Green Fenton-like catalysts for the removal of water pollutants

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ABSTRACT

Two types of surface modified magnetite (Fe_3O_4) nanoparticles, coated with either tannic acid (TA) or dissolved natural organic matter (NOM), were evaluated as magnetic heterogeneous catalysts. Simple and efficient procedures for the synthesis of the magnetic catalysts were employed, their properties being fully assessed by various characterization techniques. The catalytic activity in heterogeneous oxidation of aqueous solutions containing Bisphenol A (BPA) over the catalysts was comparatively studied. The optimum experimental parameters were: 1g/L of catalysts, 10 mM H_2O_2, under UV irradiation. The highest mineralization rates were observed for Fe_3O_4-TA catalyst. More than 80% of BPA were removed after 30 minutes of reaction time under the specified experimental conditions. The results showed that the obtained catalysts are suitable candidates for the removal of pollutants in wastewaters by means of heterogeneous reaction.

Keywords: nanocatalysts, characterization, Fenton oxidation, wastewater, bisphenol A degradation

1 INTRODUCTION

Since nowadays water pollution became an issue of increasing concern, novel greener alternatives for water decontamination are continuously sought in order to protect the environment. The use of magnetic materials as adsorbents or heterogeneous catalysts in water treatment has attracted increasing attention in the last years [1-3].

Magnetite (Fe_3O_4) nanoparticles are good candidates for these procedures due to their benign nature, and also, their properties can be tailored according to their purpose; moreover, the nanostructures' surface can be functionalized with a wide variety of non-toxic materials containing (photo)active groups, that act both as nanoparticle stabilizers and also as catalysts. The magnetic properties allow facile re-collection and possible re-use of such nanomaterials from water. All these advantages significantly contribute in reducing costs and increasing availability for large-scale applications. Thus, for the present study, tannic acid (TA) and dissolved natural organic matter (NOM) were the coatings of choice for stabilizing magnetite nanoparticles (obtained by co-precipitation method), due to their known strong binding to iron ions. Moreover, they are widly-spread, safe and inexpensive natural materials. The further use of these functionalized magnetic iron oxide nanoparticles as Fenton-like catalysts for the removal of persistent contaminants from wastewaters was the aim of the present investigation. Although other studies reported the use of these type of catalysts in the degradation of pigments or adsorption of heavy metals from water [4-6], the knowledge on their performance in the removal of hazardous water pollutants such as endocrine disruptors (i.e. Bisphenol A) is limited. Thus, the properties and catalytic activity of the above mentioned nanomaterials in heterogeneous oxidation of aqueous solutions containing BPA are discussed.

2 EXPERIMENTAL

2.1 Materials

The catalyst synthesis procedures were performed using high purity reageants (Sigma-Aldrich), while the dissolved natural organic matter (NOM), was isolated from surface water (Fuchskuhlelake, Brandenburg, Germany), up-concentrated by reverse osmosis and later freeze-dried. Deionized water (18.2 MΩ/cm), obtained with Barnstead EASYpure[TM] II Ultrapure Water System was used throughout all experimental protocols.

2.2 Catalyst synthesis

The magnetic nanocatalysts were fabricated by employing a facile cost-effective synthesis procedure (chemical co-precipitation method) as described in detail in [3]. Briefly, the iron oxide (Fe_3O_4) magnetic nanoparticles were obtained by thoroughly mixing together ferric and ferrous salt precursors (2:1 stoichiometric ratio) in the presence of a strong alkaline precipitation agent (1.7 M NaOH); the method was performed at relatively high temperature (80 °C) with continuous stirring, under normal atmospheric conditions. The as-obtained magnetic black precipitate was subsequently purified, then coated with

either TA or NOM, taking in consideration a molar ratio of 0.05 between the magnetic core and stabilizing shell. After 2 h of mechanical vigurous stirring at 40 °C, the samples were separated from suspension, repeatedly washed with water and ethanol, then dried in a vacuum oven at ~ 40 °C.

