



Catalytic reduction of Nitrophenols using silver nanoparticles-supported activated carbon derived from agro-waste

Padmaja Sudhakar*, Harnish Soni

Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodra 390 002, India



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ABSTRACT

Immobilization of Ag nanoparticles (AgNps) on solid supports has been considered as the most efficient way to prevent their aggregation and use them as catalysts. Agrowaste derived carbons provide enormous benefits such as environmental friendliness, economic viability and porosity when used as supports for AgNps. The present study was conducted to investigate the use of palm shell agrowaste derived carbon (Agnp-PSAC) as a support for Ag nanoparticles. The prepared Agnp-PSAC was characterized using Transmission electron Microscopy (TEM), Fourier-transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDAX), Raman and UV–visible spectroscopic techniques. The catalytic potential of the prepared Agnp-PSAC was investigated. Nitrophenols such as 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP) and 2,4,6 tri nitrophenol (TNP) were used as substrates. The supported Agnps could be reused upto four cycles. The reduction followed pseudo-first-order kinetics. A value added application of palm shell derived activated carbon is thus proposed.

1. Introduction

The most amenable method for removal of Nitrophenols which are reported to be toxic is by treatment with a catalyst which reduces it into 4-Aminophenol [1]. This method of remediation for nitroaromatic compounds has gained interest as it is a green process avoiding the use of organic solvents. Further the products, aromatic amines are widely used as intermediates for the synthesis of dyes, pharmaceuticals, and agrochemicals [2].

However, the traditional methods for reduction of such nitro compounds involve the use of reagents such as Raney Ni in the presence of acid [3]. The process is thus not green, but costly and environmentally hazardous. A cleaner alternative is employing NaBH_4 in water as the hydride source and using Au, Ag, Pt or Pd as catalysts for this purpose [4–6].

During reduction catalyzed by Ag, it was observed that smaller Agnps usually showed higher activity, due to a more facilitated electron transfer from surface of Agnps to reactants [7]. However, the use of small-sized Agnps as catalysts resulted in their aggregation thus minimizing the surface area of catalysts [8]. A feasible solution to overcome these drawbacks was immobilization of Agnps onto a support so as to retain both the high catalytic activity and reusability of the catalysts [9].

Supports such as mesoporous silicas (e.g., SBA-15, MCM-41) and

mesoporous γ -alumina [10], TiO_2 [11], zeolites [12], carbon nanotubes [13], graphene oxide [14], polyamino cyclodextrin [15] and polymers [16] have been used.

The formation of Agnps on biological matrices such as organic matrix derived from cuttlebone [17]; Chitosan and calcium alginate [18]; methyl cellulose [19] have also been paid particular attention in catalytic applications.

However, very little effort has been directed towards the preparation of metal catalysts supported on carbonaceous materials and the application of carbon supported Ag catalysts in hydrogen mediated reactions. Carbon offers a number of advantages over oxide and other supports, in being cost effective, stable in acid and base media and the possibility of tuning porosity, specific surface area and surface chemistry for specific catalytic applications [20]. Surface oxygen-containing functionalities on carbon act as metal-anchoring sites, lower hydrophobicity and improve support accessibility during catalyst synthesis [21]. The concentration and nature of surface groups can be tailored by treatment with oxidising agents (HNO_3 , KMnO_4 , $\text{H}_2\text{SO}_4/\text{HNO}_3$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 , and O_3) [22].

Mondal et al. prepared Ag/carbon polymer hybrid films using spin coated thin films of PAN in N,N-dimethyl formamide followed by their carbonization and incorporation of a silver salt in the solution prior to spin coating. The Ag/carbon porous films were reported to be effective in the reduction of 4-NP to AP with sodium borohydride [23].

* Corresponding author.

E-mail address: p_padmaja2001@yahoo.com (P. Sudhakar).

Cárdenas-Lizana et al. performed gas phase continuous hydrogenation of m-dinitrobenzene (m-DNB) over acid treated AC supported Au and Ag prepared by deposition-precipitation [24]. In-situ reduction of Ag nanoparticles on oxygenated mesoporous carbon fabric was performed by Ji et al. and was used for reduction of nitro aromatics. T Das et al. synthesised Fe₃O₄ nano-particles supported on coal-derived humic acid and used them as catalysts for reduction of Nitrophenol [25–27].

Our objective was to investigate the potential of activated carbon from palm shell, PSAC as support for Agnps and investigate its potential for the catalytic reduction of Nitrophenols. 4-NP, DNP and TNP were chosen as model compounds.

2. Experimental

2.1. Chemicals and reagents

AgNO₃ (Spectrochem, India), NaBH₄ (Spectrochem, India), 4-NP, DNP and TNP (Spectrochem, India) were used. De-ionized water was used for preparation of all solutions.

2.2. Synthesis of NanoSilver supported on ACs

PSAC was prepared from an agro-waste palm shell as reported elsewhere [28]. Briefly, Palm shells obtained from the coastal areas of Andhra Pradesh, India; were washed, sun dried for 24 h and ground using a jaw crusher. They were then dried at 110 °C and the cleaned powder was mixed with conc. H₂SO₄ (sp. gr. 1.64) in 1:1.5 weight ratio and allowed to stand in an oven maintained at 140–160 °C for 24 h. The resulting char was thoroughly washed with water followed by 2% solution of NaHCO₃ until effervescences ceased and then left to soak in a 2% solution of NaHCO₃ overnight. The acid treated palm shell powder (APSP) was then separated, washed with water until free of bicarbonate and dried at 105 °C. APSP was steam activated in an autoclave at 14 kg pressure for 30 min; followed by thermal activation at 900 °C in furnace for 1 h. Thus prepared carbon was named as PSAC.

