Studies Regarding the Florisil Impregnation with Ionic Liquid through Ultrasonication

A. Negrea, L. Lupa, M. Ciopec, P. Negrea, and I. Hulka

***Abstract*—The paper presents the studies regarding the impregnation of Florisil with Cyphos IL-101 using a new method of impregnation instead of the classic methods: the ultrasonication. In order to determine the efficiency of the ultrasonication methods of impregnation, the work conditions were varied, and the obtained supported ionic liquids were characterized through scanning electron microscopy (SEM), energy dispersive XRay analysis (EDX) and FTIR- Fourier transform infrared spectroscopy. From the experimental data was observed that only the amplitude of ultrasonication had a significant influence onto the impregnation process efficiency. The impregnated material obtained in the optimum conditions showed good adsorption performance in the removal process of Cs^+ developing a maximum adsorption capacity of 2.95 mg/g.**

***Index Terms*—Ultrasonication, impregnation, ionic liquid, Cs^+ adsorption.**

I. Introduction

The impregnation of a solid support, with various functionalized groups in order to enhance its adsorbent properties and selectivity, is a new trend in the removal process of various metals ions from aqueous solutions. In this way were developed four methods for the impregnation of the desired extractant into a solid support: the dry method, wet method, modifier addition method and dynamic column method [1]–[6]. Instead of the traditional methods mentioned in the specialty literature for the impregnation of a solid support, we studied in this paper, the impregnation through ultrasonication.

Due to their superior characteristic compared to organic extractants, the use of ionic liquids reached a higher attention, in special in the removal process of radionuclides from aqueous solutions [7]–[11]. The immobilization of the ionic liquids in a suitable solid support prevents the drawbacks of the liquid-liquid extraction like: the loss of the ionic liquid in water and a possible ion-exchange occurrence between the metal ion and the ionic-liquids cation [12]–[15]. Therefore the studies regarding the ultrasonication method of impregnation were realized for the system Cyphos IL-101 onto Florisil. We focused on this ionic liquid due to its commercial availability and low price, and also because in our previous studies and literature survey, Cyphos IL-101 showed to be a favourable extractant for Cs^+ removal from aqueous solutions [12], [16]–[19]. As a solid support was used Florisil, because the inorganic solid supports have several superior qualities compared with the organic solid supports such as: higher thermal and chemical stabilities, well-ordered periodic pore structure, and controllable pore diameter, and particularly in liquid radioactive waste treatment: radiation stability and great selectivity for certain radiological important species [5], [9], [11], [20]–[23]. Supported ionic liquid (SILs) have the advantages of small amount of ILs used, high interface area, short diffusion distance and accelerated transport rate [13], [24]. In order to determine the efficiency of the ultrasonication methods of impregnation, the work conditions were varied, and the obtained supported ionic liquids were characterized through scanning electron microscopy (SEM), energy dispersive XRay analysis (EDX) and FTIR- Fourier transform infrared spectroscopy. The obtained material, in the optimum conditions of impregnation, was applied in the removal process of Cs^+ from aqueous solutions and the maximum adsorption capacity was determined.

II. Experimental

For the impregnation of the studied solid support through the ultrasonication method in the first step the studied ionic liquid (Cyphos IL-101) was dissolved in acetone (0,1 g of IL in 5 mL of acetone). It was used a ratio of IL:solid support of 0.1:1, this being the main advantages of the use of solid supports ionic liquid: the use of a small amount of IL. The ultrasound impregnation was realized using a Sonorex Super 10 P ultrasonic bath, using the indirect ultrasonication method. It was varied the time of ultrasonication (10, 20, 30, 40, 50 and 60 minutes) and the amplitude (10, 30, 50, 70 and 100%).

