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# Silver recovery using electrochemically active magnetite coated carbon particles

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ABSTRACT

The electrochemical recovery of silver by employing recyclable superparamagnetic carbon materials (Cmag) is reported. The proposed strategy explores the adsorption properties and the large surface area of carbon, in conjunction with the superparamagnetic properties of magnetite nanoparticles, in order to collect $Ag^+$ ions from the solution and to promove their rapid confinement at the working electrode surface, using an external magnet. Efficient electrodeposition can be performed in this way, facilitated by the preconcentration effect at the electrode. The adsorption process at the magnetic carbon particles proceeds according to the Langmuir model, exhibiting an adsorption capability of 61.5 mg of silver per gram of Cmag. As a proof of concept, an automated system was specially designed for performing successive batch cycles, encompassing the capture, transport, confinement, electrodepositon of silver, and recycling of the magnetite coated carbon particles from the electrode. The recovery process was successfully demonstrated in this work, by processing discarded X-ray photographic films.

## 1. Introduction

Carbon materials, such as carbon black, graphite, glassy carbon and pyrolytic carbon, have been extensively employed in electrochemical processes as low cost and relatively inert electrodes (McCreery, 2007; Moreno-Castilla et al., 2012; Svancara et al., 2009). In the micro/nanoparticulate form, they provide very large surface areas for adsorption and separation processes, becoming particularly useful in the industry and water treatment (Bansal and Goyal, 2005; Davidson et al., 1979; Omri and Benzina, 2013)

Silver is a noble material employed in houseware and jewellery, exhibiting the highest electrical and thermal conductivity of all metals. Its economical relevance is increasing because of the widespread technological applications, including the recent boom of antibacterial products (Levard et al., 2012; Sen et al., 2013). As a counterpoint, its role as a contaminant species in the environment is also increasing, because of the accumulation of electronic wastes (Marambio-Jones and Hoek, 2010). For this reason, there is an intrinsic economical and environmental interest of recovering silver (Modi et al., 2012; Ratte, 1999) under sustainable conditions, as we recently reported for copper (Condomitti et al., 2012), using the so called magnetic nanohydrometallurgy process (MNHM). This process has been demonstrated by using superparamagnetic nanoparticles functionalized with ethylenediaminepropyltriethoxysilane (Condomitti et al., 2012) for capturing, concentrating and processing metal ions, with the aid of an external magnet. Now, we are exploring an alternative low cost material for MNHM, based on superparamagnetic carbon particles which are particularly suitable for upscaling in real plants.

Carbon, from many different sources, has already been successfully employed for adsorbing metal ions (Dias et al., 2007), including gold and silver from gold-plant solutions (Davidson et al., 1979). The use of magnetic carbon particles allows coupling the capture of silver ions from aqueous solution to their rapid confinement at the electrode surface, for performing their efficient electrochemical deposition and also the carrier regeneration. It should be noted that in contrast to the conventional chemical and hydrometallurgical processes, the entire procedure can be performed in the same reactor, allowing automatization and recycling under sustainable conditions, in terms of the green chemistry aspects involved.

## 2. Methodology

Superparamagnetic nanoparticles of magnetite (MagNP) of about 10–20 nm were obtained by the thermodecomposition method in the presence of oleic acid (Park et al., 2004). The MagNP generated in this process is stabilized with an oleic acid coating. After mixing with carbon powder (Aldrich, Darco® G60), in toluene, typically at 1:9 MagNp:carbon mass ratio, the black supension became strongly superparamagnetic, implying an effective interaction between the two components. After sonicating for 60 min, the suspension was separated by applying an external $Nd_2Fe_{14}B$ magnet (MagTek Co, 2.54 cm diameter, 11 kOe), and then washed with water and kept under vacuum. The final adsorbing material was essentially composed by carbon particles containing 0.16 g ($6.9 \times 10^{-4}$ mol) of $Fe_3O_4$ per gram of Cmag.

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Energy dispersive X-ray fluorescence (EDXRF) measurements were carried out using an EDX720 instrument from Shimadzu, equipped with a X-ray tube with Rh target and a Si(Li) detector. Under the working conditions, the limit of detection for $Ag^+$ ions in aqueous solution was $5 \times 10^{-4}$ mol $L^{-1}$.

For characterization purposes, magnetization measurements of the superparamagnetic nanoparticles were performed as a function of temperature in the zero field cooled (ZFC) and field cooled (FC) mode, and also as a function of magnetic field (hysteresis), using a Cryogenic Sx600 superconducting quantum interference device.

Specific surface area determinations were performed using the Brunauer–Emmett–Teller (BET) method with a surface area analyzer Quantachrome (model NOVA 4000).

Square wave voltammetry was carried out on an AUTOLAB PGSTAT30 potentiostat/galvanostat, using a rectangular quartz cuvette containing, in addition to a platinum wire counter electrode, a Luggin capillary with the Ag/AgCl (1 mol $L^{-1}$ KCl) reference electrode and a 3 mm diameter platinum disc working electrode. This electrode was placed in contact with the cuvette quartz window, using a convenient experimental setup for the application of an external magnetic field as previously described (Condomitti et al., 2011a,b). The volume used in this cell was about 3 mL.

