THE USE OF HYBRID MATERIALS (Mg3AL-LDH/IONIC LIQUIDS/CHITOSAN) IN THE RECOVERY PROCESS OF Pd IONS FROM AQUEOUS SOLUTIONS

Emilia Milos[1], Laura Cocheci[1], Adriana Popa[2], Anca Filimon[3], Lavinia Lupa[1]

[1] *Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timisoara*

[2] *"Coriolan Dragulescu" Institute of Chemistry, Timisoara*

[3] *Polycondensation and Thermostable Polymers Department, "Petru Poni" Institute of Macromolecular Chemistry*

Abstract

In this work, studies were carried out on the recovery of palladium ions from aqueous solutions by adsorption on hybrid materials, Mg_3 Al-LDH/ionic liquids/ chitosan.

To synthesize the double layered hydroxide, Mg_3 Al, the coprecipitation method at low supersaturation was used , using as sources of metal ions $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO \cdot 9H_2O)$, the ratio between the cations being $Mg^{2+}/Al^{3+} = 3:1$.

Regarding obtaining the functionalized compound with 10% ionic liquid, the same method was used, specifying that the mixture of nitrates was added, dropwise, to the ionic liquid solution, dissolved in acetone, the ratio between them being ionic liquid:acetone =1g/50mL. To maintain the pH in the desired range, a NaOH solution was used , prepared from boiled and cooled water, and the mechanical strength of the obtained adsorbents (Mg_3 Al and Mg_3 Al-IL) was increased by dispersing them in chitosan solution dissolved in 1% acetic acid, obtaining the hybrid materials: Chitosan / Mg_3 Al, Chitosan / Mg_3 Al-IL, Chitosan / Mg_3 Al/IL. The hybrid materials were characterized by X-ray diffraction, Fourier transform IR spectroscopy (FTIR) and scanning electron microscopy (SEM) coupled with an energy dispersive X-ray detector (EDX).

The X-ray spectrum of the Mg_3 Al sample, obtained by co -precipitation at low supersaturation, suggests a good compatibility of chitosan with LDH, which leads to the formation of porous networks.
For all studied materials and for all initial palladium concentrations, the adsorption capacity of the studied materials increases with increasing contact time, up to 60 minutes, after which it remains practically constant.

To clarify the palladium adsorption mechanism on the three studied materials, three kinetic models were used: the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intraparticle diffusion model (Weber-Morris), the pseudo-order kinetic model second order being the one that confirmed, the best, the experimental data, value of the correlation coefficients R^2, being approximately 1, regardless of the working temperature.

In order to study the nature of the palladium adsorption process on the studied materials, the thermodynamic parameters were calculated: enthalpy, entropy, Gibbs free energy, activation energy, the results confirming that the reactions are spontaneous, endothermic, and the palladium adsorption process on the studied materials corresponds a chemosorption.

In order to identify the mechanism of the process and evaluate, theoretically, the adsorption capacity at equilibrium, the Langmuir, Freundlich , Temkin and Redlich-Peterson isotherms were used , finding that the Langmuir isotherm best describes the palladium adsorption process on synthesized materials.

It is recommended to add the ionic liquid in the synthesis process of the hybrid material, not in the synthesis process of the LDH.

Introduction

In the conditions where the primary reserves are continuously depleted, palladium's applications are multiple, and the price of the metal in a fluctuating increase, its recovery from secondary products and waste becomes imperative. The recovery processes are multiple: melting, chlorination, dissolution in acids, co-precipitation, ion exchange, adsorption, etc. Particular attention is paid to adsorption, being one of the most promising methods due to its simplicity and high efficiency, attributes that determine the widespread use of this recovery method.

As a result, in the present work the possibility of recovering palladium ions from residual aqueous solutions was studied, by adsorption on hybrid materials, Mg3Al-LDH/ionic liquids/chitosan, proving that all the raw materials used to obtain the adsorbents proved their effectiveness.

Experimental

To synthesize the double layered hydroxide, Mg $_{3 Al, the}$ coprecipitation method at low supersaturation was used , using as sources of metal ions $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO \cdot 9H_2O)$, the ratio between the cations being $Mg^{2+}/Al^{3+} = 3:1$.