In order to evaluate if the studied solid support was impregnated with the Cyphos IL-101, the obtained SILs were characterized by energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy FTIR. The surface morphology of the impregnated materials was investigated by Scanning Electron Microscopy (SEM) using a Quanta FEG 250 Microscope, equipped with EDAX ZAF quantifier. The FTIR spectra (KBr pellets) of the obtained materials were recorded on a Shimadzu Prestige- 21 FTIR spectrophotometer in the range 4000–400 cm^{-1}. In order to established the best work conditions the obtained impregnated solid supports were used in the removal process of Cs^+ from aqueous solutions, and the dependence of the Cs^+ uptake versus the ultrasonication work

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conditions was established. In this aim a specified amount of each impregnated solid support (0.1 g) was treated with 25 mL of 10 mg/L Cs^+ solution, under continuous stirring for 1h using a Julabo shaker. After the time elapsed the samples were filtrated and the residual concentration of Cs^+ was analysed through atomic emission spectrometry using a Varian SpectrAA 280 type atomic absorption spectrometer using air/acetylene flame.

III. Results and Discussion

A. Characterization of the Impregnated Support

The experimental data regarding the SEM images of the Florisil impregnated with Cyphos IL-101 at different time of ultrasonication and at 100% amplitude are presented in Fig. 1.

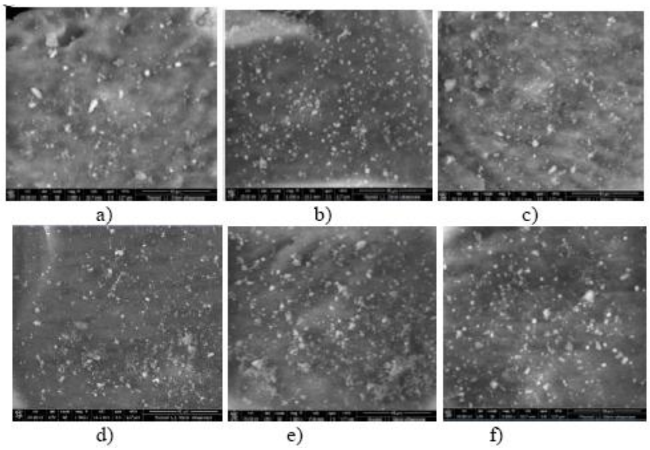


Fig. 1. SEM images of Florisil impregnated with Cyphos IL-101 using various time of ultrasonication a) 10 min; b) 20 min; c) 30 min; d) 40 min; e) 50 min; f) 60 min.

From the SEM images it can be observed that the particles of the studied IL (white particles from Fig. 1) adhered to the Florisil surface. It can be notice that the time increasing didn't lead to a significant increase of the quantity of the impregnated IL onto the Florisil surface. At the same time the increasing of ultrasonication period has an undesired effect, the conglomeration of the IL particle, their dispersion being patchy. This effect can influence the reproducibility of the Cs^+ adsorption experiments.

The SEM images of the materials obtained through impregnation of the Florisil with Cyphos IL-101 using 10 minutes of ultrasonication at various amplitudes are presented in Fig. 2.

The intensity of sonication is proportional to the amplitude of vibration of the ultrasonic source and, as such, an increment in the amplitude of vibration will lead to an increase in the intensity of vibration and to an increase in the sonochemical effects. In our case the increasing of the amplitude lead to an increase in the IL quantity which is impregnated onto the Florisil surface.

The increasing of the amplitude assures an easier transmission of the IL particles through the liquid media until reach the cavities of the solid support, the impregnation being realized inside the pore of the solid support. Therefore we will expect that the material, obtained through impregnation of the Florisil with the studied IL using the ultrasonication method for 10 minutes at an amplitude of 100%, will develop the highest efficiency in the removal process of Cs^+ from aqueous solutions.

