PALLADIUM RECOVERY BY ADSORPTION ONTO IONIC LIQUID-IMPREGNATED LAYERED DOUBLE HYDROXIDES

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Abstract
Palladium (Pd) is part of the platinum group metals (PGMs) and represents a "critical" raw material with economic importance. In our days, the secondary sources with Pd content are called "the urban mines of precious metals". Therefore, a lot of researchers focused their attention to the removal and recover studies of Pd ions from secondary sources. Regarding the recover process from aqueous solutions a lot of methods have been studied, among which adsorption process gained a special attention due to its well know advantages.
In this context, the present paper aims at the synthesis and characterization of Mg_3Al-LDH and its functionalization with IL(methyl trialkyl ammonium chloride) in order to obtain adsorbent materials with high efficiency in the removal process of Pd ions from aqueous solutions.

Introduction
It is well known that the sorption processes are more appropriate for the recovery of metal ions from diluted solutions. The challenge in the adsorption process is represented by the development of new efficient adsorbent materials. An effective adsorbent material must meet the following requirements: excellent selectivity, high adsorption kinetics and capacity, thermal and chemical stability, and ease of synthesis. These properties are fulfilled by layered double hydroxides (LDH). [1,2] For more than a decade, studies have been carried out in the functionalization of different solid supports with different functional groups to increase the adsorption capacity and the selectivity of these materials. To this end, the researchers' attention was focused on the use of ionic liquids (IL) in the processes of functionalization of solid supports. The reason for such interest comes from the almost unlimited possibilities of tunability / design of new ionic liquids for specific applications and needs, insignificant volatility, high thermal stability, and wide ionic and electrochemical conductivity. [3,4] Therefore, immobilization of IL in suitable solid supports is a solution for the removal of metal ions from aqueous solutions since the advantages of IL are combined with the properties of LDH.

Experimental
Mg_3Al-LDH was synthesized using the co-precipitation method at low-supersaturation. The functionalization of Mg_3Al-LDH with the same quantity of the studied ionic liquid (IL- methyl trialkyl – ammonium chloride) was realized through co-precipitation (sample named Mg_3Al-IL) and through ultrasonication (sample named Mg_3Al-ILUS). The obtained adsorbents were characterized by X-ray diffraction (RX), Fourier-transform IR (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The obtained adsorbent materials were used in the recovery process of Pd ions from aqueous solutions. The adsorption processes were conducted in batch mode.

Results and discussion

The XRD patterns recorded for the synthesised materials and functionalized with methyl trialkyl ammonium chloride are presented in Figure 1.

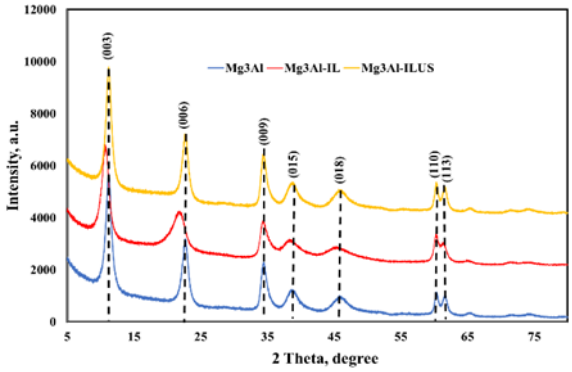

Figure 1. XRD patterns of the studied materials

The results of the characterization proved the fact that through ultrasonication, is assured a uniform distribution of the IL onto the surface of the LDH, while via co-synthesis is obtained an impregnation of the IL between the LDH layers, which will bring a higher stability of the obtained material. Palladium adsorption studies onto the studied materials were carried out in batch mode. The efficiency of the palladium adsorption onto the studied materials was determined by establishing the dependence of their adsorption capacity on the contact time, initial concentration of Pd (II) ions in the solution and temperature. The adsorption data were discussed from the kinetic and equilibrium point of view. The adsorption experimental data indicate that the adsorption process unfolds quickly, the equilibrium between Pd(II) ions and the studied adsorbent materials being achieved in 60 min. It is obvious that the functionalization of the Mg_3Al with methyl trialkyl ammonium chloride led to a an increase of approximately 50% of the maximum adsorption capacity of the studied materials in the recovery process of Pd(II) ions from aqueous solutions. The recovery degree of Pd(II) ions increased from 75.6% for raw Mg_3Al to over 95% for the functionalized materials. Data presented show that the kinetics of Pd(II) removal by adsorption on the studied material is described by a pseudo-second-order expression, because the correlation coefficient is very close to 1 and the theoretically predicted equilibrium sorption capacity is close to the value experimentally determined. Langmuir isotherm studies were conducted in order to investigate the maximum adsorption capacity and the affinity of the studied material towards Pd(II).

The Langmuir isotherm describe better the adsorption process of Pd(II) ions onto the studied material, comparted with other isotherm models due to the values of the obtained correlation coefficient which are close to unity. Moreover, the maximum adsorption capacity of the studied material obtained from the Langmuir plot is very close to that obtained experimentally.

Conclusions

It was observed that the presence of IL onto the LDH structure double the maximum adsorption capacity of the studied materials.

The maximum adsorption capacity of the studied materials increases in the order: $Mg_3Al \ll Mg_3Al\text{-}ILUS < Mg_3Al\text{-}IL$. Comparing the maximum adsorption capacities developed by the layered double hydroxide with or without functionalization with methyl trialkyl ammonium chloride, in the process of Pd(II) recovering from the aqueous solution, with the adsorption capacities developed by other adsorbent materials reported in the literature, it can be concluded that the layered double hydroxide Mg_3Al is an efficient adsorbent, especially if it is functionalized with the studied IL.

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