

Bio-synthesis of Pd and Ag nanoparticles supported on celestine and their catalytic performance for reduction of Cr(VI) and methyl orange

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Article Info	ABSTRACT
Article type: Research Article	This study reports the green synthesis of palladium (Pd) and silver (Ag) nanoparticles (NPs) supported on celestine using an aqueous extract of <i>Amaranthus caudatus</i> flowers as both a reducing and stabilizing agent. The synthesized nanocomposites were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and energy-dispersive X-ray spectroscopy (EDS), revealing well-dispersed spherical Pd and Ag NPs with average sizes below 60 nm anchored on the celestine surface. The nanocomposites demonstrated excellent catalytic activity and reusability in the reduction of Cr(VI) ions (using formic acid) and methyl orange (MO) azo dye (using NaBH ₄). Notably, Pd NPs/celestine achieved complete reduction of a 10 ppm MO solution in just 30 s, outperforming Ag NPs/celestine (90 s), indicating superior electron transfer efficiency from NaBH ₄ to MO molecules. These findings highlight the potential of Pd-based catalysts for efficient pollutant degradation.
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1. Introduction

Azo dyes and hexavalent chromium (Cr(VI)) have been acknowledged as the most critical and strategic contaminants in water and wastewater, originating from industrial processes [1-3]. These substances pose significant threats to human and animal health due to their carcinogenic and mutagenic properties. Various approaches, including adsorption, photodegradation, chemical reduction, coagulation, ion exchange, and membrane separation, have been employed to effectively eliminate pollutants from wastewater systems [4-8]. Reduction/decolorization process, utilizing NaBH_4 or HCOOH as reducing agents, converts hazardous materials into less toxic organic or inorganic compounds [9-11].

Recently, the usage of Ag and Pd nanoparticles (NPs) because of their high specific surface area, chemical stability, and suitable catalytic activity in different chemical reactions such as arylation of phenols, coupling reactions, synthesis of heterocycles, and reduction of toxic azo dyes have been significantly studied [12-16]. Since metal NPs are prone to aggregate, immobilizing them on the surface of different supports such as bentonite, zeolite, perlite, kaolin, graphene oxide, Fe_3O_4 , ZrO_2 , and CuO leads to their higher reactivity and facile reusability [17-20]. In this field, celestine (or celestite) ore can be used as a support due to its chemical and thermal stability.

The biosynthetic route employing plant extracts for the synthesis of metal NPs offers several advantages, including simplicity, elimination of toxic compounds, lower processing temperatures, and improved control over particle size [21,22]. Flavonoids and non-flavonoids polyphenols in different organs of plants can effectively reduce the metal ions and stabilize the formed NPs [23,24].

Amaranthus Caudatus as an important source of phenolic compounds, has several pharmaceutical activities such as anticancer, antibacterial, anthelmintic, antipyretic, antinociceptive, antidiabetic, antiallergenic, cardioprotective, and hepatoprotective properties [25-27].

In the present work, Pd and Ag NPs were immobilized onto the surface of celestine ore using *A. Caudatus* flower extract. Biosynthesized nanocomposites were used as catalysts to reduce Cr(VI) ions or methyl orange (MO) azo dye from water.

2. Experimental

The celestine ore has the following chemical composition (in %): SrO , 54.57; SO_3 , 42.14; CaO , 1.03; SiO_2 , 0.23; MgO , 0.32; Na_2O , 0.01; K_2O , 0.04; Al_2O_3 , 0.01; Fe_2O_3 , 0.09 and TiO_2 , 0.01. This natural strontium sulfate was provided from the Koohsefid area in Qom, Iran. The flowers of the *A. Caudatus* plants were collected from the city of Kamu in the Isfahan province of Iran. AgNO_3 and PdCl_2 were purchased from Aldrich. The concentration of Cr(VI) and MO solutions was monitored using a Lambda-35 UV-Vis spectrophotometer. FTIR spectra of celestine and its Pd and Ag nanocomposites were recorded using a Cary

630 FTIR spectrometer. The X-ray diffraction (XRD) patterns were obtained by a Philips PW 1730 X-ray diffractometer ($\text{CuK}\alpha = 1.5406$). FESEM-EDAX analysis of prepared nanocomposites was performed on the Cam Scan MV2300.

