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Orange peel + nanostructured zero-valent-iron composite for the removal of hexavalent chromium in water

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ABSTRACT

In this work we used the Pulsed Plasma in Liquid technique to synthesize zero-valent iron nanostructures. We used a DC Power Source to produce such plasma on water and methanol. The obtained particles were characterized by TEM to determine their shape and size and Mossbauer Spectroscopy to investigate the chemical state of the iron present. We found that 80% of the particles produced in water are composed of metallic iron and when methanol is used 97% of the particles are metallic iron. Once the Fe colloid was formed, orange skin was impregnated with these nanostructures for the removal of in water solution. The Cr(VI) removal experiments were done in a batch system in the presence of the composites at an inicial concentration of 50 ppm of Cr(VI). When using the iron nanostructures supported on the orange peel, the percentage of removal is 100% in the case of nanostructures formed in water and 96% when obtained in methanol.

1. Introduction

Hexavalent chromium (Cr(VI)) species are a serious environmental problem since they are known to be toxic, mutagenic and carcinogenic. Furthermore, the treatment of these species in water is difficult since they do not form insoluble precipitates at any pH value. There are two main processes to deal with this problem: the first one is to adsorb the Cr(VI) ions in a material and then, such material is removed from the water; the second one is to reduce Cr (VI) to Cr(III). The ionic species of Cr (III) have a significantly lower toxicity than those of Cr(VI) and are capable of forming insoluble compounds easily removed by precipitation. Therefore, the reduction method is preferred. There are a number of well-known chemical and electrochemical methods to achieve the reduction of Cr(VI) that have been in use for a long time [1].

Recently, iron oxide has been used to eliminate Cr(VI) by adsorption [2–5]. Also, Zero Valent Iron (ZVI) nanostructures are used to reduce Cr(VI) to Cr(III). This nanostructures are usually employed protected with a covering stabilizer or supported on a different material that can be easily removed by filtration or precipitation [6–10]. Among the different methods to obtain metallic nanoparticles, Pulsed Plasma in Liquids (PPL) has emerged as a convenient low-cost technique that produce nanostructures without the formation of byproducts. Also, the nanostructures surface is free from any covering molecule, thus it can interact freely in chemical reactions, sorption processes, etc. [11–15]

Therefore, in this work we have used PPL to produce pure and uncovered ZVI nanostructures. Then, we have supported them on orange peel to produce a composite. Such new material has been used in the removal of Cr(VI) in water solution. Orange peel is an environment friendly natural material that is a waste after the orange juice has been extracted. Orange peel has been already used successfully by our group in previous works showing its adsorption/reduction capabilities [16,17].

2. Materials and methods

2.1. Iron nanostructures synthesis and characterization

Iron rods (99% of purity) with approximate dimensions of 5 × 5 × 20 mm were used as the moving electrodes during the iron nanostructures production by PPL. The two liquid media used were distilled water and reagent grade methanol (Sigma-Aldrich). A commercial DC Power Source was used at 30 V. The PPL experi-

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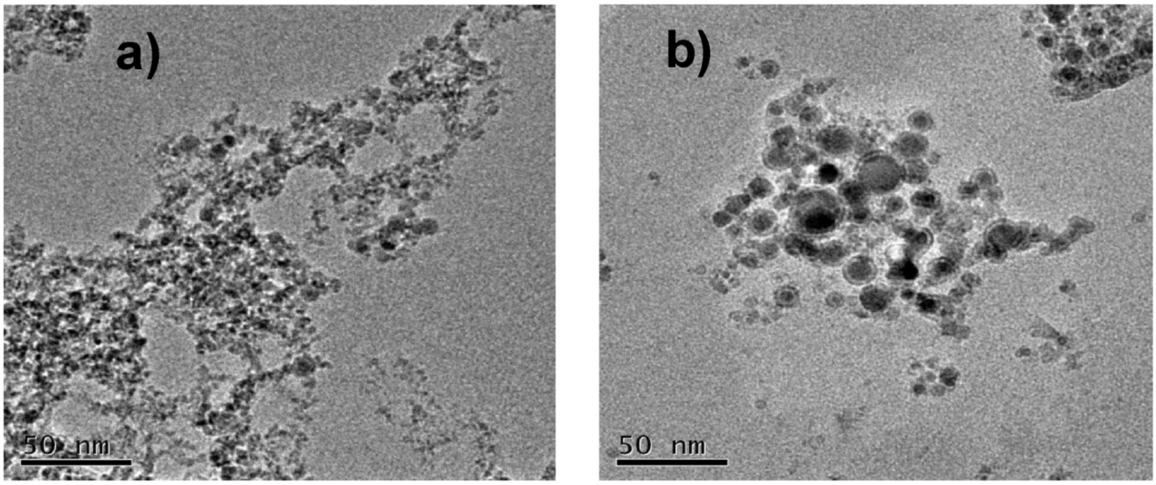