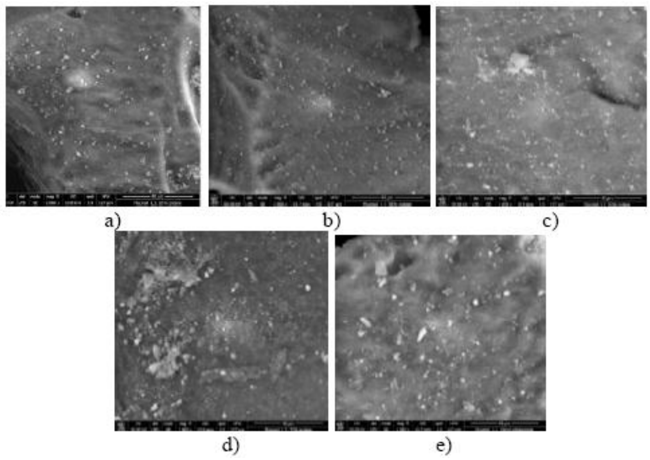


Fig. 2. SEM images of Florisil impregnated with Cyphos IL-101 using various amplitude of ultrasonication.
a) 10 %; b) 30 %; c) 50 %; d) 70 %; e) 100 %.

The impregnation of the Florisil with Cyphos IL-101 through ultrasonication was highlighted by the EDX analyse.

The content of phosphorous and chlorine (two elements specific for the studied IL) from the obtained impregnated materials resulted from the EDX analysis is presented in Table I.

TABLE I: The Quantification of P and Cl for the Obtained Impregnated Materials Resulted at EDX Analysis

Time of ultrasonication	P, wt %	Cl, wt %	Amplitude of ultrasonication	P, wt %	Cl, wt %
10 min	0.40	1.62	10%	0.15	0.46
20 min	0.42	1.63	30%	0.23	0.68
30 min	0.47	1.66	50%	0.25	0.81
40 min	0.48	1.65	70%	0.36	1.11
50 min	0.56	1.61	100%	0.40	1.62
60 min	0.56	1.63			

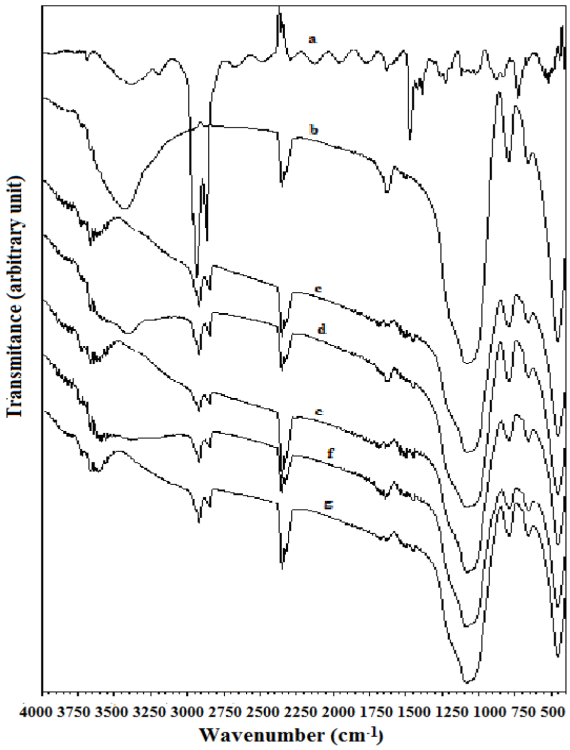


Fig. 3. The FTIR spectra of the a) Cyphos IL-101; b) Florisil before impregnation; c) Florisil impregnated at a 10% ultrasonication amplitude; d) 30%; e) 50%; f) 70%; g) 100%.

EDX analyze confirmed that the impregnation of the Florisil with the studied IL, through ultrasonication method, occurred. From the experimental data presented in Table I, it can be concluded that the highest quantity of IL impregnated onto the Florisil was lead in case of solid support impregnation at a 100% amplitude for 10 minutes.

Because from the SEM and EDX analyze was observed that the ultrasonication time hasn't a significant influence onto the impregnation process, only the samples obtained at various amplitude were submitted to the FTIR analyze. The FTIR spectra of the studied IL, studied solid support before and after impregnation at various amplitudes are presented in Fig. 3.

