



Non-thermal plasma synthesis of sea-urchin like α -FeOOH for the catalytic oxidation of Orange II in aqueous solution



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ABSTRACT

In this study, a template-free synthesis of iron oxyhydroxide nanostructures by gliding arc plasma at atmospheric pressure was evaluated. The results showed that exposure of a Mohr's salt solution to the plasma discharge induces a rapid oxidation–precipitation of iron(II) into a non-porous and amorphous iron(III) (hydr) oxide. After ageing in temporal post-discharge for three hours, the amorphous iron (hydr) oxide was transformed into crystalline goethite (α -FeOOH). The presence of goethite was confirmed by FTIR, Raman spectroscopy and thermogravimetric analysis. Textural analyses showed that the material is mesoporous with a BET surface area of $134 \text{ m}^2 \text{ g}^{-1}$. SEM pictures revealed that the plasma-synthesized goethite particles consist of sea-urchin like hollow spheres. The catalytic activity of such goethite in the Fenton degradation of Orange II (organic dye) showed that this material can be used as heterogeneous catalyst for effective removal of organic pollutants from wastewater. This study establishes that the plasma discharge of gliding arc type can be used as a green and cheap efficient route for the synthesis of porous metal oxide nanostructures.

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1. Introduction

During the last decade, iron (hydr) oxides have drawn significant interest for their potential applications in the field of wastewater treatment because of their demonstrated excellent adsorption and catalytic capacities, and their environmentally benign nature [1–6]. Among them, iron (hydr) oxides with three dimensional nanostructures composed of hierarchically assembled nanosized building blocks have several advantages for adsorption and catalysis, such as their high surface area and their easy separation [7–8]. However, the conventional methods used for the production of iron (hydr) oxides with hierarchical nanostructures are quite expensive because they need the use of templates such as ethylene glycol, and other chemicals including urea and tetrabutylammonium bromide [7]. Another disadvantage of these methods is that they are not environmentally friendly. To overcome the above disadvantages,

Faria et al. have recently developed a new green method for the synthesis of iron oxyhydroxide with nanosized particles and high surface area [9]. Briefly, they mixed an alcoholic solution of sodium hydroxide with iron(II) solution, and then, they added hydrogen peroxide to the mixture to form a δ -FeOOH precipitate. During this process, sodium hydroxide and hydrogen peroxide were used as precipitating and oxidizing reagents, respectively. Based on this previous work, we developed a new surfactant-free method to prepare iron oxyhydroxide by using gliding arc plasma with humid air as feeding gas. Our hypothesis is that the hydroxyl radicals created by the plasma discharge can simultaneously act as oxidizing and precipitating reagents for the fabrication of iron oxyhydroxide. Indeed, Depenyou et al. highlighted the formation of lepidocrocite (γ -FeOOH) while treating a carbon steel by gliding arc plasma [10]. The plasma discharges in humid air are known to induce acidifying and oxidizing effects in an aqueous target solution. In such plasmas, a part of the thermal energy carried on by the arc is transferred to the surrounding “parent species” of the feeding gas (i.e. O_2 , N_2 and H_2O) and thus favours the cleavage of H–OH and O=O bonds. This feature requires less energy than for N≡N bond breaking and allows rising gaseous moieties from their fundamental energy level to some excited state. Thus, the NO^\bullet and HO^\bullet radicals mainly

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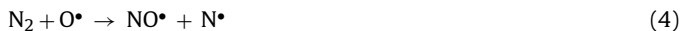
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formed in the arc by electron impact as shown in Eqs. (1)–(4) were identified and quantified by emission spectroscopy [11].



The first aim of our study is to investigate whether the gliding arc plasma species (mostly HO^\bullet radicals) can be used as reagents for the synthesis of hierarchical iron oxyhydroxide nanostructures. The most important merit of this process as compared with other methods consists in the fact that it only requests mild conditions and a short processing time. Moreover, this process can be considered as a green and cheap route, since the only chemical used to produce the reactive species is a water saturated air which is non-pollutant, available and renewable. The second objective of our work is to evaluate the catalytic performance of the plasma-synthesized material in the heterogeneous Fenton removal of organic pollutants from water.

The plasma-synthesized materials were characterised by X-ray powder diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR), Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and nitrogen physisorption. The catalytic performances were evaluated for the bleaching of an Orange II dye solution. Orange II is a toxic and non-biodegradable azoic dye often present in textile and food industrial wastewater.

