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# Green synthesis of seashell supported silver nanoparticles using *Bunium persicum* seeds extract: Application of the particles for catalytic reduction of organic dyes

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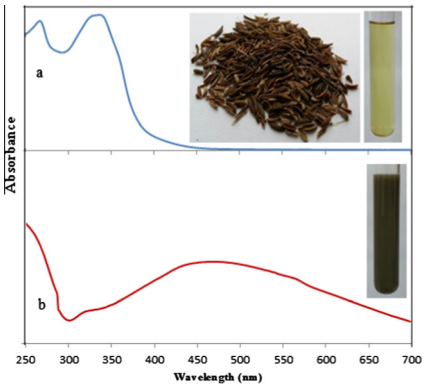
## HIGHLIGHTS

- Green synthesis of Ag NPs/seashell by extract of seeds of *B. persicum*.
- Ag NPs/seashell was characterized by FT-IR, FE-SEM, EDS, TEM, TG-DTA, XRD and UV–Vis.
- Catalytic reduction of 4-nitrophenol, Methyl Orange, Congo Red and Methylene Blue.
- The catalyst could be easily recovered and reused several times.

## GRAPHICAL ABSTRACT

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## ABSTRACT

In the present work, silver nanoparticles were immobilized on the surface of seashell using *Bunium persicum* seeds extract as a reducing and stabilizing agent. The seashell supported silver nanoparticles was characterized by FT-IR spectroscopy, X-ray diffraction (XRD) pattern, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and Thermogravimetric-differential thermal analysis (TG-DTA). The diameter of Ag NPs on the seashell was predominantly found within the range 20–50 nm. The catalytic performance of the prepared catalyst was investigated for reduction of 4-Nitrophenol (4-NP), Methyl Orange (MO), Congo Red (CR) and Methylene Blue (MB) at room temperature. It was found that the Ag NPs/seashell is a highly active and recyclable catalyst for related reactions and can be recovered and reused several times without significant loss of its catalytic activity.



## 1. Introduction

Azo dyes and nitroarene compounds are well known as toxic, bio-refractory and carcinogenic pollutants in wastewaters. Therefore, it is necessary to find the effective methods to remove these contaminants [1,2].

Reduction process in the presence of metal nanoparticles (MNPs) and $NaBH_4$ is a new and rapid technique for the removal of pollutants from water [3,4].

The reactivity of MNPs is more than the particulate metal counterpart because of their small sizes and large surface areas. Among MNPs, silver nanoparticles (Ag NPs) have attained a particular

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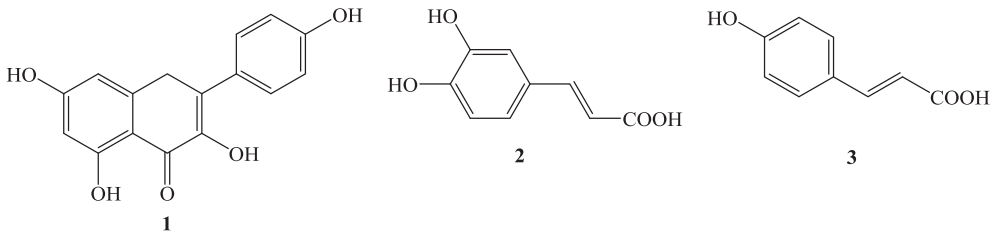


