>FWHM [°2Th.]</th>
<th>d-spacing, [Å]</th>
<th>hkl values</th>
<th>Crystallite size [nm]</th>
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<td>1 0 3</td>
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<td>1.44257</td>
<td>1 1 0</td>
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</tr>
</tbody>
</table>
6.3.1.6. AFM

![AFM Topographical Image of AgNPs](image)

**Fig.8.** AFM topographical image of AgNPs

Average crystallite size (nm) 24.26
AFM analysis principally tells the homogeneity and the particular size of the AgNPs. In this study, the AgNPs reduced by CRGE extract were characterized by AFM for determining its particle size, morphology and aggregation of the particles. Figures 8, 9 and 10 have been notified that the biologically reduced nanoparticles are in the range of 10 nm. Then the obvious particle nature of the AgNPs is also observed from their surface.
topography (Fig. 9). The size distribution of the AgNPs is showed in the histogram, which range from 1 to 5 nm. The nanoparticles are maximum at 5 nm is also showed in the line shape. The statistics graph is also showed that the size distribution of nanoparticles, these range approximately from 1 to 11 nm. Besides, the uniform spherical nature of AgNPs is also established from the inset image observed from AFM (Fig. 10). As a result, it is clearly confirmed that the AgNPs are formed without aggregation and are spherical in nature [28].

6.3.1.7. TGA & DTA

![TG curve of the AgNPs at different temperatures](image)

Fig. 11. TG curve of the AgNPs at different temperatures
Fig. 12. DTA curve of the AgNPs at different temperatures

Fig. 13a and b. TG curve of the free and Hg^{2+} loaded AgNPs
Fig.14a and b. DTA curve of the free and Hg$^{2+}$ loaded AgNPs

The weight loss of AgNPs through the heating process was investigated (Fig.11). The TG curve of AgNPs exposed weight loss at two regions related to the loss of water (8% by weight) at temperature about 100°C and the loss of organic binder (50% by weight) at the temperature range of 200–500°C. Such total weight loss at 30–500°C of TG curve linked to the total weight of organic binder added. No more major weight loss peak was observed in the temperature range above 500°C. Fig.12 shows the loss of water and organic binder of AgNPs was confirmed by one endothermic and exothermic peak around at 100 and 480°C corresponding to the evaporation of water and the oxidation of organic binder. From DTA curve, it is confirmed that the limiting temperature for the safer use of AgNPs was 100°C as the AgNPs degrade thermally after 100°C [29]. The TGA (Fig.13a and b) & DTA (Fig.14a and b) analysis of the free adsorbents and metal loaded adsorbents are showed a move in temperature dominant peaks related with the
loaded metal. This change in the temperature shows that the metal binding process taking place at the surface of adsorbents. This corresponds to the fundamental peaks of control (free adsorbents), Hg (II) treated adsorbents and their respective possible band peaks in the TGA and DTA analysis [30].

6.3.2. Effect of opposing ions

The percentage of adsorption of AgNPs for removal of mercury from aqueous media was nearly about 95-98%. However, Alkali and alkaline earth
metals like Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) are universally detected collectively with heavy metal ions in polluted waters. Hence it is essential to find the opposing effect of these innocent cations on heavy metals adsorption by AgNPs. Here, we studied the effects of Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) on Hg (II) adsorption by the AgNPs adsorbent. Outcomes in Fig.15 propose that Na\(^+\) addition causes minor effect on Hg (II) adsorption in the trial concentration series, whereas the divalent competing ions Mg\(^{2+}\) and Ca\(^{2+}\) result in a remarkable drop in Hg (II) uptake on adsorbents. This is clear for the dissimilar behavior for monovalent cations and divalent cations because divalent cations are generally of low hydration energies and have a tendency to be sooner adsorbed [31]. Simultaneously while rising the concentration of Mg\(^{2+}\) and Ca\(^{2+}\) from 0 to 8 times of the Hg (II) concentration results to an
apparent drop of its percentage of adsorption from 100 to 30–40 for AgNPs as well as farther increase in all these competing ions still to 5 times of Hg (II) concentration does not result in further observable capacity decrease. All the above results confirmed that AgNPs shows more superior adsorption toward mercury over these competing cations. Also, mercury ion can be selectively sequestrated by AgNPs by the inner-sphere complexation of Hg (II) on AgNPs [32]. As the spent AgNPs was regenerated by HCl (0.5M)–NaCl (0.8M) binary solution for cyclic use and the results are shown in Fig.16. It was indicated that the preloaded mercury can be efficiently regenerated with 25-30BVregenerates with slight capacity loss.

6.4. Conclusion

The results existed in this work confirmed that AgNPs has the potential to be an ecofriendly and efficient nano-biosorbent for removal of Hg (II) from aqueous media and
industrial wastewater. Then the AgNPs revealed more favorable mercury adsorption in the presence of other competing cations \( \text{Na}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \) at larger levels. In this present work, we have built-up a simple and green method to synthesize AgNPs with diameters in the range of 1–100nm using the CRGE as reductant and capping agent. The grass extract has a syndicate effect in reducing the silver salt solution and hindering the particle growth. This green chemistry approach also serves in scaling up and economic viability of the synthetic process. Further, it is also notable that the reduction of silver ions and stabilization of AgNPs may occur through the involvement of tannins and flavonoids present in CRGE. This biosynthesis may also favors lower toxicity to environment denoting its merit and prompt for preference in various industrial and medical applications. Besides, the exhausted AgNPs are tractable to an effective regeneration by HCl (0.5M)–NaCl (0.8M) binary solution for continual use with slight capacity loss.

6.5. References:


Silver Nanoparticles Impregnated Resorcinol-Formaldehyde tailored Polymer Matrix for Biological and Environmental Applications

Abstract:

Zero valent silver nanoparticles (AgNPs) are usually synthesized through wet chemical methods by using the rather normally venomous and inflammable chemicals. The current study aims at a simple and eco-friendly biosynthesis of AgNPs using Cyperus rotundus grass extract (CRGE) as reducing agent without involving chemical agents associated with environmental toxicity. This method let’s construct AgNPs with the size
of 1–100nm disseminated in a green solution (plant extract). The AgNPs were impregnated in a Resorcinol-formaldehyde resin (RFR) by polycondensation method. The existence of AgNPs alters considerable properties of RFR in expressions of morphology and adsorption capacity for heavy metals retention. The AgNPs loaded RFR (RFR-AgNPs) exerted a significant Hg (II) adsorption and prominent antibacterial efficacy against the water-borne diseases causing gram-negative (*Escherichia coli, Salmonella typhi*) and gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacteria. The polymeric nanocomposites have great potential for utilization in the prevention and treatment of microbial diseases and heavy metals pollution for environmental applications.

*Keywords:* Zero valent silver nanoparticles; Resorcinol-formaldehyde resin; polymer nanocomposites; antibacterial; mercury (II) removal.

### 7.1. Introduction

The development of industries has exasperated the contamination of water bodies such as oceans, lakes, rivers and groundwater ensuing from heavy metal ions is a universal environmental problem. The existence of heavy metals in water bodies has increased apprehension for the eminent harmful effect of such contamination toward human beings, animals and plants. Among the heavy metals, mercury well-known as a type of extremely poisonous and non-biodegradable metal also possibly will cause health hazard while even at very low concentration in water [1]. Thus, the removal of