



Original Research Article

Synthesis and characterization of biocompatible and magnetic ESW-Fe₃O₄-Cit nanocomposite by a green one-pot route

Elaheh Mosaddegh^{1*}, Asadollah Hassankhani¹

¹ Department of New Materials, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, PO Box 76315-117, Kerman, Iran.

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ABSTRACT

Magnetic nanocomposite, ESW-Fe₃O₄-Cit, was synthesized via a novel, low cost and green co-precipitation method using eggshell waste nanopowder and FeSO₄. In the present procedure, eggshell (ES) nanopowder was prepared from food waste by collecting, washing, and ball milling. Nano eggshell waste (ESW) was modified by FeSO₄ and trisodium citrate under natural conditions without additional alkali and a protective atmosphere. Trisodium citrate was used as a modifier and stabilizing reagent to form well dispersed small size and coated magnetic nanoparticles which should be ascribed to a large reduction of the surface electrostatic charge of the nanoparticles. The ESW-Fe₃O₄-Cit nanocomposite exhibits larger magnetization (14.6 emu/g) as compared to the uncoated composite (7.68 emu/g). Trisodium citrate causes an interesting increase in magnetic properties after coating on the magnetic eggshell waste nanopowder, due to the prevention of agglomeration causing self-Neel and Brownian Relaxation. The magnetic nanocomposite was fully characterized by FTIR spectroscopy, TEM and FESEM images, XRD, Zeta potential, DLS, and VSM analysis.

Keywords: Fe₃O₄, eggshell waste, MNPs, nanocomposite, VSM.

Introduction

Natural porous materials have various functions and characteristics superior to the synthesized and artificial ones [1,2] making them more interesting for research. In addition, the porous structure of these natural materials makes them use less material to form a higher surface area under equivalent conditions compared to artificial ones [3,4]. In recent years, the study of eggshell structure has been a fascinating area of research due to its interesting natural porous structure [5]. Eggshell wastes (ESW) are abundant, inexpensive, and biodegradable biomaterials, which are composed of more than 90% calcium carbonate [6]. ESW shows relatively lower density and phase continuity in the composite as compared with mineral CaCO_3 . Thus, ES wastes can be used as an excellent and potential candidate for cheap and lightweight bulk quantity and low load-bearing composite preparation [7]. Composite materials supported by metal oxide molecules, specifically iron oxide, have important applications in areas such as catalysis and electronics. The use of an inorganic or ceramic matrix in a composite structure allows narrow dispersion of metal oxide particle size, and homogeneous distribution [7]. These properties of the composites as well as high surface area ratio to volume leads to superior magnetic properties and promising new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionics, nanowires, sensors, and tissue fluids [8]. In this regard, the porous ceramic structure of eggshell with the ability to provide nucleation sites and minimize the aggregation of particles is an excellent host to prepare magnetic nanoparticles (MNPs), biocompatible composites, and novel materials with high conductivity and magnetic properties [9,10]. In recent years, special attention has been devoted to eggshell waste treatment and recycling due to the green aspects of technology [11-13]. In recent years, a lot of efforts have been made to apply eggshells as value-added products [14-16].

In this work and based on our interest in the synthesis of new nanocomposites [17-20], a new and highly effective strategy is developed for the synthesis of novel ES- Fe_3O_4 -Cit core-shell nanocomposite by using eggshell, a bioceramic, as support material for supporting MNPs and trisodium citrate (Na_3cit) as *coating and magnetic susceptibility agent*. Fe_3O_4 MNPs were synthesized by a co-precipitation method at 60 °C without any protective atmosphere.

The porous structure of ES is alkali and can raise the pH of metal ion solution to 9.5 during the MNPs synthesis procedure. So, the chemical co-precipitation method needs no additional alkali and ESW can act as support and base together. To our knowledge, this is the first report on the

green synthesis of MNPs supported on eggshell waste as a natural and biocompatible composite. The structure, chemical composition, morphology, dispersion, Zeta potential, and magnetic properties of Fe₃O₄ MNPs were investigated in detail.