**Scheme 1.** The major components of *B. persicum*.

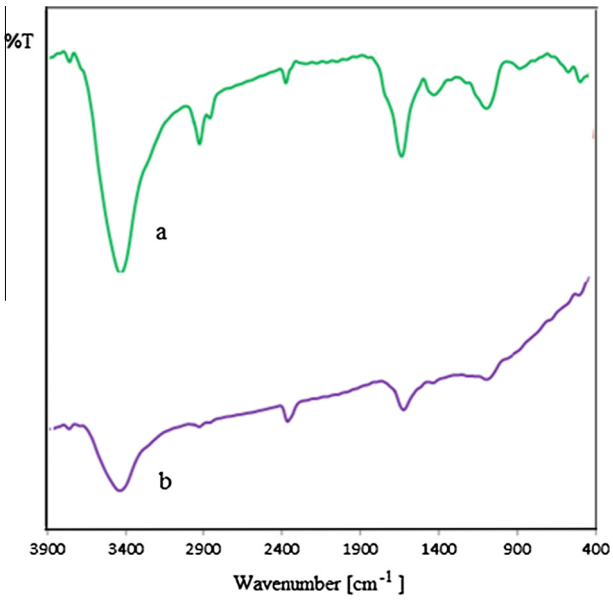


**Fig. 1.** FT-IR spectra of *B. persicum* extract (a) and Ag NPs prepared using aqueous extract of *B. persicum* (b).

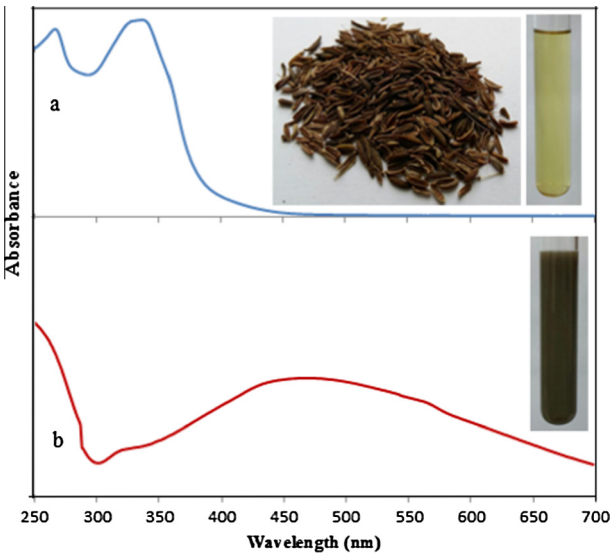


**Fig. 2.** UV–Vis spectra of *Bunium persicum* seeds extract (a) and synthesized Ag NPs using aqueous extract of *B. persicum* (b).

attention due to their stability, good conductivity, high catalytic, antibacterial, anti-viral and antifungal activities [5,6]. Despite the high catalytic activity of Ag NPs, their agglomeration is inevitable. To overcome the agglomeration of MNPs, heterogeneous catalysts have been prepared by immobilizing MNPs onto inorganic materials such as $TiO_2$ [3], zeolites [7], magnetic-materials [8], graphene [4,9], bentonite [10] and gums [11]. Immobilization of MNPs on different supports decrease nanoparticles agglomeration, increase their stability and facilitate their separation and recovery. The heterogenization of homogeneous catalysts on natural supports such as zeolite and bentonite can partly circumvent the drawbacks of the immobilization not only for ecological reasons, but also from an economical point of view [7,10].

Natural ceramics, especially seashells with pearly layers exhibit superior structural robustness, despite the brittle nature of their ceramic constituents [12–14]. They have a layered brick-and-mortar architecture with calcium carbonate ($CaCO_3$) conventional platelets as the bricks and protein as the mortar. Seashells have generated sustained interest amongst researchers in the last few decades [12–14]. However, to the best of our knowledge, there is no report to date on using of seashell as a support for immobilization of Ag NPs.

Recently, the development of new methods for the synthesis of MNPs by plants extract has continued to increase dramatically [3,4,7–11]. Plants extract mediated synthesis of NPs can be useful for preparing nanomaterials to control the size, shape and distribution size. During this type of green syntheses which is carried out in an aqueous environment under mild conditions, no need of toxic reducing and stabilizing agents. The biosynthetic techniques for the synthesis of MNPs by using plants extract are very desirable and has several merits over chemical and physical synthetic methods, such as use of nontoxic solvents such as water, very mild reaction conditions, simplicity, elimination of toxic and dangerous materials, elimination of high pressure, energy, temperature and cost effectiveness as well as compatibility for biomedical and pharmaceutical applications [3,4,7–11].

*Bunium persicum* is an Iranian plant which is valued for its antispasmodic, carminative, antiobesity, antimicrobial and antioxidant properties [15–18]. Gamma-terpinene and cuminaldehyde are the major components which are found in the oil extract and kaempferol (**1**), caffeic acid (**2**) and *p*-coumaric acid (**3**) (Scheme 1) are found as antioxidant components in the methanol extract [15].

Very recently, our research group have been studied and reported the synthesis of metal or metal oxide NPs using plants extract [19–22]. In continuation of our previous efforts on MNPs catalyzed reactions [19–22], we herein present for the first time, synthesis of seashell supported Ag NPs by a simple and green method using *B. persicum* seeds extract. The catalytic activity of the prepared catalyst was investigated for reduction of various dyes.

## 2. Experimental

### 2.1. Instruments and reagents

High-purity chemical reagents were purchased from the Merck and Aldrich chemical companies. All materials were of commercial reagent grade. The seashell used in this study originated from Mazandaran Sea, Mazandaran Province, Babolsar City, Iran. FT-IR