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Green arbitrated synthesis of Fe_3O_4 magnetic nanoparticles with nanorod structure from pomegranate leaves and Congo red dye degradation studies for water treatment

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ABSTRACT

An efficient, cost effective and eco-friendly approach has been developed for the synthesis of Fe_3O_4 magnetic nanorods (MNRs) using aqueous extract of *Pomegranate* leaves (PG). The synthesized PG-Fe_3O_4 MNRs were characterized by using different microscopic and spectroscopic techniques. The synthesized PG-Fe_3O_4 MNRs confirmed by Raman scattering and X-ray photoelectron spectroscopy reveal that PG-Fe_3O_4 MNRs are well dispersed with uniform size (45–60 nm) and exhibits high specific surface area of 14.6 $m^2\ g^{-1}$ calculated using BET adsorption-desorption method. The magnetic behavior of PG-Fe_3O_4 nanorods was studied using vibrational sample magnetometer (VSM) at 300 K, and the results obtained shows enhanced magnetic properties of saturation magnetization (M_s, ~59.0 emu/g), remnant magnetization (M_r, ~15.5 emu/g) and coercivity (H_c, 220 Oe). Furthermore, we also reported the use of the synthesized PG-Fe_3O_4MNRs as an adsorbent to dispose of the Congo red (CR) containing waste water, which exhibited more favorable adsorptive properties as compared to the bulk-metal oxides with low surface area.

1. Introduction

The stable and nontoxic magnetic iron oxide nanoparticles (Fe_3O_4 NPs) have been applied in diverse fields such as detection and separation of proteins [1], to improve the sensitivity of magnetic resonance imaging [2], immunoassay [3], drug and gene delivery [4–6] etc. Nevertheless, the use of the nanoparticles has also attracted a lot of attention in the field of catalysis [7], targeted drug delivery [8,9], cancer therapy [10], proton exchange membrane [11], sensor [12], bio-sensing applications [13] and magnetic resonance imaging [14,15]. Likewise, some iron oxides and their composite have proved as effective materials for dye degradation by adsorption [16–21] due to their high surface area and diverse nanostructures. So far, different approaches have been used for the synthesis of Fe_3O_4 MNPs such as hydrothermal/solvothermal [22], sonochemical [23], micro-emulsion [24], electrochemical [25], sol-gel [26] and co-precipitation methods [27]. However, the green synthesis of nanoparticles has been proved to be a cost-effective environmental friendly and an alternative to chemical and physical methods. The previous reports on the green synthesis of Fe_3O_4 MNPs [28–33] have been very costly, hence we report a facile and low cost environmentally benign green synthesis in this study.

In the present study, naturally abundant *Pomegranate* leaves were used for the synthesis of Fe_3O_4 nanoparticles by the green route. *Pomegranate* leaves are found growing wild in the warm valleys and outer hills of the Himalaya between 900 m and 1800 m altitude. It is cultivated throughout India, the largest area being in Maharashtra. Its leaves are useful in treating digestive problems, skin problems, low appetite, insomnia and certain other medical conditions. However, in this study, we report *Pomegranate* leaves extract as capping and reducing agent for synthesis of PG-Fe_3O_4 MNRs. Moreover, a facile complete green synthesis of PG-Fe_3O_4 MNRs has been developed using the *Pomegranate* leaves extract {Tannins (punicalin and punicafolin), flavones glycosides, luteolin and apigenin} [34,35]. The formation of PG-Fe_3O_4 MNRs is shown in Scheme 1. Further, the synthesized PG-Fe_3O_4MNRs were characterized by various microscopic and spectroscopic techniques. The silver, copper and zinc nanoparticles compared iron nanorods exhibit much higher stability in rigorous environments, as well as at high temperatures and pressures. PG-Fe_3O_4 MNRs exhibit surface area and larger pore volumes. In this work, we used these PG-Fe_3O_4 MNRs as typical examples to study their dye adsorption ability which is injurious to the environment and to public health. Hence, we had selected Congo red as the absorbed dye.

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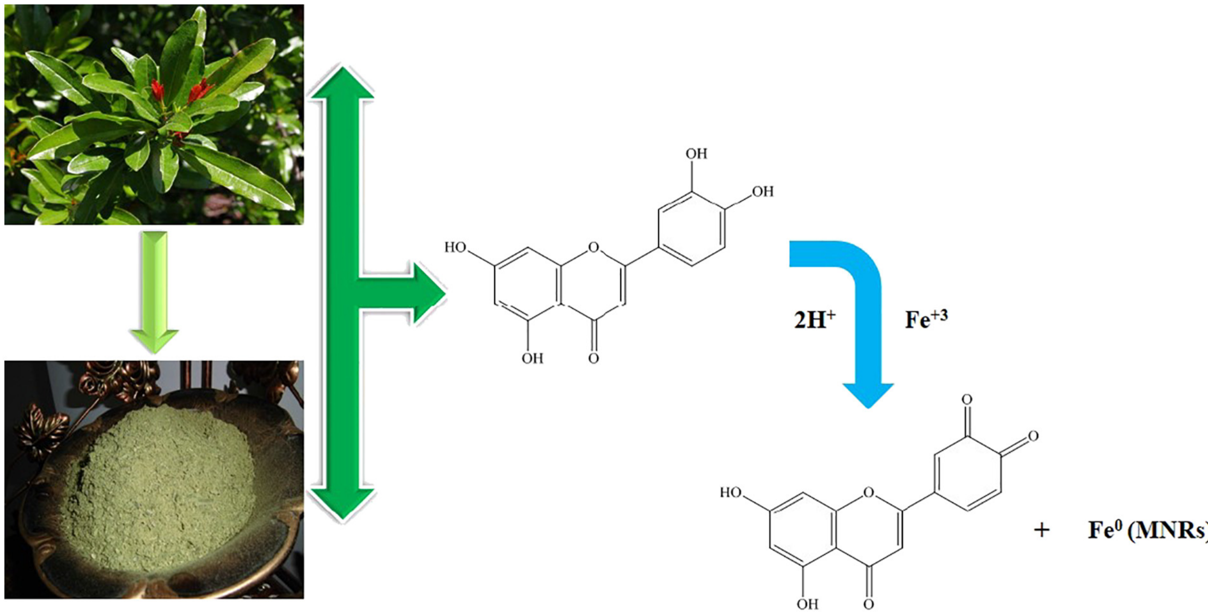