The impregnation of the Florisil with the studied IL, in all the cases is confirmed by the IR peaks around 2957 cm^{-1}, 2933cm^{-1}, 2858 cm^{-1} and 1395 cm^{-1} were the stretching vibration of CH_3 and CH_2 in Cyphos IL 101. The bands at 1100 cm^{-1}, 1050 cm^{-1} and 800 cm^{-1} are attributed to the group of vibrations ν_a (C-C)+ ν (M-O)+P-C stretching [25]-[28].

B. *Adsorption of Cs^+ from Aqueous Solutions*

In order to determine the adsorption performance of the obtained impregnated materials, these were used in the removal process of Cs^+ from aqueous solutions. The adsorption performance was expressed as the metal uptake, *q*, mg/g, and the corresponding mass balance expression is [8], [19], [21]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where C_0 and C_e are the concentrations of Cs^+ (mg/L) in the solution initially ($t = 0$) and at equilibrium, respectively, V is the volume of the solution and m is the mass of adsorbent. In order to determine the optimum conditions of impregnation through ultrasonication the dependence of Cs^+ uptake versus the impregnation conditions (time and amplitude of ultrasonication) was established. The experimental data are presented in Fig. 4.

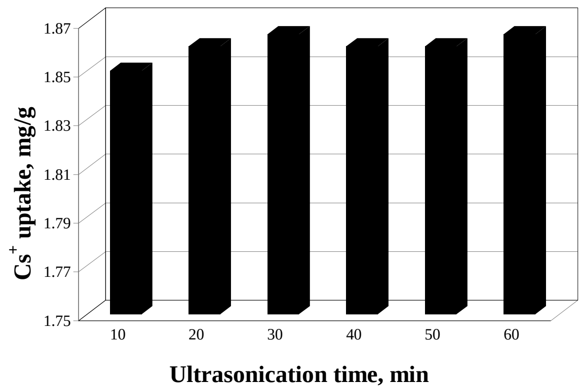
It can be observed that the increasing time of the impregnation process through ultrasonication didn't lead to an increasing of the adsorption performance of the obtained materials. Instead the increasing of the amplitude had this effect. This means that the Cs^+ uptake is dependent by the quantity of IL impregnated onto the Florisil. These results are in agreement with the conclusions resulted from the analysis of the impregnated materials.

The material obtained in the optimum conditions of impregnation (10 minutes of ultrasonication at amplitude of 100%) was treated with Cs^+ aqueous solutions having various concentrations (5-50 mg/L) in order to determine its maximum adsorption capacity.

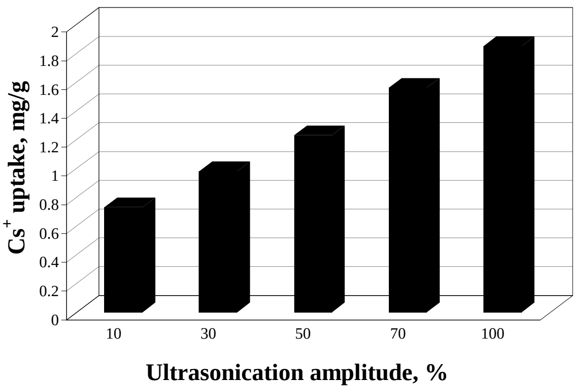
The experimental data were fitted with the Langmuir isotherm. The relation between the amounts of Cs^+ adsorbed by the adsorbent can be expressed by the linearized Langmuir adsorption isotherm as [5], [11], [12]:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \quad (2)$$

where q_e is the amount of Cs^+ adsorbed per unit of the adsorbent (mg/g), K_L the adsorption constant related to the enthalpy of adsorption (L/mg), C_e the equilibrium concentration of the Cs^+ (mg/L), q_m the maximum adsorption capacity (mg/g).



a)



b)

Fig. 4. Cs^+ uptake versus the ultrasonication work conditions. a) time, b) amplitude