Materials and Methods

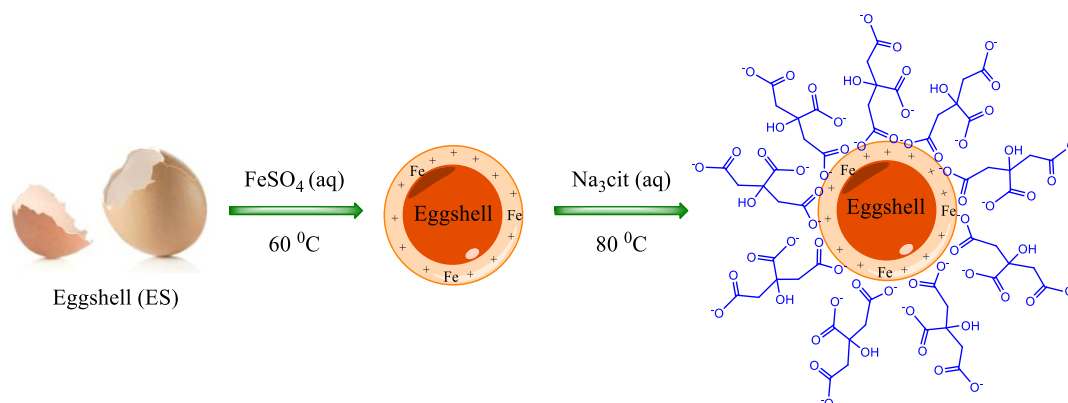
Materials

All chemicals, used in this work, were of analytical reagent grade, purchased from Merck, and used with no further purification. Double-deionized water was used for all dilutions. IR spectra were obtained with MATSON 1000 FT-IR spectrophotometer. X-ray diffraction (XRD) with an X-Pert Philips PW340/60 diffractometer (40kV and 30mA) and Cu_{Kα} radiation ($\lambda=0.154$ nm) was used to analyze the crystal structure of the milled powders. TGA experiments were carried out using an STA 409 PC Luxx thermal analysis machine (NETZSCH, Germany) under a flow of nitrogen. The morphology of the cross-section of the film was examined with transition electron microscopy (TEM) (Philips, CM 120). The Milling was carried out in a planetary ball mill using a hardened chromium steel vial (250 ml) at room temperature under an argon atmosphere. Zeta Potential (mV) and particle size were determined in a Nano Size ZS apparatus. For zeta potential measurements the ground material was suspended in water and homogenized with ultrasound for 6 min.

Magnetic nanocomposite preparation

The ESWs were prepared according to the previously described method⁵. Initially, the collected household empty chicken ESs were washed with warm tap water to remove the polluting and the adhering membrane.

The ESWs were, further, washed with distilled water and dried at 80 °C for 1 h. Then, the planetary milling of the ESWs was carried out for 2 h. Following, 1.0 g of the ESW powder was mixed simply with 100.0 mL of FeSO₄ solution at the concentration of 1000 mg L⁻¹ to achieve a narrow size distribution MNPs by the co-precipitation method. The suspension was stirred vigorously in a baker at 60 °C. The color of the suspension was immediately changed to light brown and finally, the black ESW-Fe₃O₄ nanocomposite was produced after 2 h (Scheme 1).



Scheme 1. Synthesis of ESW-Fe₃O₄-Cit nanocomposite

Stabilization of magnetic nanocomposite

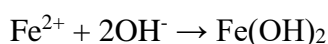
50 mL of the trisodium citrate (Na₃C₆H₅O₇) 1.5 M as an electrostatic stabilizer was added into the final suspensions to modify the surface of the obtained nanocomposite. The suspension was stirred for 18 h at 80 °C. Then, the mixture was kept at room temperature to cool down and the resulting particles were magnetically separated and washed with deionized water several times to remove any excess salts from the suspension. The products were then dried at 60 °C in an oven for further characterization.

