OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 3, March 2010, p. 340 - 344

Sol-gel synthesized sorbents for Cu^{2+} and Cd^{2+} separation from solutions

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The aim of this work was synthesis and characterization of new hybrid materials by grafting phenylphosphonic acid on silica gels. The obtained hybrid were characterized by FT-IR spectroscopy, Thermal Analysis (TG, DTG, DTA), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). IR spectra indicate the formation of Si-O-P bonds, by the presence of a large band in the 850-1300 cm^{-1}. Results obtained by the thermal analysis confirm the high stability of the obtained compounds. TEM and SEM micrographs showed the mesoporous structure of the analyzed materials. The adsorbant capacity of the obtained materials for removal of Cu^{2+} and Cd^{2+} ions from aqueous solution has been investigated. The maximum capacity of the synthesized hybrid materials was 2.016 mg/g for Cu^{2+}, and 0.51 mg/g for Cd^{2+} ions. The obtained results allow us to propose utilization of these new hybrid materials as sorbents for the removal of heavy metal ions from aqueous solutions.

(Received January 26, 2010; accepted March 12, 2010)

Keywords: Hybrid material, Sol-gel synthesis, Sorbent

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1. Introduction

The rapid development of some industrial domains has generated an enormous demand of new materials whose properties can be controlled. Many traditional materials such as metals, plastics or ceramics don't provide technological requirements for different new applications. By combining the suitable molecular-scale organic component with an inorganic component, hybrid materials are obtained, which have complementary properties to those of component parts.

Many possible combinations between organic and inorganic species ensure the production in an unlimited number of new materials, characterized by properties different from the traditional materials and therefore, a broad spectrum of their future applications [1-3].

In recent years there has been a growing concern for the use of hybrid materials in environmental protection. This use is based on their ability to function as sorbents, respectively to adsorb on the surface of solid various cations from aqueous or non-aqueous solutions. In this aim, the organic component is represented by a chelate group with high tendency to form metal complexes with various metal ions from solution. Covalent grafting of chelate molecules on the inorganic supports is the current practice used to obtain functionalized surfaces.

In recent years, organophosphoric compounds present a great interest as coupling molecules [4-9]. The great advantage of the use as coupling molecules of organophosphoric compounds is that in sol-gel process the M-O-P bonds by hetero-condensation are formed. This process is cinetic favorized due to the protonation of alkoxy groups by the acidic P-OH groups [4-10].

Bonding to the inorganic part, M-O-P involves the formation of stable bonds. The stability and the easiness of M-O-P bonds formation is well illustrated by many exemples of hybrid materials containing organophosphorus coupling molecules reported in the literature [9-15].

Depending on the inorganic substrate and organophosphorus coupling molecules, these hybrid materials have applications in various fields such as: catalysis [16], optical devices [17] or biomedical area [18, 19].

In this work, hybrid materials have been synthesized by grafting phenylphosphonic acid on silica gels. The sorbent capacity of this hybrid materials for removal of Cu^{2+} and Cd^{2+} ions from aqueous solution has been investigated.

2. Experimental

The sol-gel method has been used for synthesis of organic inorganic hybrids. The synthesized compounds are presented in Table 1.

Table 1. The hybrid materials synthesized by the sol-gel method.

product code	Reagents			Molar ratio
PP1	C_6H_5-PO(OH)$_2$	Si(OC$_2$H$_5$)$_4$	NH$_2$-C$_3$H$_6$-Si(OCH$_3$)$_3$	1:1:1
PP2	C_6H_5-PO(OH)$_2$	Si(OC$_2$H$_5$)$_4$	-	1:1
PP3	C_6H_5-PO(OH)$_2$	-	NH$_2$-C$_3$H$_6$-Si(OCH$_3$)$_3$	1:1

2.1 PP1 hybrid material

Tetraethylorthosilicate (5.6 ml) was added dropwise to a solution of phenylphosphonic acid (4 g) in 10 ml absolute ethanol at room temperature under stirring; then, 3-aminopropyltrimethoxisilane (4.5 ml) was added. The mixture was stirred another hour at room temperature then 10 ml of deionized water and 0.3 ml 1N HCl were added under stirring. The mixture was maintained two hours under stirring at room temperature, then the mixture was aged three days at room temperature, dried at 70 °C for 24 hour and analyzed.