Regarding obtaining the functionalized compound with 10% ionic liquid, the same method was used, specifying that the mixture of nitrates was added, dropwise, to the ionic liquid solution, dissolved in acetone, the ratio between them being ionic liquid:acetone =1g/50mL. To maintain the pH in the desired range, a NaOH solution was used , prepared from boiled and cooled water, and the mechanical strength of the obtained adsorbents (Mg_3Al and Mg_3Al-IL) was increased by dispersing them in chitosan solution dissolved in 1% acetic acid, obtaining the hybrid materials: Chitosan / Mg_3Al, Chitosan / Mg_3Al-IL, Chitosan / Mg_3Al/IL. The hybrid materials were characterized by X-ray diffraction, Fourier transform IR spectroscopy (FTIR) and scanning electron microscopy (SEM) coupled with an energy dispersive X-ray detector (EDX).

To explain the mechanism of the adsorption process, kinetic, thermodynamic and equilibrium studies were carried out.

Results and discussion

The X-ray spectrum of the Mg_3Al sample, obtained by co -precipitation at low supersaturation, suggests a good compatibility of chitosan with LDH, which leads to the formation of porous networks.

For all studied materials and for all initial palladium concentrations, the adsorption capacity of the studied materials increases with increasing contact time, up to 60 minutes, after which it remains practically constant.

The structural and morphological characterization of the synthesized materials was achieved by: X-ray diffraction (XRD); Fourier transform IR spectroscopy (FTIR); scanning electron microscopy (SEM);

Diffractograms of the synthesized hybrid samples were compared with the X-ray diffractograms of the raw materials used (chitosan , Mg 3 Al, Mg 3 Al-IL). The X-ray spectrum of the Mg 3 Al sample obtained by co -precipitation at low supersaturation confirms the fact that layered double hydroxide was obtained as the main crystalline phase, being able to highlight the specific basal peaks of planes (003) and (006) at the angle 2Ө=11, 5°, respectively 2Ө=22.8° and the non-basal peaks corresponding to planes (110) and (113) present at angles 2Ө around 60 degrees. In the case of the layered double hydroxide sample functionalized with

methyl trialkyl ammonium chloride (Mg 3 Al-IL), was observed a shift of the basal peaks to smaller 2Ѳ angles, a decrease in their intensity and an increase in the base indicating the intercalation of the ionic liquid between the LDH layers. X-ray diffraction studies of pure chitosan show very broad peaks at the angles $2\Theta = 10°$ and $2\Theta = 20°$, results similar to the data presented in the specialized literature . In hybrids samples are observed disappearance of chitosan peak at $2\Theta = 10°$, and the very wide peak from $2\Theta = 20°$ became weak. These results suggests that chitosan has a good compatibility with LDH, which leads to formation of some porous network of chitosan and LDH, respectively IL, demonstrating that the preparation method was effective for obtaining the studied hybrid materials.

While the chitosan particles have a very smooth surface, the morphology of the Mg3Al sample is in the form of hexagons arranged neatly in overlapping layers, typical of layered double hydroxides. By functionalizing it with methyl trialkyl ammonium chloride through co - synthesis, it is observed that the layers are disordered due to the penetration of the ionic liquid between the layers, the surface of the sample appearing in the form of cotton flowers. The synthesized hybrid samples show very different surface morphologies, with more compact surfaces containing small, well-dispersed LDH particles. EDX spectra confirm the obtaining of hybrid materials.

To clarify the palladium adsorption mechanism on the three studied materials, three kinetic models were used: the pseudo-first-order kinetic model, the pseudo-second-order kinetic model and the intraparticle diffusion model (Weber-Morris), the pseudo-order kinetic model second order being the one that confirmed, the best, the experimental data, value of the correlation coefficients R^2, being approximately 1, regardless of the working temperature.

In order to study the nature of the palladium adsorption process on the studied materials, the thermodynamic parameters were calculated: enthalpy, entropy, Gibbs free energy, activation energy, the results confirming that the reactions are spontaneous, endothermic, and the palladium adsorption process on the studied materials corresponds a chemosorption.

In order to identify the mechanism of the process and evaluate, theoretically, the adsorption capacity at equilibrium, the Langmuir, Freundlich , Temkin and Redlich-Peterson isotherms were used , finding that the Langmuir isotherm best describes the palladium adsorption process on synthesized materials.

Conclusion

It can be found that the functionalization of the adsorbent materials with the studied ionic liquid leads to an increase in their adsorptive efficiency, which means that the functional groups in the ionic liquid contribute to the palladium removal process from aqueous solutions. It is found that the method of obtaining the adsorbent material also influences the efficiency of the Pd recovery process from aqueous solutions, so it is recommended to functionalize the adsorbent material with the studied ionic liquid in the hybrid materials synthesis process, not in the LDH synthesis.

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