Results and Discussion

Characterization of nano eggshell/Cu catalyst

XRD analysis

ESW has an alkali nature and Ca(OH)₂ can be formed at its surface when mixed with an aqueous solution, increasing the *pH* of the aqueous suspension up to 9.5. So, ESW acts as a bifunctional agent (alkali and support) to precipitate Fe²⁺ without any use of more external alkali. Also, the preparation of MNPs was performed under an oxygen atmosphere. In this procedure, Fe(OH)₂ was oxidized by O₂ in the air to form FeOOH. Combination of Fe(OH)₂ and FeOOH at 60 °C produced magnetic Fe₃O₄ particles [21-23]. In contiguity of ES support with Fe₃O₄ which was produced according to:



and



the Fe_3O_4 crystals grew on the porous surface of the support as NPs. It indicated that the use of ES support in the co-precipitation method under air can produce Fe_3O_4 with no need to involve Fe^{3+} as precursors. Surface stabilization of the nanocomposite was carried out via a one-pot procedure by using trisodium citrate. Therefore, the novel stabilized ESW- Fe_3O_4 nanocomposite was produced under mild, green, and approximately natural conditions. The morphology of the nanocomposite can be deduced from the XRD pattern as we have described previously [24].

As shown in Fig. 2, the main peak at $2\theta=29.4$ was identified as the major phase of CaCO_3 in the structure of mineral CaCO_3 and the obtained composite [5]. Comparing the XRD patterns of ESW (Fig. 1a) and nano ESW- Fe_3O_4 -Cit(Fig. 1b) corroborated that the peaks observed at (220), (311), (400), (422), (511), (440), (533) and (731) were related to the inverse cubic spinel phase of Fe_3O_4 MNPs which are by those reported in the literature [25]. The XRD patterns comparison implied the formation of ESW- Fe_3O_4 nanocomposite which suggests that the crystalline structure of Fe_3O_4 MNPs can be remained after supporting and surface modification with sodium citrate. Further, the presence of iron was approved with energy dispersion x-ray (EDX) analysis of uncoated nanocomposite that showed high levels of Fe (26.2%), Ca (26.5%), O (29.9%) and carbon (13.4%) with small amounts of Si (2.7%), Al (0.7) and Na (0.7%). An average diameter of as-synthesized nanocomposite stabilized with sodium citrate was calculated by using the Scherrer equation ($D=K\lambda/(\beta \cos\theta)$), and it is about 20 nm.

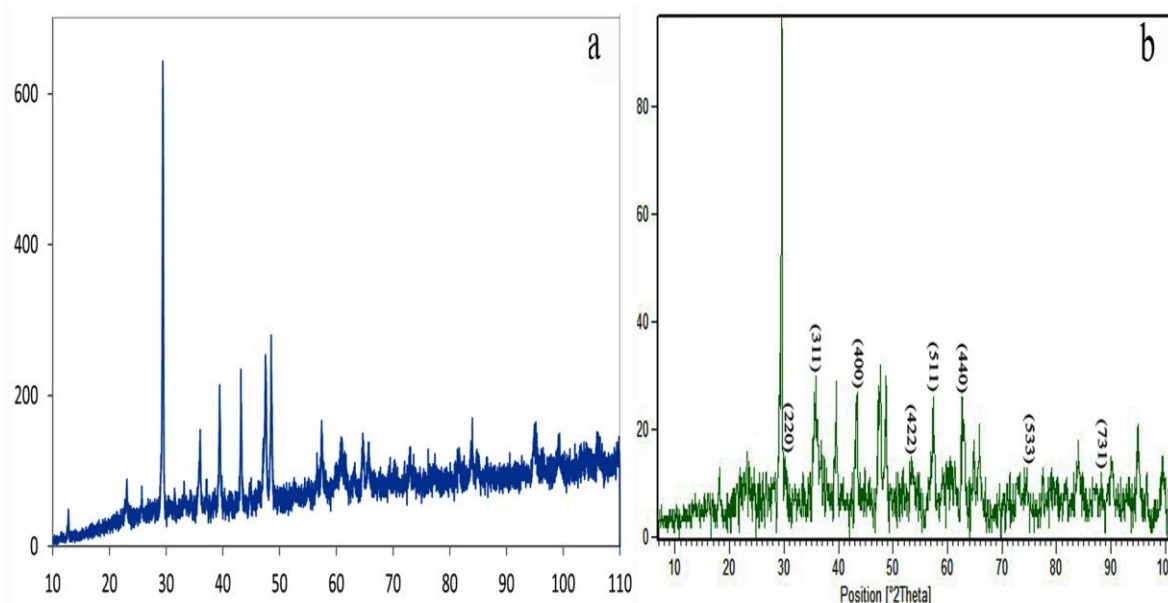


Figure 1. XRD pattern of raw ESW(a) and stabilized ESW- Fe_3O_4 -Citnanocomposite (b).