2.2 PP2 hybrid material

Tetraethylorthosilicate (5.6 ml) was added dropwise to a solution of phenylphosphonic acid (4 g) in 10 ml absolute ethanol at room temperature under stirring. Then 10 ml of deionized water and 0.3 ml 1N HCl were added under stirring and the mixture was maintained two hours under stirring at room temperature. Then the mixture was aged three days at room temperature, dried at 70 °C for 24 hour and analyzed.

2.3 PP3 hybrid material

3-aminopropyltrimethoxisilane (4.5 ml) was added dropwise to the solution of phenylphosphonic acid (4 g) in10 ml absolute ethanol at room temperature under stirring. Then 10 ml of deionized water and 0.3 ml 1N HCl were added under stirring. The mixture was maintained two hours under stirring at room temperature. Then the mixture was aged three days at room temperature, dried at 70 °C for 24 hour and analyzed.

2.4 Sorption of divalent metals from aqueous solution on hybrid materials[20]

Metal ions separation from aqueous solutions was performed by a batch technique at room temperature. 0.5 grams of hybrid materials were added to a solution containing 100 mg Me^{2+} in 0.1 N HNO_3 and maintained under mechanical stirring for 7 hours. The residual Me^{2+} content in solution was determined on samples (1 mL) taken from the mixture as follows: at 10 min. interval in the first hour, at 15 min. interval in the second hour and at 30 min. interval in the last 5 hours. Each sample was diluted (ratio 1:25) and the concentration of Me^{2+} was determined by atomic adsorption spectroscopy.

The amount, q (mg/g), of Me^{2+} sorbed, was calculated as follow:

$$q = \frac{\left(C_{f0} - C_{ft}\right) V \cdot 10^{-3}}{G} \text{ (mg/g)} \quad (1)$$

where: C_{f0} –, C_{ft} – are the initial and the equilibrium Me^{2+} concentration (mg/L) in the solution at 0 and t times; V – is the volume of the solution (mL), G- is the mass of hybrid sample (g).

2.5 Analysis

The obtained materials were characterized by Fourier transform infrared spectroscopy (PRESTIGE 21-Shimodzu), scanning electron microscopy (SEM) with a Philips XL-20 microscope, transmission electron microscopy (TEM) with Philips Tecnai microscope, thermal properties of materials were characterized through thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which were performed on a TGA/SDTA 851-LF1100 – Mettler instrument at a heating rate of 10 °C/min under air atmosphere and temperature range from 20 to 1100 °C, The concentrations of Cu^{2+} and Cd^{2+} (mg/L) in solution were determined by atomic absorption spectrometry on a Varian SpectrAA 110 coupled with GTA-110, at the wavelength λ= 324,8 nm for Cu^{2+} and λ= 228,2 nm for Cd^{2+}.

3. Results and discussion

Some general remarks concerning the analysis of the IR spectrum of PP1 hybrid material (Fig. 1):

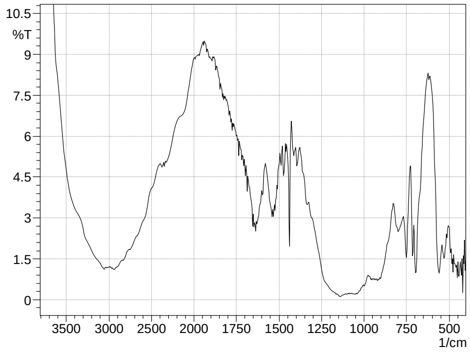


Fig. 1. FT-IR spectrum of the PP1 hybrid material.