The nano silver supported on to PSAC (Agnp-PSAC) was synthesised by a one pot process. About 1.25 g of PSAC was agitated with 50 mL of 0.1 N AgNO₃ solution for 30 min followed by addition of 0.1% (w/w of AgNO₃) NaBH₄. The whole reaction mixture was kept in dark for 4 h and then filtered through whatman filter paper no. 42, and then washed with conductivity water until excess of AgNO₃ solution was removed. The residue was then allowed to dry at ambient conditions.

2.3. Characterizations of NanoSilver supported on ACs

Agnp-PSAC was characterized by XRD, SEM-EDX, FTIR, TEM, Zeta Analyser, Raman and UV–vis spectroscopic techniques

Zeta potential of an aqueous suspension of PSAC in the pH range of 1.0–11.0 was measured using particle size analyser equipped with zeta potential measurement (90Plus/BI-MAS model, Brookhaven Instruments Corporation). **Fourier Transform Infrared Spectroscopy (FTIR)** spectra were collected using Perkin-Elmer RX1 model in the wavenumber range 400 to 4000 cm⁻¹. **Scanning Electron Microscopy (SEM)** analysis enables the direct observation of the changes in the surface microstructures of the adsorbent due to the chemical surface modifications and the elemental composition. The topography of PSAC and Agnp-PSAC was visualized by using a SEM microscope (LEO 1430 VP). **Transmission Emission Microscopic Analysis (TEM)** was performed by drying aqueous solution of Agnp-PSAC on –1500 mesh Cu coated TEM grid (Tecnai-12, FEI-Netherlands) for analysis. Images were taken by single tilt holder with CCD Camera. Tecnai software was used for noise filtering. X-ray diffraction (XRD) measurements were performed on a Philips X'pert MPD X-ray diffractometer to determine the phases formed in ACs. The X-ray source used was Philips high intensity ceramic sealed tube (3 kW) with Wavelength Cu-K α radiation (1.5405 Å). **Raman analysis** was carried out using Mini Ram-II (B&W

TEK) Raman Spectrometer with “CLEANLAZE” laser technology (excitation at 785 nm) and TE cooled 2048 pixel CCD array spectrometer in the range 200 cm⁻¹ to 2800 cm⁻¹. **UV–Visible** spectral measurements were carried out using a JASCO-Japan made spectrophotometer (V-630 model) working in the range 1100 nm–190 nm.

2.3.1. Assay of silver loaded in Agnp-ACs

About 0.1 g sample of Agnp-AC was dried in an oven at 105 °C until constant weight and then digested with 10 mL nitric acid (16 M) in an evaporating dish almost to dryness; further 10 mL nitric acid was added and again digested to dryness. About 15 mL of water was added to the digest and boiled for 10–15 min; the suspension was filtered and thoroughly washed with de-ionized water. The resultant filtrate and washings were combined and diluted to 10 mL with de-ionized water. The silver concentration in the obtained solution was determined using ICP-OES (Optima 3300 RL, Perkin Elmer).

2.4. Catalytic reduction of Nitrophenol

The potential of Agnp-SPAC as catalyst has been evaluated for the reduction of 4-NP, DNP and TNP. In neutral or acidic condition, 4-NP exhibits a strong absorption peak at 317 nm. Upon addition of NaBH₄ to 4-NP, the increased alkalinity of the solution leads to the formation of 4-nitrophenolate ions with a new absorption band at 400 nm [29] providing a simple means to monitor the nitrophenol reduction reaction.

The catalytic reduction experiment was carried out in 10 mL glass vial. In a typical setup, 0.02876 mmol 4-NP was mixed with 8 mL water followed by 20 mg of Agnp-PSAC and 0.7 mmol NaBH₄. A 100 μ L of reaction mixture was taken and diluted to 5 mL in a volumetric flask and the progress of reaction was monitored by taking UV–visible absorption spectra in the wave length range of 200–600 nm at regular time intervals.

3. Results and discussions

3.1. Characterisation

3.1.1. UV–visible spectroscopy

Fig. 1a shows UV–vis spectra of all four catalysts and their respective pristine carbons. It is observed that PSAC and Agnp-PSAC exhibited strong absorption in the visible light region due to their black color [30].

The absorption at 200–350 nm is attributed to the characteristic absorption of the AgCl while the absorption at 350–800 nm can be ascribed to the characteristic surface plasmon resonance (SPR) absorption of Ag nps [31]. However, the weak absorbance may be due to the dispersion of Ag on the surface of ACs.

3.1.2. FTIR analysis

The PSAC loaded with silver exhibited increase in intensity of the bands at 1102 cm⁻¹, 1180 cm⁻¹ and 1402 cm⁻¹ (Fig. 1b). This could be attributed to oxidation of active oxygen functionalities. Further, there was increase in intensity of the band at 3350 cm⁻¹, representing the O–H stretching in C–OH. The band at 900–600 cm⁻¹ could be assigned to Ag–O vibrations [32].

3.1.3. XRD analysis

XRD patterns of as prepared catalysts are shown in Fig. 1c. The well defined intense peaks in the diffraction pattern indicated crystallinity of the Agnps. Characteristic 2 θ values of silver nano particles were observed at 38.04°, 44.22°, 64.39° and 77.36° for Agnp-PSAC that could be readily indexed to the (111), (200), (220) and (311) reflections of fcc structure of silver respectively [33] while a broad diffraction peak at 2 θ ~ 23.5° corresponds to the (002) diffraction of graphite plane arising from the carbon support. The broadness of the peak could be due to

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