2.1. Preparation of *A. Caudatus* flower extract

A 250 mL beaker containing 10 g of the dried *A. Caudatus* flowers and 120 mL distilled water was heated at 40 °C for 20 min. The obtained extract was filtered and applied for the synthesis of Pd and Ag NPs in the following steps.

2.2. Preparation of Pd NPs/Celestine nanocomposite

1 g of celestine was dispersed in 25 mL of *A. Caudatus* extract at ambient temperature using a mechanical stirrer. Subsequently, a solution containing 0.1 g PdCl_2 dissolved in 7 mL acetonitrile was added to the mixture and then heated at 50 °C. Following 30 minutes, the resulting Pd NPs/Celestine nanocomposite was thoroughly rinsed with distilled water and subjected to drying at ambient temperature.

2.3. Preparation of Ag NPs/Celestine nanocomposite

80 mL of *A. Caudatus* flower extract was added to a mixture of celestine ore (1g) dispersed in AgNO_3 solution (25 mL, 0.1 M). Then, this mixture was stirred continuously for 30 min at 50 °C. The obtained Ag/Celestine nanocomposite was washed twice with distilled water and subsequently dried at ambient temperature.

2.4 Catalytic reduction of Cr(VI) ion or MO azo dye using prepared nanocomposites

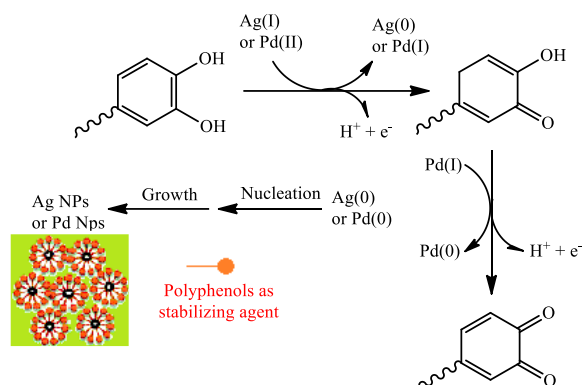
The celestine and its Pd and Ag nanocomposites (8 mg) were dispersed in 3.4 mM Cr(VI) solution containing 1 mL 88% formic acid as a reducing agent. Also, 8 mg of these catalysts were applied for the reduction of the MO solution (25 mL, 10 ppm) by utilizing the newly prepared NaBH_4 solution (25 mL, 5.3×10^{-3} or 10.6×10^{-3} M). The changes in the Cr(VI) and MO concentration were monitored using UV-Vis analysis at λ_{max} of 350 and 465 nm, respectively.

3. Results and discussion

3.1. Preparation of Pd and Ag NPs

As depicted in Scheme 1, the aqueous flower extract of *A. Caudatus* contains various water-soluble phytochemicals, such as flavones and terpenoids, which can undergo enol-form into the keto-form conversion (tautomeric transformations) and subsequently reduce metal ions. Additionally, these compounds play an important role as stabilizing agents

due to their hydroxyl and carbonyl functional groups for the synthesized Pd and Ag NPs [28].



Scheme 1. The plausible mechanism of Ag and Pd NPs preparation in the presence of the plant extract.

3.2. Characterization of the prepared catalysts

The FT-IR spectra of the prepared celestine, Ag NPs/Celestine, and Pd NPs/Celestine are presented in Figure 1. The observed bands at approximately 1090–1200 and 610–640 cm^{-1} are assigned to the SO_4^{2-} bands [29, 30]. The peaks around 1400–1650 cm^{-1} in Figures 1b and 1c are related to the constituents of *A. Caudatus* extract that has been absorbed on the Pd and Ag NPs surfaces as stabilizing agents [31]. The broad peaks at wavenumbers 3800–4500 cm^{-1} can be attributed to O–H stretching vibrations [32,33].