- in the 1300-3500 cm^{-1} region are superimposed the characteristic bands corresponding to the aromatic vibration, of CH_2 groups, alkyl-NH_2, respectively OH;

- in the 650-850 cm^{-1} region appear the deformation vibration of -C-H bands corresponding to the aromatic ring, deformation vibrations of CH_2 groups and alkyl-NH_2

- IR spectra indicate the formation of Si-O-P bonds, by the presence of a large band in the 850-1300 cm^{-1} region where are overlapping and the characteristic vibrations of the Si-O and P=O links.

The morphology of the materials was illustrated by SEM şi TEM microscopy.

SEM picture of the PP1 sample, given in Fig. 2 shows a mesoporous structure.

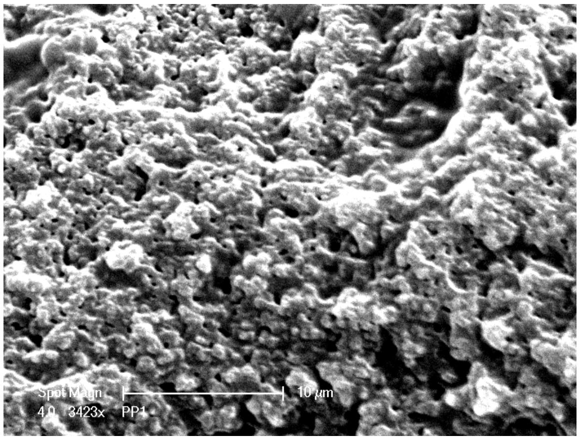


Fig. 2. SEM image of PP1 sample.

TEM image of the PP1 hybrid material (Fig. 3.) shows the presence of mesopores with little and large diameter

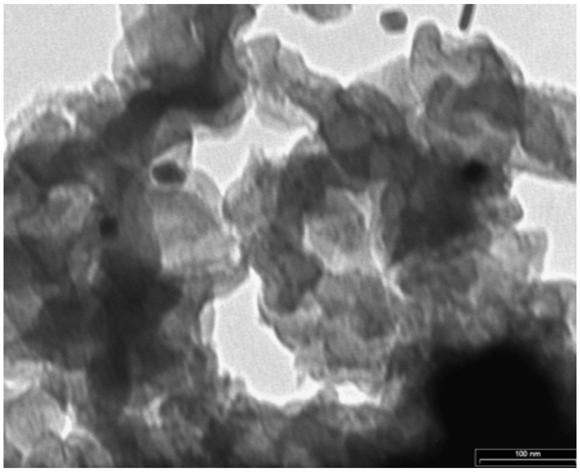


Fig. 3. TEM image of PP1 sample.

Fig. 4 shows the DTA-TG curves for sample PP1. A weight loss < 5 wt-% before 200 °C is due to evaporation of physically absorbed water in the hybrid material. Between 340-550 °C on DTA curve are shown a series of exothermic effects attributed to combustion of residue organic from material. These efects are confirmed by a weight loss on TG curve.

Organic-inorganic hybrid materials are characterized by high thermal stability (> 300 °C) owing to Si-O bond strength.