2.3 Catalyst characterization

The nanocatalysts were fully characterized by X-ray diffraction (XRD, Shimadzu LabX XRD-6000 diffractometer), nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2020[TM] Physisorption system - Norcross, USA), energy dispersive X-ray spectroscopy (EDX, Bruker XFlash® 5030 SDD X-ray spectrometer - Berlin, Germany), high-resolution scanning electron microscopy (SEM, Supra 40 Carl Zeiss - Oberkochen, Germany) and high resolution transmission electron microscopy (HRTEM, Zeiss Libra 200 MC TEM/STEM electron microscope), Fourier transform infrared spectroscopy (FTIR, Jasco 660 Plus spectrometer) and vibrating sample magnetometry (VSM, MicroMag Model 2900/3900 magnetometer).

3 RESULTS AND DISCUSSION

Both samples exhibit good cristallinity as confirmed by XRD analysis. Fig. 1 shows the XRD patterns of TA and respectively NOM coated iron oxide nanoparticles, which were found to be typical for cubic Fe_3O_4 phase with spinel structure, the peak positions being consistent with those from the standard data for magnetite.
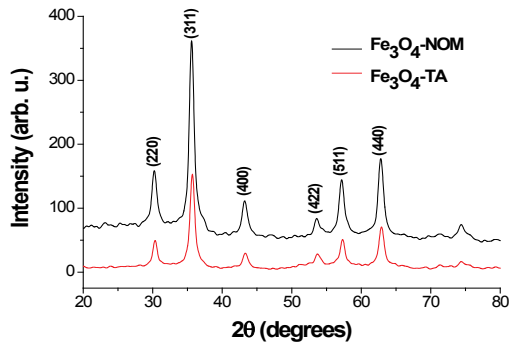

Figure 1: The XRD patterns of Fe_3O_4-TA and Fe_3O_4-NOM

BET measurements revealed similar values of the surface area of both sensitized nanomaterials (Table 1) consistent with those reported in the literature. The plots of pore size distribution (Fig. 2 a,b), determined by the BJH method, show the presence of a dominant peak in the mesoporous range (2–50 nm); the mesopores on spheres can be attributed to the interspaces of constituent particles. The pore diameter and volume for both catalysts were also determined (see Table 1). Overall, the Fe_3O_4-TA catalyst is characterized by a larger surface area with larger pores than those of Fe_3O_4-NOM sample.

Catalyst type	BET surface area (m²/g)	BJH pore size (nm)	Pore volume (cm³/g)
Fe_3O_4-TA	52.971	24.373	0.3023
Fe_3O_4-NOM	49.250	20.297	0.2499

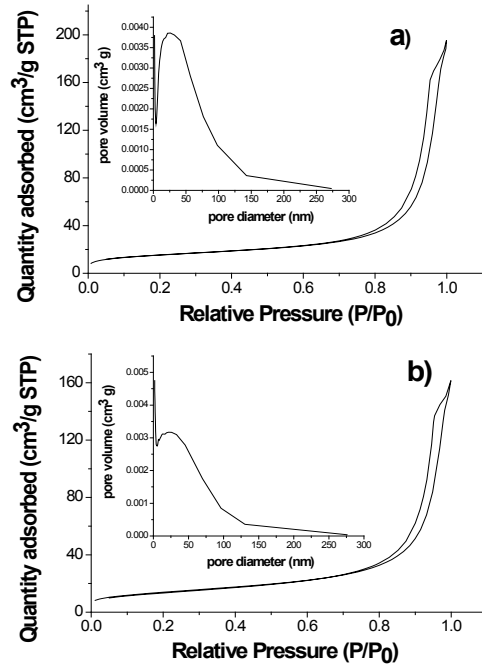Table 1: Surface properties of the studied nanocatalysts.