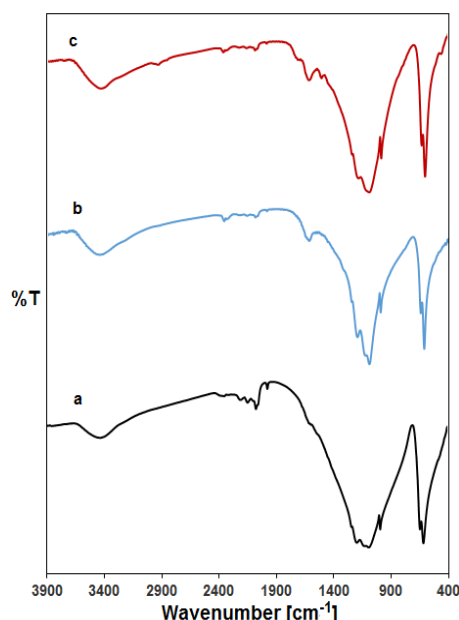


Figure 1. FT-IR spectra of (a) celestine, (b) Ag NPs/Celestine, and (c) Pd NPs/Celestine.

The crystalline structures of the celestine and its synthesized Pd and Ag nanocomposites were evaluated using XRD analysis (Figure 2). The observed diffraction peaks at about 2θ values of 27.1, 28.1, 30.1, 32.8, and 44.3° can be ascribed to the (021), (210), (121), (211), and (212) planes for celestine [34]. The

peaks at 2θ values of 37.3 and 44.1 in Figure 2b can be attributed to the (111) and (200) crystal planes of Ag NPs with a face-centered cubic structure (JCPDS card No-87-0719), respectively [35]. In the XRD pattern of Pd/Celestine (Figure 2c), no specific peaks related to the Pd phase are found, possibly due to the high dispersion of the Pd NPs stabilized on the support surface or their amorphous phase [36].

The FESEM images of Pd NPs/Celestine and Ag NPs/Celestine (Figures 3 and 4) indicate the well-dispersed spherical Pd and Ag NPs prepared by the plant extract on the celestine support. Furthermore, the EDS spectra of these nanocomposites confirm the presence of Pd and Ag elements.

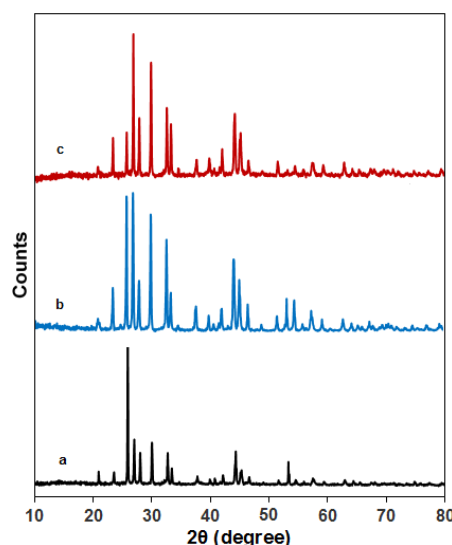


Figure 2. X-ray diffraction of celestine (a), Ag NPs/Celestine (b), and Pd NPs/Celestine (c).

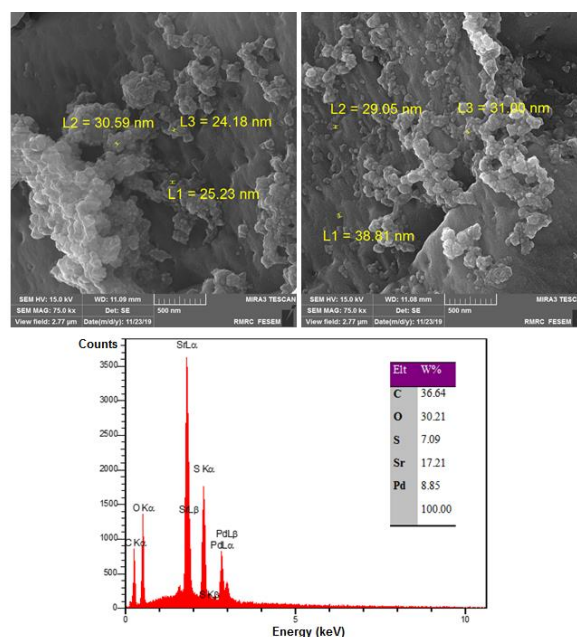


Figure 3. FESEM images and EDS spectrum of the Pd NPs/Celestine nanocomposite.