The adsorption process was investigated by mixing 0.0100 g of Cmag with 20 mL aqueous solutions containing different concentrations of silver nitrate (Synth Co.). The suspensions were left in a thermostated shaker at 25 °C for 1 h. After this period of time, the Cmag particles containing silver ions were separated magnetically, with the aid of an external magnet and analyzed with the EDXRF instrument, in order to construct the adsorption isotherms.

A mobile, automated setup for the MNHM process was elaborated, as shown in Fig. 1. The reactor consisted of a 350 mL inverted glass bottle, cut at the base in order to introduce the mechanical stirrer, auxiliary electrode (Platinum or graphite), and the flexible hose for injecting/draining the solution. The screw cap at the bottom was modified in order to accommodate a working disk electrode (copper or silver coated copper). The magnet was positioned at a controlled distance below the working electrode. The applied potentials, stirring, magnet positioning and draining functions were computer controlled, using a programmable Arduino microprocessor.

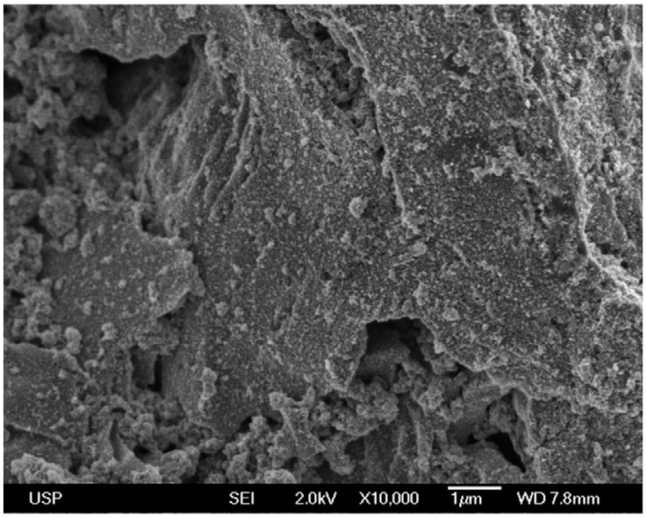

**Fig. 2.** SEM image of the superparamagnetic carbon material (Cmag).

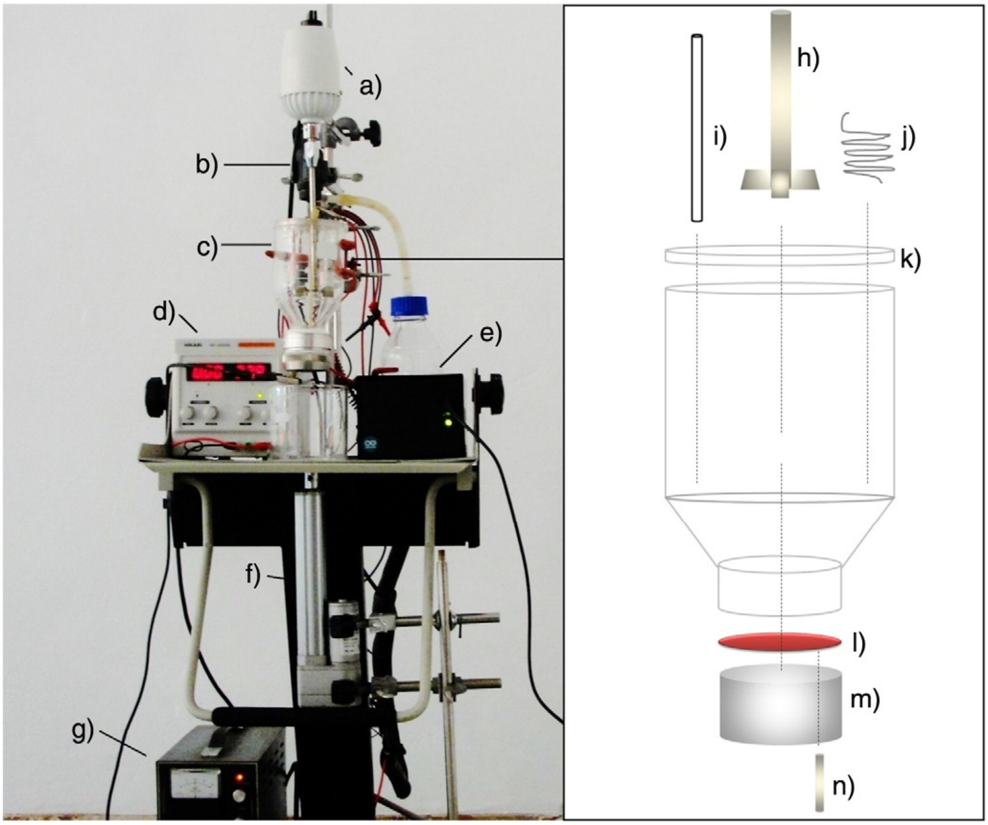

**Fig. 1.** Programmable reactor for the MNHM process: a) mechanical stirrer, b) suction pump, c) compartment reaction, d) potential source, e) CPU, f) linear actuator for positioning the magnet, g) power source, and the reaction compartment shown at right, with h) rod of stirrer, i) hose, j) auxiliary electrode, k) lid top, l) working electrode, m) electrode holder and bottom cover, and n) electric contact.