Figure 2: The nitrogen adsorption-desorption isotherm and pore size distribution curve (inset) of Fe_3O_4-TA catalyst (a) and Fe_3O_4-NOM catalyst (b).
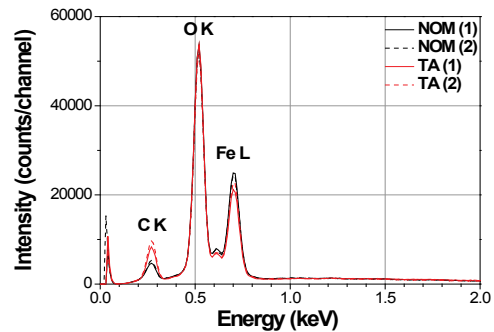

Figure 3: 5 kV EDX spectra measured at two locations on each sample, Fe_3O_4-NOM (black) and Fe_3O_4-TA (red); the EDX spectra were normalized on the O K line intensity.

The EDX investigation at 5 kV provided more surface sensitive analysis. The results at 5 kV were validated by EDX measurements at 20 kV acceleration voltage. As it can be seen from Fig. 3, the Fe_3O_4-TA sample contains significantly more C and Fe (relative to O) than the Fe_3O_4-NOM sample.
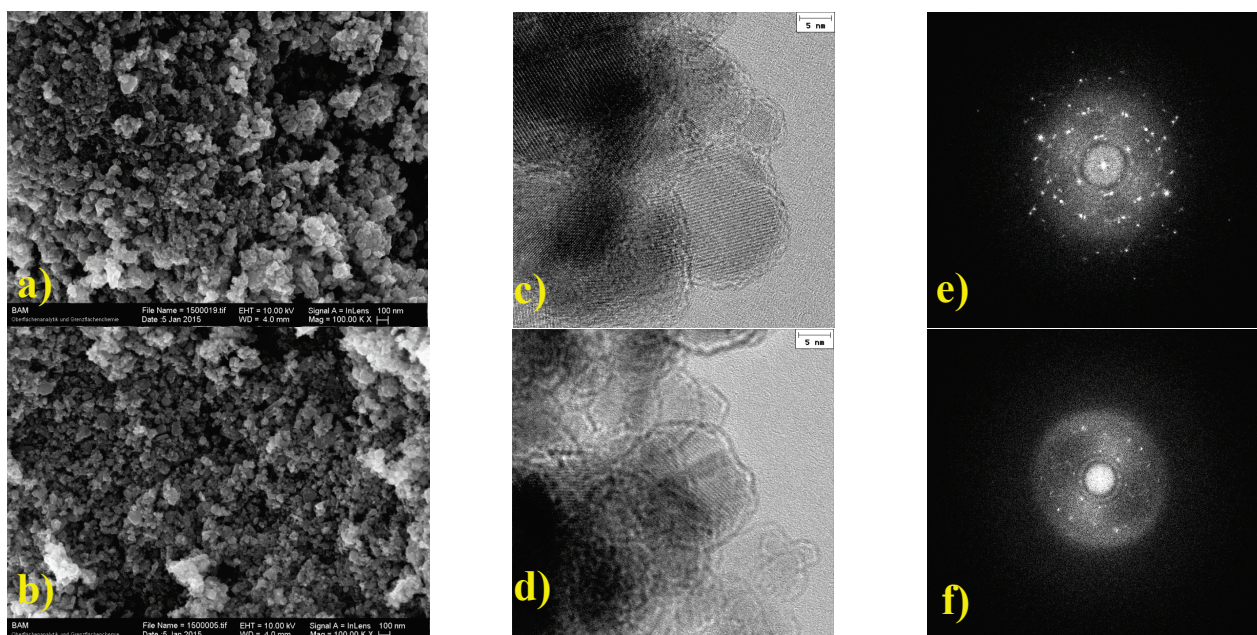
Figure 4: SEM micrographs (left), HRTEM images (middle) together with the corresponding SAED patterns (right) of the Fe$_3$O$_4$-TA (up) and Fe$_3$O$_4$-NOM (down) catalysts
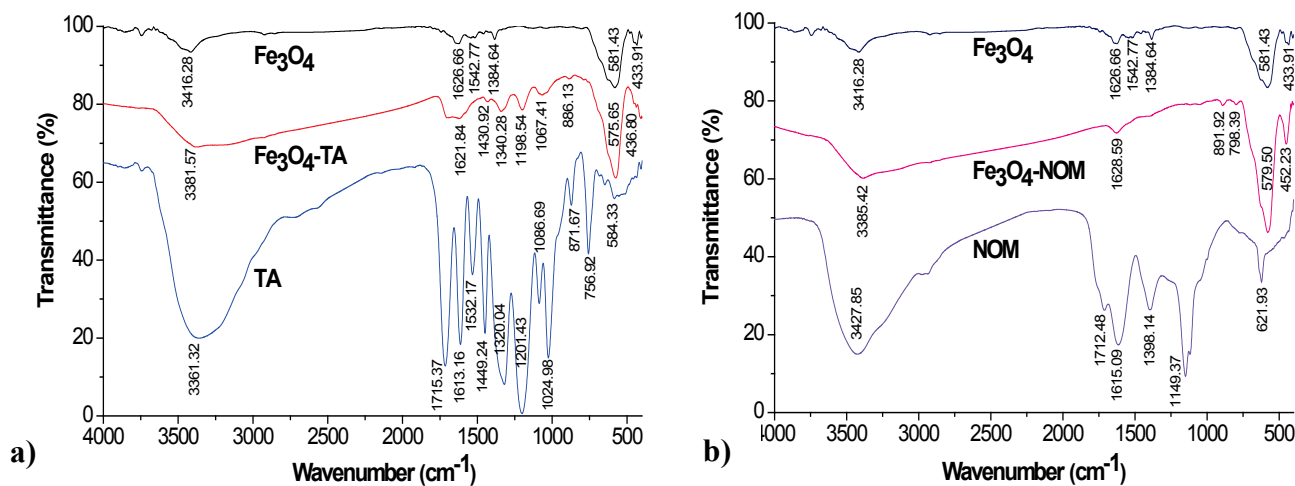

