"Gheorghe Asachi" Technical University of Iasi, Romania

SILICA IMPREGNATED WITH CYPHOS IL-101 FOR Cs$^+$ ADSORPTION

Adina Negrea, Lavinia Lupa∗, Mihaela Ciopec, Petru Negrea

Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Blvd. Vasile Parvan no. 6, 300223, Timisoara, Romania

Abstract

A series of experiments were performed to quantify the adsorption of Cesium on Silica impregnated with trihexyl(tetradecyl)phosphonium chloride (Cyphos IL-101). Non-radioactive cesium solution was used as a surrogate of the radioactive ^{137}Cs. The obtained impregnated Silica with the studied ionic liquid was characterized through scanning electron microscopy, energy dispersive X-ray analysis and Fourier transform infrared spectroscopy in order to put in evidence that the impregnation with the ionic liquid occurred. The adsorption process has been investigated as a function of pH, solid:liquid ratio, adsorbate concentration, contact time and temperature. Three kinetic and two equilibrium models were employed to interpret the test results. The results indicate that the adsorption fitted well with the pseudo-second order kinetic model. Simple thermodynamic model has been applied to the isotherm sorption data and the relevant thermodynamic parameters were determined from the graphical representation of this model.The isotherm data was well described by Langmuir isotherm model. The reported results showed that the impregnated silica with Cyphos – IL 101 studied in this paper is an efficient adsorbent material for the removal of cesium ions from aqueous and wastewater solutions.

Key words: Cs$^+$ adsorption, ionic liquid, impregnation, silica,

Received: February, 2014; Revised final: August, 2014; Accepted: August, 2014

1. Introduction

Radioactive ^{137}Cs ion is a significant component of nuclear waste and nuclear fallout. Cs$^+$ separation from aqueous solutions is mostly needed, due to its destructive effects on the environment. It is potential dangerous to human health and also to the environment, because of its relatively long half-live (30 years), high solubility/mobility and strong γ emitting radiation. Furthermore, it can be easily incorporated in terrestrial and aquatic organism because it is chemically similar to potassium (Abd El-Latif and Elkady, 2011; El-Kamash, 2008; Negrea et al., 2013a, b; Nilchi et al., 2011).

A lot of methods for cesium removal from aqueous solution have been studied such as: ion exchange, reverse osmosis, ultrafiltration etc. Unfortunately all these methods presents some limitations (ex. high operation and capital costs, blockage problems, difficult to be regenerated and recovered, easily damaged due to radiation), therefore the finding of an efficient methods for the radionuclides removal, which minimize these limitations, still represents a challenge (Abdel Rahman et al., 2011). In this way the specialty researchers used the liquid/liquid extraction as one of the effective methods for cesium removal from aqueous solutions (Luo and Dai, 2004; Xu et al., 2010; Zhao et al., 2005). However, general liquid/liquid based extraction technology has some disadvantages: the possible release of the hazardous and expensive extractants, lower mass transfer rate and longer equilibrium time.

These problems can be overcome by immobilizing the extractants in a solid support (Gallardo et al., 2008; Negrea et al., 2013a; Lemus et al., 2011; Zhu et al., 2012). Recently ionic liquids, a new class of extractants, have been used as alternative replacement for traditional volatile compounds, for the preparation of the impregnated

---

∗ Author to whom all correspondence should be addressed: e-mail: lavinia.lupa@upt.ro

solid supports. In addition, ionic liquids display good physical properties including higher thermal stability, viscosity, density, lower solubility in water and lower vapor pressure (Gallardo et al., 2008; Guo et al., 2011; Kalidhasan et al., 2012; Lemus et al., 2011; Liu et al., 2009; Mahmoud, 2011; Sun et al., 2009; Xu et al., 2009; Zhu et al., 2012). In comparison with the conventional polymeric matrix resin, the inorganic type has several superior qualities required for the treatment of waste waters compared to organic resins like: rapid adsorption and eluation kinetics, high mechanical strength, better resistant ability against temperature and γ-radiation (Liu et al., 2009; Mahmoud, 2011; Zhang and Hu, 2010).