Fig. 1. TEM images of a) Fe nanostructures formed in water and b) Fe nanostructures formed in methanol.

ments were performed during two different intervals of time, the first one was done during 10 min to prepare the composites, and the second one during 1 h to obtain enough material (~50 mg) to perform Mössbauer measurements. The mass of the nanoparticles was estimated by weighting the Fe electrodes before and after the PPL experiments. To study the morphology and size of the nanostructures Transmission Electron Microscopy (TEM) was performed. One drop of the Iron colloids was placed on a carbon coated TEM grid (SPI Supplies) and left it to dry at room temperature. To be able to study the obtained Fe nanoparticles by Mössbauer Spectroscopy (MS), ~50 mg of Iron nanostructures were transferred from the liquid medium (water or ethanol) to a commercial epoxy resin precursor to avoid oxidation in air. After that, the resin containing the nanoparticles was chemically cured. The encapsulated Fe nanostructures were then studied by MS in a Wissel spectrometer operating in the constant acceleration mode and using a ^{57}Co/Rh. The reported isomer shifts are referred to metallic iron.

2.2. Orange peel + iron nanostructures composite preparation and characterization

Orange peel (Citrus Cinencis 'Valencia') was dried during one day at 80 °C and milled to obtain a dry powder. Afterwards, it was mixed with the iron nanostructures colloid and left the mixture stirring during 3 h. After that, the composite was allowed to sink to the bottom of the flask and then separated by decantation. In all cases we prepared 0.4 g (5% wt. of Fe) of composite. A small amount of the composite was placed in a Scanning Electron Microscopy (SEM) sample holder and left to dry at room temperature.

2.3. Chromium removal

The Chromium solution was prepared from $K_2Cr_2O_7$ (Sigma-Aldrich, 99% purity) at a concentration of 50 ppm with respect to Cr. The wet composites (0.4 g, 5 wt.% of Fe) were immediately mixed with 10 mL of the Cr(VI) solution during one hour at room temperature under magnetic stirring and a pH of 3. After that, the composite was left to sink during 1 min and 200 μ L of the remaining solution were taken for the Cr(VI) concentration determination. Such determination was done using the dyphenilcarbazide colorimetric method already explained in previous works [16,17]. Shortly, a solution of dyphenilcarbazide at pH 3 forms a pink complex with Cr(VI), which is spectroscopically analyzed at 542 nm using a UV Vis spectrophotometer.

2.4. XPS characterization of the composites

For the X-ray Photoelectron Spectroscopy (XPS) measurements, a small amount of composite was placed in a piece of carbon tape and introduced to the spectrometer. XPS wide and narrow spectra were acquired using a JEOL JPS-9200, equipped with a Mg X-ray source (1253.6 eV) at 300 W, the area of analysis was 3 mm^2, and the vacuum around 7.5×10^{-9} Torr for all samples. The spectra were analyzed using the Specsurf^{TM} software included with the instrument. All spectra were charge corrected with respect to the adventitious carbon signal (C1s) at 284.5 eV. The Shirley method was used for the background subtraction, while for the curve fitting we used the Gauss-Lorentz method.

3. Results and discussion

3.1. Iron nanostructures characterization

Fig. 1 shows the TEM images of Fe nanostructures prepared by PPL in distilled water and methanol. When using water, small particles are formed that agglomerate forming bigger "network-like" structures as seen on Fig. 2a. Since no stabilizer was used, the formed particles tend to agglomerate rapidly forming such structures. On the other hand, when methanol is used the formation of bigger spherical particles is observed as well as the network structure (Fig. 2b). Clearly, the liquid media plays an important role on the size and shape of the nanostructures formation. According to Chen et al. [13], methanol may be capable of partially stabilize the formed nanoparticles and this could be the reason we see individual spherical nanoparticles when using this liquid.

To determine the oxidation state of the Fe atoms on our samples Mössbauer Spectroscopy was used. On Fig. 2 we show that the majority of our samples are composed of Fe^0. In the case of water, 80.34% of the iron is in the metallic iron and the rest is for Fe ions (15.19% and 4.47% for Fe^{+3} and Fe^{+2} respectively). As for methanol, only 2% is Fe^{+3} ions; the rest is composed of 7.5% ZVI in nanometric sizes (less than ~10 nm) and 89.5% bigger forms. Therefore, the liquid medium not only affects the shape and form of the obtained nanostructures but their composition as well. In water, oxidation is expected to happen, however, as evidenced by Mössbauer Spectroscopy such oxidation is not complete and 80% of the Fe atoms remain in the metallic state. On the other hand, when using methanol as the liquid medium, the obtained nanoparticles are composed of 98% Fe^0. This could be due to the possible "stabilization" from methanol mentioned earlier. As discussed later, Fe^0