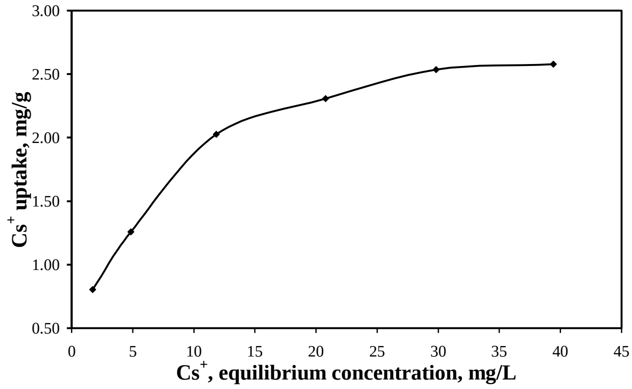


Fig. 5. The equilibrium isotherm of Cs^+ adsorption onto the Florisil impregnated with Cyphos IL-101 through ultrasonication.

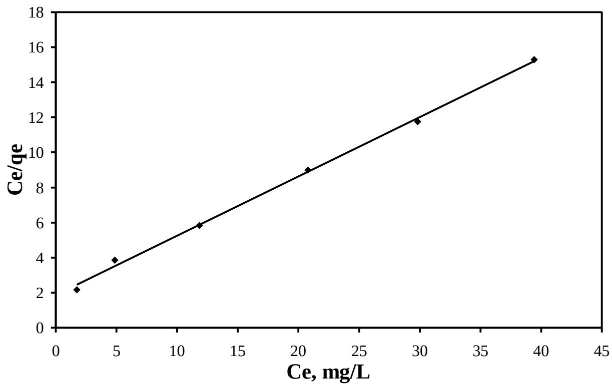


Fig. 6. Langmuir plot of Cs^+ adsorption onto the Florisil impregnated with Cyphos IL-101 through ultrasonication.

The equilibrium isotherm and the Langmuir isotherm of Cs^+ adsorption onto the Florisil impregnated with Cyphos IL-101through ultrasonication are presented in Fig. 5 and Fig. 6, respective.

From the experimental data can be observed that the Cs^+ uptake increase with equilibrium concentration of caesium increasing. Then, it approached a constant value at high equilibrium concentrations. The maximum adsorption capacity obtained by the studied material in the removal process of Cs^+ from aqueous solutions is 2.6 mg/g.

It can be noticed that the Langmuir model effectively describes the Cs^+ adsorption onto the studied material, the obtained correlation coefficient being close to 1 (R^2=0.9978). From the slope and intercept of the Langmuir plot (Fig. 6) were determined the K_L (K_L=0.182 L.mg) and q_m (q_m=2.95mg/g) parameters. It can be observed that the maximum adsorption capacity obtained experimentally is close to those obtained from the kinetic plot, this means that the Langmuir isotherm describe the Cs^+ adsorption onto the entire concentration interval studied. Compared with our previous studies when was used a contact time between adsorbent and adsorbate of 2 h [19], or with the literature studies when was used a contact time of 10 days and obtained a maximum adsorption capacity of 0.2128 mg Cs^+/g of adsorbent [29] we can conclude that the studied method of impregnation enhance the adsorption properties of the studied materials in the removal process of Cs^+ from aqueous solutions.

IV. Conclusions

The present paper showed that the ultrasonication method can be used for the impregnation of solid support with ionic liquid. From the experimental data was observed that only the amplitude of ultrasonication had a significant influence onto the impregnation process efficiency. Therefore, the optimum work conditions in order to obtain an impregnated solid support with an IL are: ultrasonication time of 10 minutes using amplitude of 100%. Through ultrasonication method of impregnation the particles of the IL adhere inside the cavities of the used solid support, not only at the surface, in this way being avoid the loss of the IL in the aqueous phase. This method is advantageous because the impregnation is realized in a shorter time, and some steps, like washing of the materials, are skipped. The impregnated material obtained in the optimum conditions showed good adsorption performance in the removal process of Cs^+ developing a maximum adsorption capacity of 2.95 mg/g.

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