FTIR spectra analysis

FTIR spectroscopy is another key tool to investigate the nature of the surface metallic sites of the molecules. The FTIR spectra of the nanocomposite structure (Fig. 2) show the typical carbonate absorptions at about 2517 (HCO_3), 1799 (CO), 1422, and 710 (C–O), and 876 cm^{-1} (OCO). Both coated and uncoated composites show a broad band at about 3420 cm^{-1} which is due to surface hydroxyl groups stretching vibration from adsorbed water. The strong FTIR band observed at around 599 cm^{-1} can be attributed to the Fe–O–Fe stretching vibration mode of Fe_3O_4 [25]. The bands at 1020 and 1154 cm^{-1} were just observed for modified nanocomposite that indicates the binding of the citrate anions to the magnetite surface of nanocomposite [26–28]. Also, the peak around 2979 cm^{-1} is due to the stretching vibration of the alkyl chain.

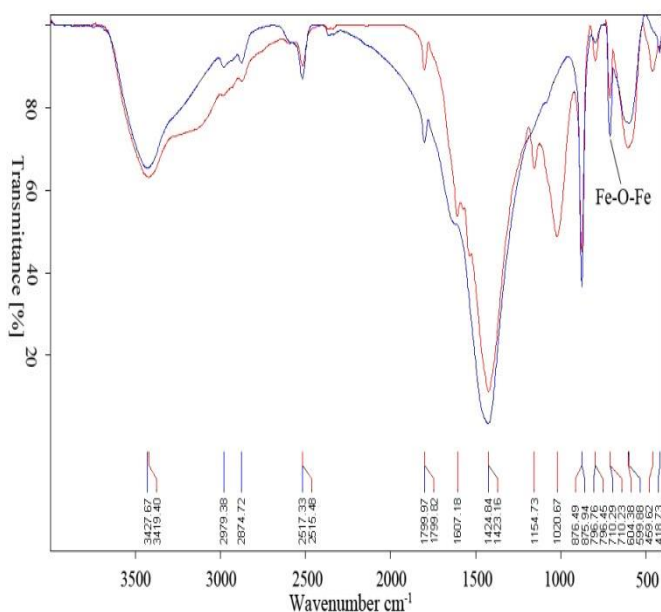


Figure 2. FTIR spectra of $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ nanocomposite before (blue line) and after (red line) stabilizing by sodium citrate.

Electron microscopic investigation

Transmission electron microscopy (TEM) images of paramagnetic nanocomposite before and after treatment with sodium citrate has provided in Fig. 3a and b, respectively. The shell of sodium citrate as a coating agent of the nanocomposite core was shown in fig. 4b that proves the core/shell structure of the modified nanocomposite. The modified nanocomposite shows better dispersion capability than that of untreated ones, which should be due to the repulsion of electrostatic force and high surface energy of the particles after modification by sodium citrate. The TEM image is in agreement with the data resulting from the Scherrer equation (Fig. 3b). In general, the narrow size and great dispersion of MNPs on the porous support provide a large contact area with spherical morphology and narrow size distribution.