In this work a fairly cheap IL: Cyphos IL-101 (trihexil (tetradecyl)phosphonium chloride) was used as extractant which was impregnated onto the silica support by the conventional method and the obtained impregnated material has been subjected to FTIR-Fourier transform infrared spectroscopy, scanning electron microscopy (SEM) and energy dispersive XRay analysis (EDX).

The impregnated Silica with Cyphos IL-101 was used in the adsorption process of Cs^+ from aqueous solutions. In order to determine the adsorption performance of the Silica impregnated with Cyphos IL-101, in the removal process of Cs^+ from aqueous solutions, equilibrium, kinetic and thermodynamic studies were used.

2. Experimental

The Silica inorganic support was purchased from Merck and the Cyphos IL-101 was supplied from Sigma-Aldrich. The impregnation of the Silica with the studied IL was described in our previous published paper (Negrea et al., 2013). The FTIR spectra (KBr pellets) of the obtained impregnates Silica with Cyphos IL-101 was recorded on a Shimadzu Prestige- 21 FTIR spectrophotometer in the range 4000–400 cm^{-1}.

The surface morphology of the impregnated material was investigated by Scanning Electron Microscopy (SEM) using a Quanta FEG 250 Microscope, equipped with EDAX ZAF quantifier. The SEM image was obtained using a magnification of 2000x. The aqueous solutions of cesium ions were prepared by adequate dilution of stock solution of 1000 mg/L (Merck standard solutions). In all the experiments distilled water was used.

In the first step, the optimum quantity of the IL which can be impregnated onto the Silica support was determined in order to determine the highest adsorption capacity of the cesium ions from aqueous solutions. For this 1 g of Silica was mixed with different quantities of IL (0.05, 0.1, 0.2, 0.4 and 0.6 g), and for all the obtained impregnated samples was used 0.1 g which were treated for 2 h with 25 mL of Cs^+ aqueous solution having 10 mg/L. The dependence of the Cs^+ adsorption capacity versus the quantity of the IL impregnated onto Silica was established.

Adsorption studies were carried out by batch technique using a Julabo SW23 shaker with a constant shaking rate. To determine the pH range at which the maximum uptake of Cs^+ would take place onto the impregnated silica, a well determined quantity of the impregnated material (0,1 g) was treated with 25 mL of Cs^+ 10 mg/L solution having various initial pH values range from 2 to 12, for 2 hours at 298 K. The pH of the synthetic solutions was adjusted using 0.1 N NaOH or 0.1 N HCl, in order to attain the desired pH for a specific period of contact time. After the establishment of the optimum pH, the influence of various solid:liquid (S:L) ratio on the efficiency of adsorption process was studied. After the time elapsed the sample were filtered and the Cs^+ ion concentration was determined through atomic emission spectrometry using a Varian SpectrAA 280 type atomic absorption spectrometer using air/acetylene flame.

To study the effect of contact time on adsorption, the experiments were carried out with samples of 0.1 g of impregnated Silica with IL in 25 mL of 10 mg/L Cs^+ solutions. The suspension were kept in contact different times (30 – 240 min) at three different temperatures (25, 35, 45 °C). After contact time elapsed, the suspensions were filtered and the filtrate was collected for Cs^+ analysis.

The effect of the initial concentration of Cs^+ was studied. Therefore 0.1 g of impregnated Silica was suspended in 25 mL of Cs^+ solution of different concentration (range: 5-50 mg/L). The suspension were stirred for 2 h at room temperatures, after the completion of experiment, the suspensions were filtered and analysed for Cs^+ residual concentration.

The adsorption capacity of the Silica impregnated with Cyphos IL-101 was determined using Eq. (1) and represent the amount of Cs^+ (mg) adsorbed by 1 g of impregnated Silica.

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

where: C_0 and C_t are the concentrations of Cs^+ ions (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.

The experimental results are given as an average of three sets of experimental results obtained in identical working conditions.

3. Results and discussion

3.1. Characterization of the silica impregnated with IL

The dependence of the adsorption capacity of the impregnated Silica with IL in the removal process of Cs^+ from aqueous solutions versus the quantity of the IL impregnated onto Silica is presented in Fig. 1.

By increasing the quantity of the IL impregnated onto the SiO_2 the adsorption capacity increase until it reach a constant value.