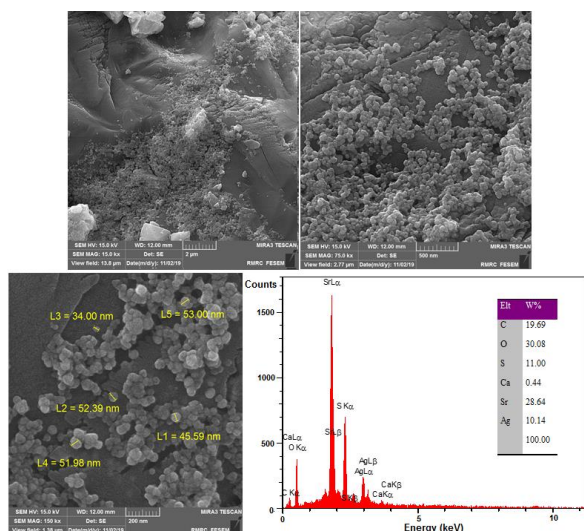


Figure 4. FESEM images and EDS spectrum of the Ag NPs/Celestine nanocomposite.

3.3. Catalytic activity of the Pd NPs/Celestine and Ag NPs/Celestine catalysts for the MO and Cr(VI) reduction

The development of heterogeneous catalysts with exceptional activity in the degradation of pollutants has presented a significant role in the field of environmental applications [37-39]. In this study, the effectiveness of the Ag NPs/Celestine and Pd NPs/Celestine catalysts was evaluated in the reduction/decolorization of the Cr(VI) ion and MO dye as representative pollutants (Scheme 2). The alterations of absorption bands in the UV-Vis spectra of MO and Cr(VI) solutions in the catalytic reductions using Pd NPs/Celestine are depicted in Figure 5a and Figure 5b, respectively. The reduction time of the 3.4 mM Cr(VI) solution containing 1 mL of 88% formic acid using Pd NPs/Celestine was 25 min. However, a significant reduction of Cr(VI) solution was not observed within 60 min using Ag NPs/Celestine. Additionally, the reduction times of the MO solution (10 ppm) were 30 and 90 s in the presence of Pd NPs/celestine and Ag NPs/Celestine catalysts, respectively. The observed results suggest that Pd NPs are more effective than Ag NPs in the electron transfer from reducing agents (NaBH_4 or formic acid) to the selected pollutants [28].



Scheme 2. Green synthesis of Pd and Ag NPs supported on celestine and their catalytic investigation in the reduction/decolorization of MO and Cr(VI).

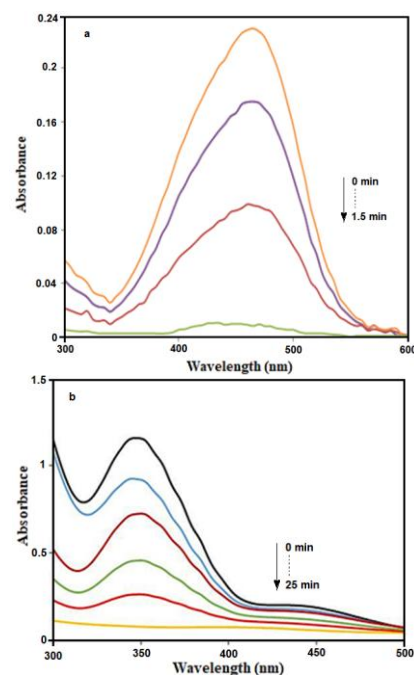


Figure 5. UV-Vis spectra changes of MO (a) and Cr(VI) (b) during the catalytic reduction.