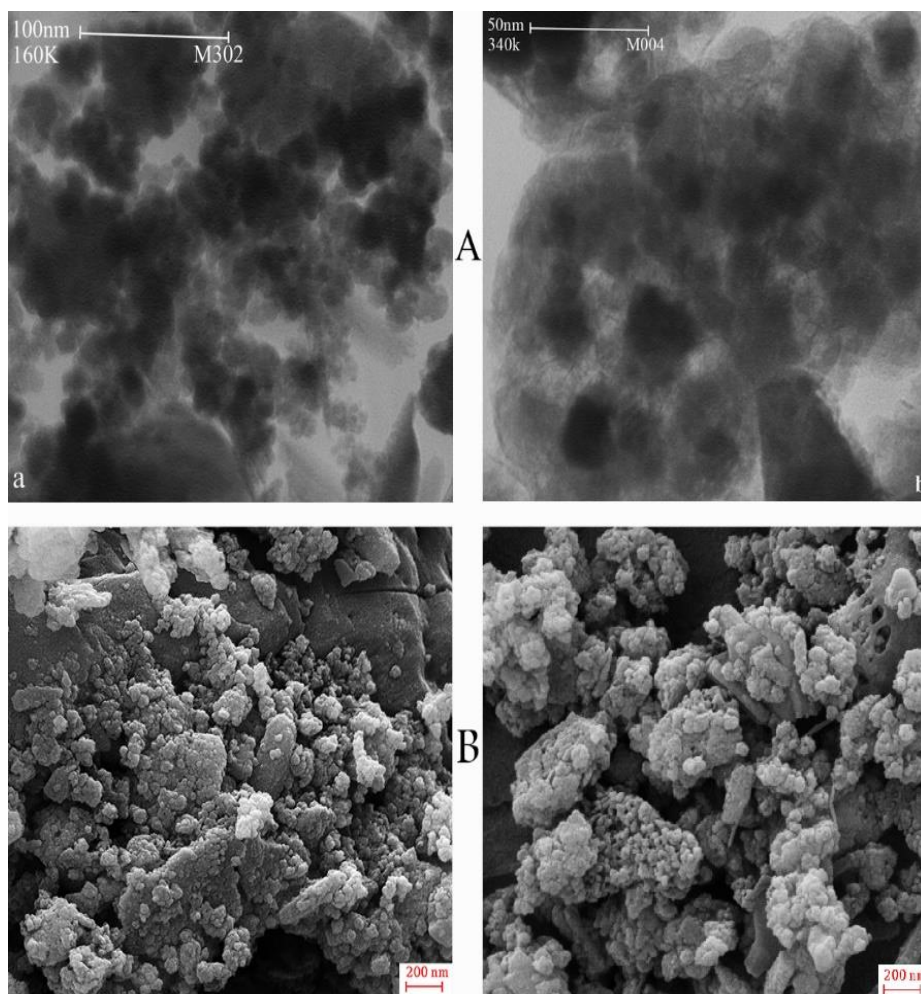


Figure 3. (A)TEM image of ESW-Fe₃O₄ nanocomposite (a) untreated, (b) treated by Na₃cit; (B) FESEM images of ESW-Fe₃O₄-Cit nanocomposite.

Particle size distribution

The size distribution of the ESW-Fe₃O₄ composite modified by Na₃cit dispersed in water is shown in Fig. 4 which indicates that the mean size of the modified paramagnetic nanocomposite in volume is lower than 100 nm. A high zeta potential indicates a high surface charge and thus, it will provide nanoparticles with good colloidal stability through a strong Coulombic repulsion. The measurement was shown negative charges of -18.4 mV on the surface of the composite. It appeared that each molecule of citrate has three carboxylate groups, one of them coated to the surface of the composite particles. So, the negative charge of the surface is due to the non-ligated carboxylate groups of the citrate molecules [29-31]. The surface charge of the adsorbent determined by DLS and zeta potential data confirmed that eggshell-supported MNPs were incorporated within the core of the composite. The protective shell of citrate chains provided the nanoparticles with steal-thinness in addition to stability.