2. Experimental methods

2.1. Preparation of α -FeOOH nanostructures

The design of the reactor used for the preparation of iron oxyhydroxide was described in our previous works [12–14] and consists of a pair of aluminium electrodes symmetrically disposed on both sides of an atomizing nozzle (diameter = 1 mm) and connected to an AC 220 V/10 kV–1 A high voltage transformer which delivers a mean current of 160 mA (600 V) in operating conditions (Fig. 1). The selected feeding gas is water saturated air. Air is provided by a compressor and then saturated by water by passing through a bubbling flask maintained at 25 °C before being blown between the electrodes at a flow rate of 800 L h⁻¹. A plasma plume is generated by an electric arc formed between the electrodes when the high voltage is applied. This arc is then pushed away by the gas flow and glides along the electrodes until it collapses. A new arc is then formed and the cycle resumes. During this cycle, the length of the

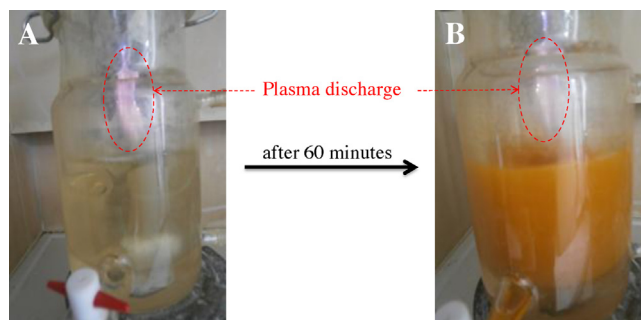


Fig. 2. The plasma reactor containing a 32.5 mM iron(II) solution before (A) and after plasma-treatment for 60 min (B); the observed yellow-brown suspension witnesses the presence of iron(III) oxide/hydroxide in the medium.

arc increases and its temperature decreases, so that the arc turns from a thermal plasma to a quenched plasma.

Ammonium iron(II) sulphate hexahydrate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ (purity = 99.997%) was purchased from Sigma–Aldrich (Belgium) and was used as received. $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was chosen because of its better stability to air oxidation as compared to other iron(II) salts. In a typical procedure, 13 mmol of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 400 mL of deionized water and disposed normally to the axis of the glass reactor (Fig. 2A) at a distance of about 2.5 cm from the electrodes tips. The reactor was cooled down by a water draught and the temperature was kept around 50 °C to limit evaporation and vapour stripping. The solution was exposed to the plasma discharge for different times t^* (i.e. 0, 15, 30, 60, and 120 min) under magnetic stirring. During this process, the pH of the medium was measured in order to follow the acidification of the target solution exposed to the plasma discharge. After the discharge was switched off, the obtained precipitate was collected by vacuum filtration using a 0.45 μm millipore filter, washed with deionized water and dried at 80 °C for 24 hours. The powder obtained after each exposure time was weighted. For the optimum exposure time predetermined, the yellow-brown precipitate obtained (Fig. 2B) was further aged in the reactor at 98 °C for 1–3 h with plasma shut off before being collected. The obtained products were, respectively, named as A1–A3. The non-aged material was named as A0.

2.2. Characterizations

X-ray diffraction (XRD) analyses were performed on a Siemens D5000 diffractometer using the $\text{K}\alpha$ radiation of Cu ($\lambda = 1.5418 \text{ \AA}$). The 2θ range was recorded between 5° and 70° at a rate of 0.02 °s⁻¹. The ICDD–JCPDS database was used to identify the crystalline phases. The Fourier transform-infrared spectra were recorded using an Equinox IFS55 spectrometer (Brücker) equipped with a DTGS detector. The absorption spectra were obtained by the recording of 100 scans between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The powders were diluted in an analytical grade KBr (Janssens Chimica 99%) by a weight factor of 100, and then pressed into self-supporting disks before analysis. SEM micrographs were taken with a LEO 983 GEMINI microscope equipped with a field emission gun. The uncoated samples were exposed to an acceleration voltage of 1 kV. Textural analyses were carried out on Micromeritics Tristar 3000 equipment using N₂ adsorption/desorption at –196 °C. Before measurement, the samples were outgassed at 90 °C overnight under vacuum. The specific surface area was calculated using the Brunauer–Emmet–Teller (BET) equation whereas the pore size distributions were derived from the desorption branches using the Barrett–Joyner–Halenda (BJH) model. Confocal Raman spectroscopy was done on DXR Raman

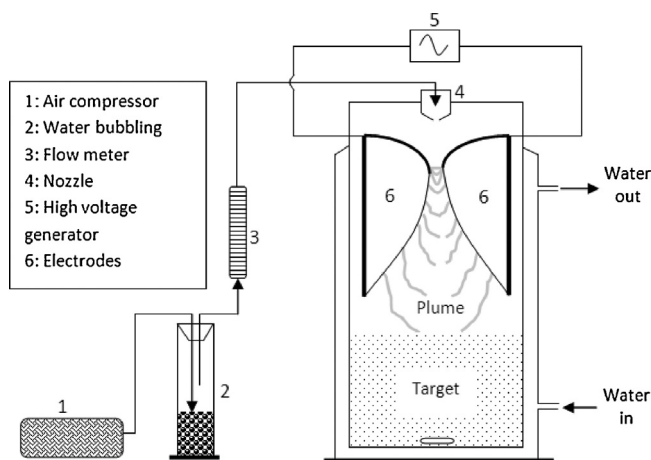


Fig. 1. Scheme of the gliding arc plasma reactor.

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