3.4. Recycling of catalyst

Here, the recycling of Pd NPs/Celestine and Ag NPs/Celestine nanocomposites for the MO reduction was investigated. The FESEM images and EDS spectra of the recycled catalysts after four times are shown in Figures 6 and 7. The results show that the Pd and Ag NPs amounts and their morphology have not significantly changed. Hence, there is only a slight decrease in the catalytic activity of recycled nanocomposites due to their good stability and reusability. The MO reaction time in the presence of the recycled Pd NPs/Celestine and Ag NPs/Celestine was about 30 and 100 s, respectively.

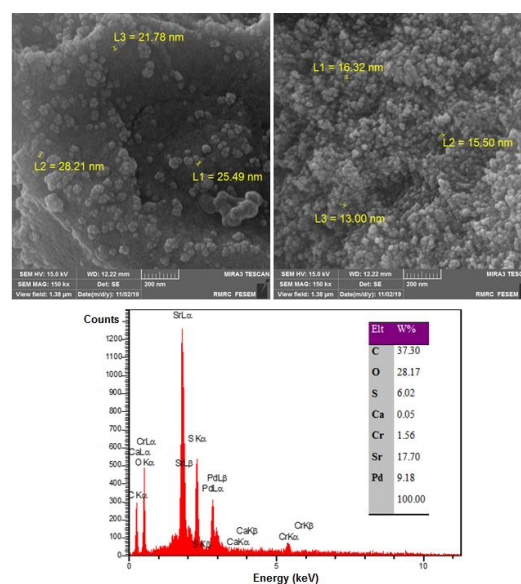


Figure 6. FESEM images and EDS spectrum of the recycled Pd NPs/Celestine nanocomposite.

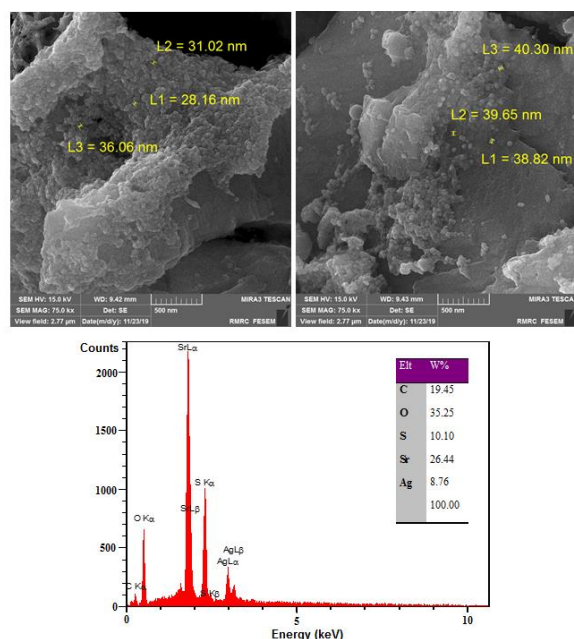


Figure 7. FESEM images and EDS spectrum of the recycled Ag NPs/Celestine nanocomposite.

4. Conclusions

This study successfully synthesized palladium (Pd) and silver (Ag) nanoparticles (NPs) supported on celestine using a green approach with *Amaranthus caudatus* extract as both reducing and stabilizing agent. Comprehensive characterization (FTIR, XRD, EDS, FESEM) confirmed the formation of well-dispersed spherical Pd and Ag NPs (<60 nm) on the celestine surface. The Pd NPs/celestine nanocomposite exhibited superior catalytic activity over its Ag counterpart in the reduction of methyl orange (MO) and Cr(VI), achieving complete decolorization of MO in just 30 s and reduction of Cr(VI) within 25 min using NaBH₄ and formic acid, respectively. Notably, both catalysts retained high stability and reusability over four consecutive cycles, with no significant loss in activity. These findings underscore the potential of Pd NPs/celestine as an efficient and sustainable nanocatalyst for environmental remediation of toxic pollutants.

Conflict of Interests

The authors declare no conflicts of interest.

Acknowledgements

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