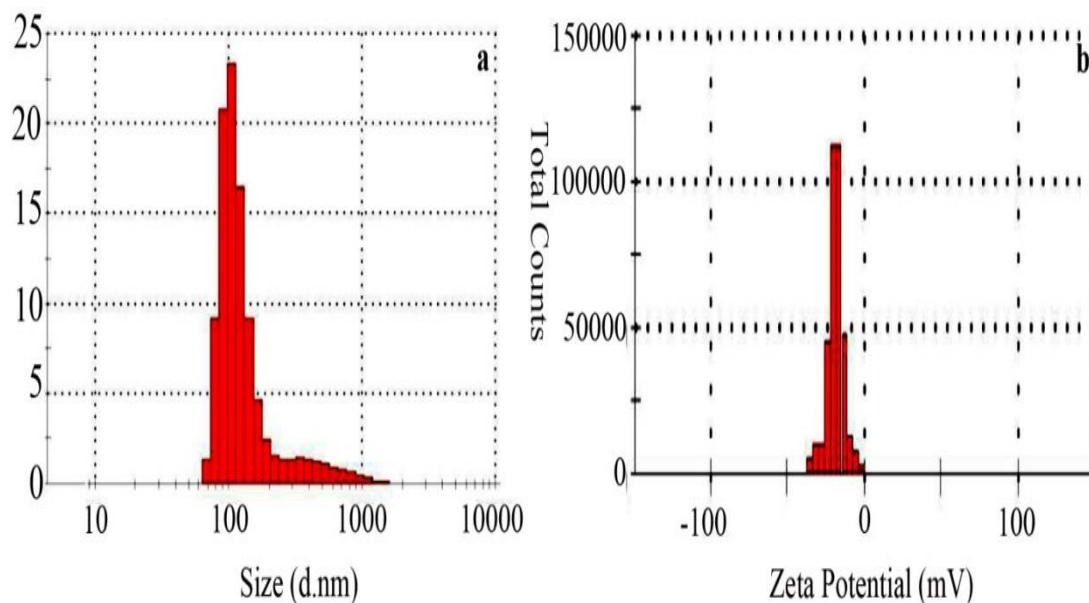


Figure 4. Size distribution (a) and Zeta potential (b) of the magnetic nanocomposite.

VSM analysis

VSM plot of treated magnetic nanocomposite (Fig. 5a) compared with those of untreated one (Fig. 5b). The treated nanocomposite with the magnetization of 14.6 emu/g shows higher magnetization properties compare to the untreated one with the magnetization of 7.68 emu/g. The NPs not only remained magnetic, but also, their magnetic properties increased after coating, due to the prevention of agglomeration causing self-Neel and Brownian Relaxation [32].

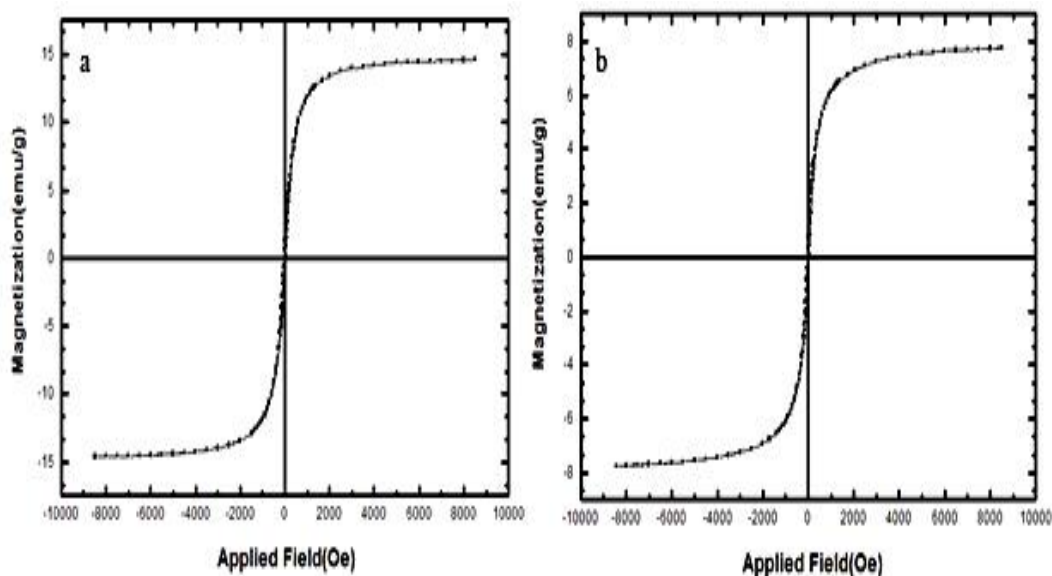


Figure 5. VSM plot of Na₃cit coated nanocomposite (a) and untreated one (b).

Conclusions

In summary, a facile and alkali-free synthesis of stabilized magnetic ESW-Fe₃O₄ nanocomposite has been established without any protective atmosphere by the simply heterogeneous stirring of an aqueous FeSO₄ solution with ES support. It has been reasonably suggested that the MNPs were formed by thermal co-precipitation methods on the nano-porous structure of the ES support. The magnetic nanocomposite was successfully coated by using Na₃cit with high stabilization and prevention of agglomeration. Finally, the synthesis of biodegradable nanocomposites based on eggshell waste is interesting because of the potential to design new materials and devices in various fields such as catalysis, medicine, electronics, ceramics, pigments, and cosmetics.

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