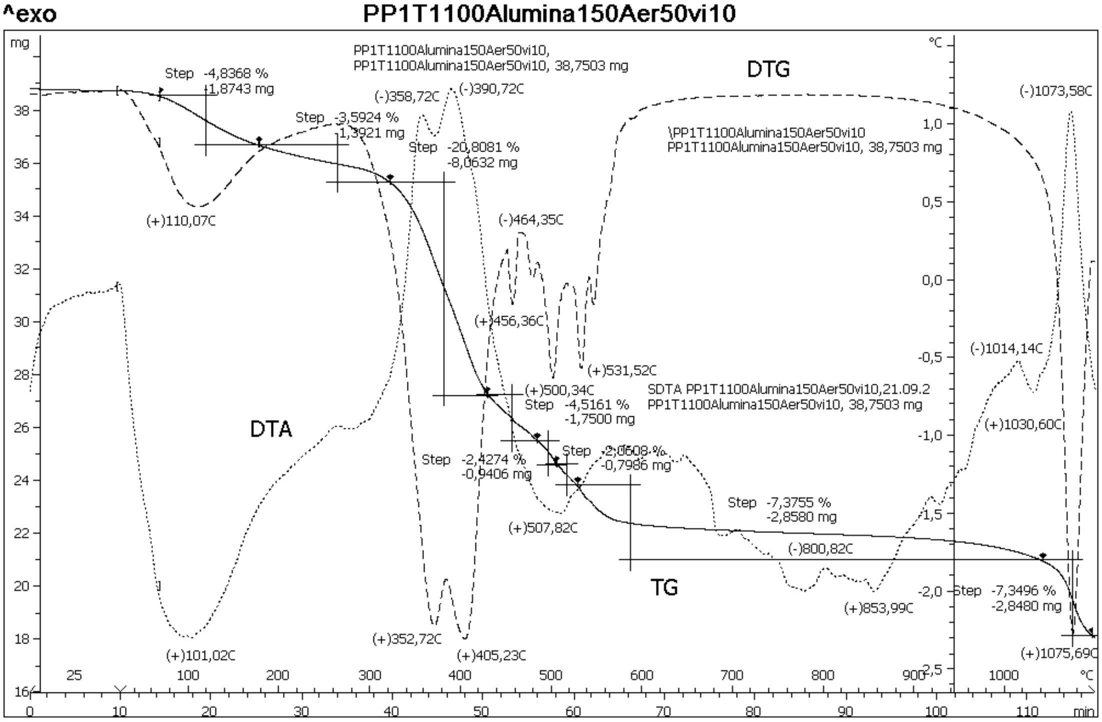
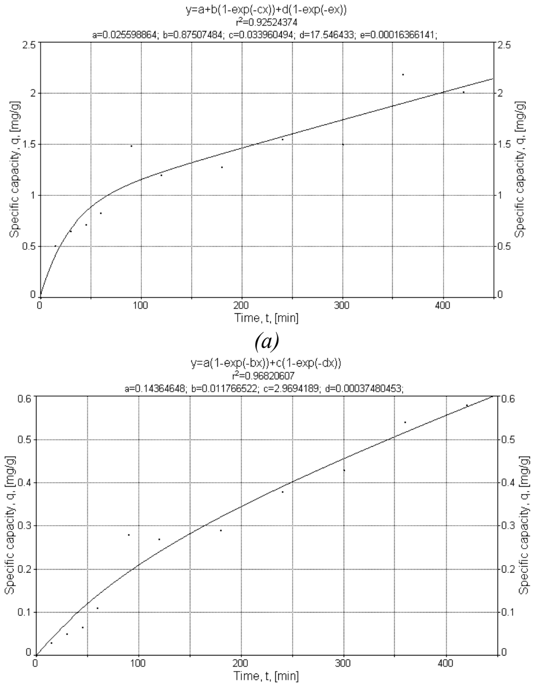


Fig. 4. Thermogravimetric analysis of sample PP1 hybrid.