Figure 5: FTIR spectra of bare Fe$_3$O$_4$, of Fe$_3$O$_4$-TA and TA (a); FTIR spectra of bare Fe$_3$O$_4$, of Fe$_3$O$_4$-NOM and NOM (b);

The morphology of the samples' surface and the size of the primary particles were examined by high-resolution SEM (Fig. 4 a,b) and TEM (Fig. 4 c,d). The SEM images show the primary nanoparticles of rather spherical-like shape having sizes between 10 and 20 nm; the data is in agreement with the ones obtained by TEM; the high-magnification TEM images evidence the thin surrounding layer (below 1 nm) of the coating material (Fig. 4 c,d). The diffraction rings indicate that the magnetite cores are polycrystalline as revealed by the SAED pattern (Fig. 4 e,f).

FTIR measurements were further carried out in order to assess the binding of the active material onto the iron oxide

surface. Fig. 5 a and b show the FTIR spectra of Fe$_3$O$_4$-TA, and Fe$_3$O$_4$-NOM respectively, compared to those of pure TA and NOM, and also compared to the uncoated magnetite spectral data. The FTIR bands of coated and uncoated Fe$_3$O$_4$ at wavenumbers lower than 600 cm^{-1} are ascribed to the Fe−O vibrations of iron oxide. In the Fe$_3$O$_4$-TA spectrum (Fig. 5a), the phenolic groups of TA are seen in the region ~1000–1343 cm^{-1}, while the absorption bands between 1400 cm^{-1} and 1650 cm^{-1} are related to aromatic −C=C− bonds [7]. In the case of pure NOM spectrum (Fig. 5b), the peaks at 1616.cm^{-1} and 1712 cm^{-1} correspond to the stretching vibration of C=O bond in carboxylic salt and free

carboxylic acid respectively [5]; these are also present in the Fe_3O_4-NOM catalyst spectrum at ~1628 cm^{-1} suggesting the interaction of carboxilate group with the FeO surfaces. The FTIR measurements also reveal that TA formed stronger interactions with Fe_3O_4, compared to NOM.

