## Adsorption of palladium ions by magnetite nanoparticles

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Platinum group metals (PGMs) which are widely used in car catalytic converters have been in high demand, in spite of a low natural abundance in the earth crust. Due to scarcity and high value of these metals, there is an increased interest towards their recovery from wastes such as spent catalyst. Palladium togheter with platinum is the metal more used as catalyst. This metal is generally fixed in the washcoat surface of the catalytic converter and allows the oxidation of carbon monoxide (CO) and hydrocarbons (HC) in order to decrease the contamination caused by car exhaust fumes [1].

Several works have been dedicated to the recovery of metals by different methods including solvent extraction, ion exchange, membrane separation and so on, but most of these methods suffer from some drawbacks such as high capital and operational costs. Therefore, efforts are made to develop low-cost materials for the recovery of metals and the use of nanoparticles is a really good alternative.

Nanomaterials have been shown to possess distinctive mechanical, magnetic, optical, electronic, catalytic and chemical properties that contribute to promising applications in electronics, energy, biomedicine, environmental remediation and recently recovery of metals [2 - 4]. Their small size gives them a high surface area-to-volume ratio and facilitates the interaction with several kinds of chemical species. As magnetic separation has been shown to be a useful solid-solid phase separation technique, magnetic nanoparticles like magnetite nanoparticles are excelent candidates for adsoption of different metals [5].

In the present work we conduct a research on the adsorption of palladium from hydrochloridic acid solution onto magnetite ( $Fe_3O_4$ ) nanoparticles. The magnetite nanoparticles have been synthesized by several methods, such as co-precipitation, freeze drying, polyol and modified polyol [6-7]. The analysis of X-ray powder diffraction indicated that all the samples were a single phase of magnetite. The transmission microscopy analysis shows that depending on the synthesis method different average particle sizes are obtained (see table 1).

For the adsorption experiments, 1mg of the different Fe<sub>3</sub>O<sub>4</sub> nanoparticles were re-dispersed with 1 ml of TMAOH (tetramethylammonium hidroxide) and added into a 10 ml disolution of 8.58 ppm of Pd. The pH of the solution was adjusted at 2.5 and the contact time was 2 hours under sonication.

The aqueous phase was separated from solid phase by magnetic settlement applying external magnetic field. The liquid phase was analyzed by ICP-MS in order to determinate the concentration of the palladium cations that have not been adsorbed into magnetite nanoparticles. This way was possible to calculate the percentage of palladium recovered from the initial dissolution.

The results show that with the polyol method only a 70% of the palladium present in the initial dissolution is adsorbed onto the magnetite ( $Fe_3O_4$ ) nanoparticles. This low percentage can be explained due to the organic coating of the magnetite nanoparticles. The freeze drying method allows a 79 % of palladium adsorption, while the co-precipitation allows an 85 %. The best results are obtained with the modified polyol method, where the smallest nanoparticles are observed and a 90% of palladium can be adsorbed. The adsorption values are summarized in table 1.

Table 1.- Nanoparticle average sizes and Pd adsorption percentage

Synthesis Method	Nanoparticle Average Size (nm.)	% Pd adsorption
Co-Precipitation	7	85
Freeze drying	8.5	79
Polyol	9	70
Modified polyol	2.6 and 10	90

These results point out that all of these methods are adequate for the synthesis of magnetite nanoparticles, which can be used for the adsorption of palladium. However, the modified polyol shows the best performance for the separation of palladium from diluted hydrochloric acid solutions.

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