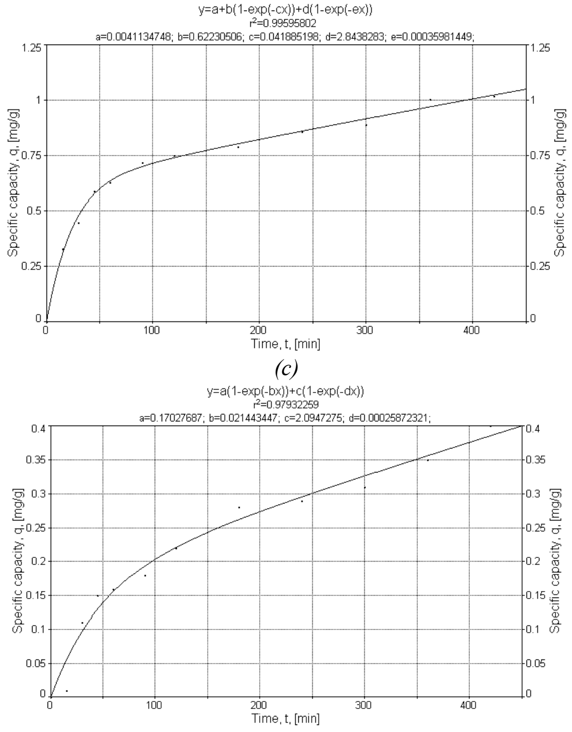
The adsorption capacity of the PP1, PP2 and PP3 hybrid materials as a function of time are shown in Figs. 5-7.



(a)

(b)

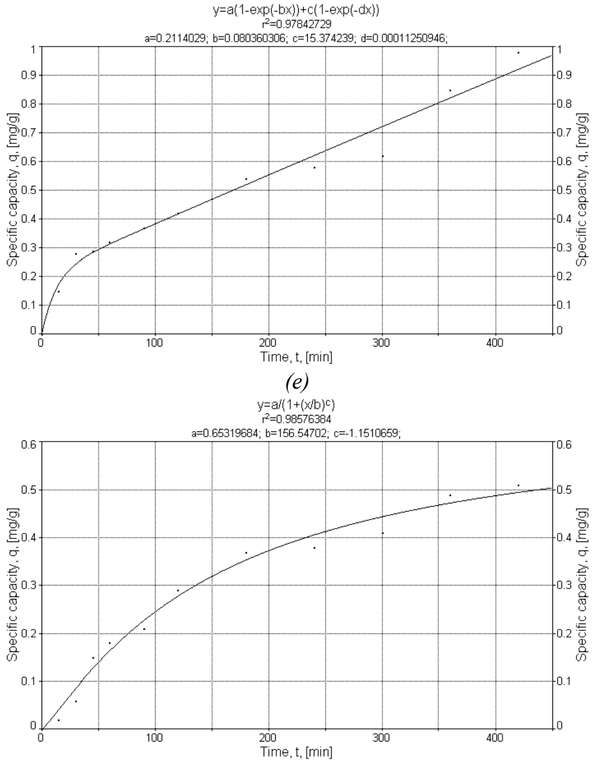
Fig. 5. Specific adsorption capacity (Cu^{2+} – (a), Cd^{2+} – (b)) as a function of time, for the PP1 hybrid material, at pH=1 and 25 °C.



(c)

(d)

Fig. 6. Specific adsorption capacity (Cu^{2+} – (c), Cd^{2+}– (d)) as a function of time, for the PP2 hybrid material, at pH=1 and 25 °C.



(e)

(f)

Fig. 7. Specific adsorption capacity (Cu^{2+}– (e), Cd^{2+}– (f)) as a function of time, for the PP3 hybrid material, at pH=1 and 25 °C.

4. Conclusions

Organophosphorus acids and their derivatives are highly promising coupling molecules that allow the anchoring of organic groups to inorganic solids. The obtained hybrid materials by sol-gel method were characterized by IR Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) and thermogravimetric analysis (DTA).

For this study the batch method was used and the following aspects were observed: - good results exist for the PP1 hybrid material in the sorption process of Cu^{2+}; - The equilibrium of the adsorption of Cu^{2+} and Cd^{2+} ions on the PP1 PP2 and PP3 hybrids was not reached during the 420 minutes that the process was followed. It is therefore necessary to follow the process longer.

Acknowledgements

The authors are grateful to Dr. Viorica Parvulescu (Institute of Physical Chemistry, Spl. Independentei, Bucharest, Romania) for SEM and TEM Images of hybrid materials.

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