The above findings can also explain the higher saturation magnetization (Ms = 68.0 emu/g) of Fe_3O_4-NOM than that of Fe_3O_4-TA (Ms = 58.2 emu/g), as depicted in Fig. 6. The obtained results are in agreement with those reported in literature for the magnetization curves of coated Fe_3O_4 recorded at room temperature.
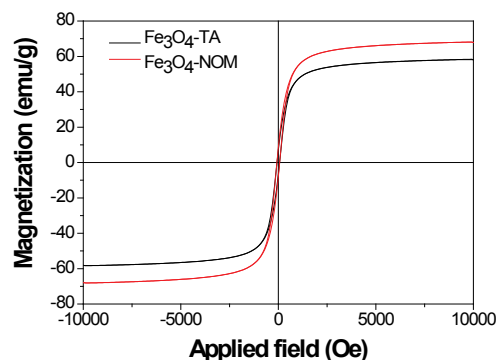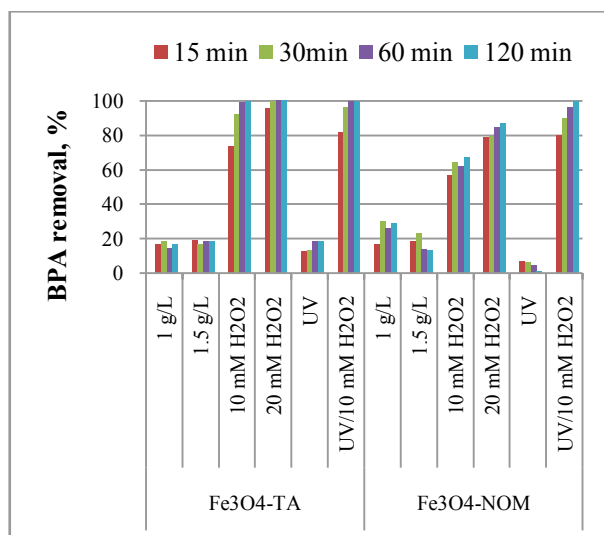

Figure 6: Magnetization curves of the two nanocatalysts

Figure 7: The effect of catalyst loading, H_2O_2 dosage and UV light on BPA removal over the two catalysts. Initial conditions: 0.5 μM of pollutant, 1 g/L catalyst.

Following catalysts' characterization, the catalytic activity in heterogeneous oxidation of aqueous solutions containing a model pollutant (Bisphenol A, BPA) was comparatively studied. BPA, used as a raw material for polycarbonate and epoxy resins, is known to accumulate in nature without decomposition and has been found to be weakly estrogenic [8].

The effect of catalyst loading, H_2O_2 dosage and UV light on the degradation performance of the oxidation

process was investigated. Moreover, the stability and reusability of the catalysts were also established (data not shown).

The optimum experimental parameters were found to be 1 g/L of catalyst, 10 mM H_2O_2, under UV irradiation. More than 80% of BPA were removed by each catalyst after 30 minutes of reaction time under the experimental conditions given above (Fig. 7). The higher overall performance of the Fe_3O_4-TA material can be observed, while Fe_3O_4-NOM exhibited a lower reactivity compared to Fe_3O_4-TA.

4 CONCLUSION

The synthesis, characterization and performance of two green Fenton-like catalysts were investigated at the laboratory scale in the present study. Tannic acid and dissolved natural organic matter were the reactive materials of choice grafted on the surface of magnetite cores. The results obtained in catalytic Fenton heterogeneous reactions showed the suitability of both catalysts for the efficient degradation of persistent pollutants in wastewaters.

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