Scheme 1. Formation of PG-Fe_3O_4 MNRs by using *pomegranate* leaves.

2. Materials and experimental methods

2.1. Materials

The mass fraction purity of all the chemicals was used without further purification and sodium acetate was purchased from Sigma Aldrich with (99%) purity. In the synthesis procedure of FeCl3.6H2O double deionized water was used.

2.2. Preparation of the leaf extract

The *Pomegranate* leaves are collected and carefully washed with double deionized water to remove the muck particles and the leaves were dried under umbrageous at room temperature for 24 h in dust free condition and grinded with mortar and pestle into powder. Furthermore, 100 mL of double deionized water was added to 10 g of *Pomegranate* leaves powder and this mixture was refluxed for 1 h at 80 °C, and the extracted aqueous solution changes its color from watery to pale yellow. The composition was allowed to cool to the room temperature and filtered by using Whattman No. 1 filter paper. Finally, the *Pomegranate* leaves extract solution was stored at 4 °C for further process.

2.3. Synthesis of PG-Fe_3O_4 magnetic nanorods

Green synthesis of Fe_3O_4 MNRs was carried out using the eco-friendly method. In a conventional reaction 0.1 M $FeCl_3$ solution was prepared by adding 1.623 g of $FeCl_3$ in 100 mL of water. Afterwards, 0.1 M $FeCl_3$ solution was added to the aqueous leaf extract solution in 2:1 ratio besides 6.46 g of sodium acetate was dissolved in this mixture and stirred vigorously for 3 h at 85 °C. Consequently, the resulting solution turned black in color after 3 h identify the formation of Fe_3O_4 MNRs. Furthermore, the resulting solution was cooled to room temperature and the black product obtained was isolated by

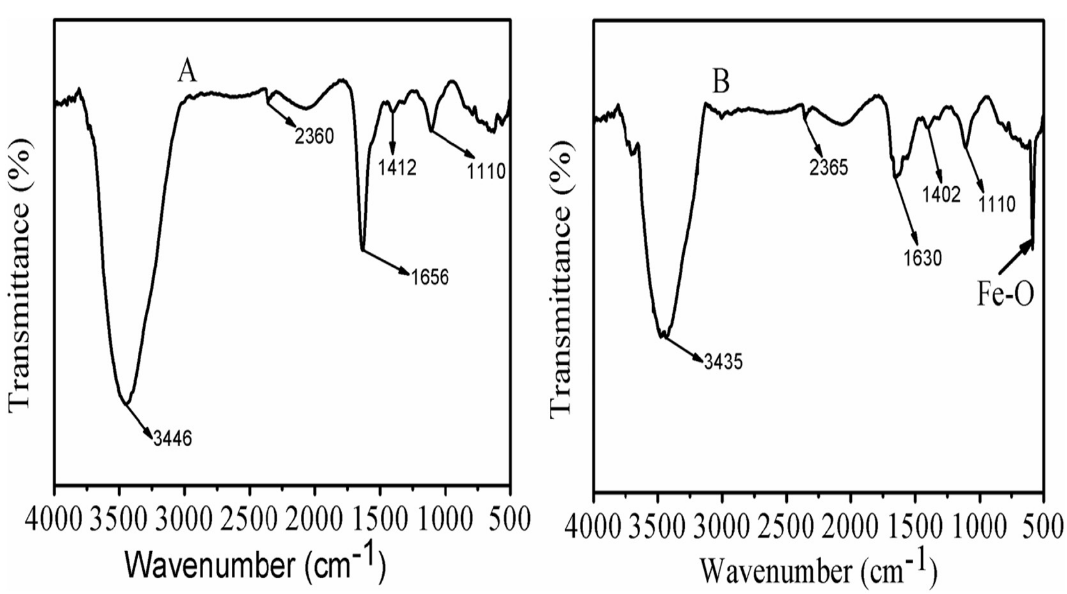

Fig. 1. FT-IR spectrum of (A) pomegranate leaves extract and (B) PG-Fe_3O_4 MNRs samples.