This means that the optimum ratio IL: SiO_2 is 0.1:1, when the porous network of the SiO_2 is densely filled with the IL leading to an efficiently binding of the Cs^+ ions. Therefore for the further studied 1 g of SiO_2 was impregnated with 0.1 g of Cyphos IL-101.
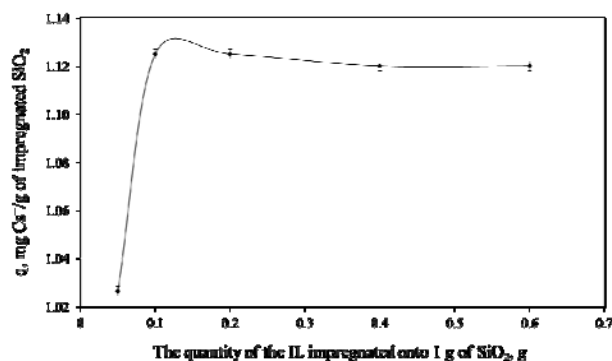

Fig. 1. Effect of the quantity of the IL impregnated onto SiO_2 on the adsorption capacity

The impregnation of the SiO_2 support was evidenced by the EDX analysis. The diagram is presented in Fig. 2 and can be observed the characteristic peaks of P and Cl which are component of the ionic liquid.
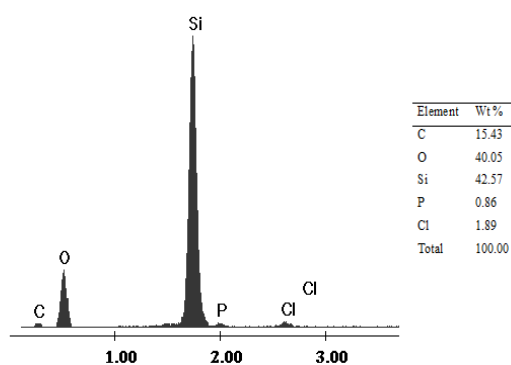

Element	Wt%
C	15.43
O	40.05
Si	42.57
P	0.86
Cl	1.89
Total	100.00

Fig. 2. EDX diagram and chemical composition of the SiO_2 impregnated with IL

The SEM images of the silica impregnated support before and after impregnation are presented in Fig. 3. It can be observed that the particles of Cyphos IL-101 are bounded on the smooth surface of the silica supports, therefore the morphology of the solid supports surface, after impregnation become patchy.
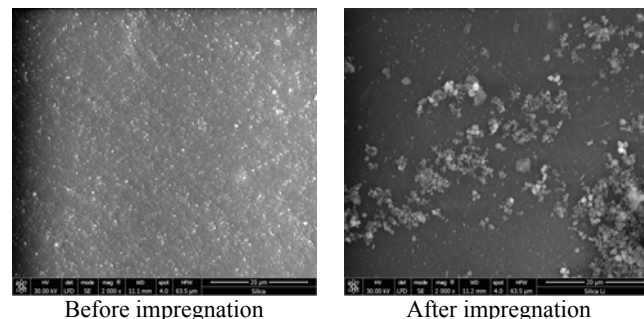

Before impregnation   After impregnation

Fig. 3. SEM-images of the Silica support

The impregnation of the Silica with Cyphos IL-101 was also evidenced by the Fourier transform infrared spectroscopy FTIR (Fig. 4.). The impregnation is confirmed by the assignments of the IR vibration which are characteristic for the IL (3455 (s,b) cm^{-1} - νOH bonded; 2957 (w) - ν_a (CH_3); 2933 (w) - ν_a (CH_2); 2858 (w) - ν_s (CH_3); 1395 (m) - P-C stretching ν_s (CH_2); 1100 (vs) - P-C stretching ν_a (C-C); 1050 (vs) - P-C stretching ν (M-O); 800 (w) - P-C deformation (out of the plane)) (Cholico-Gonzales et al., 2013; Negrea et al., 2013; Plinio, 2003).

3.2. Effect of pH on Cs⁺ adsorption process

In order to investigate dependence of the maximum adsorption capacity on pH, experiments were conducted in the pH range 2 to 12 and the results are depicted in Fig. 5. The adsorption capacity of the impregnated SiO_2 increases gradually with an increase in pH value, until it reaches a constant value.
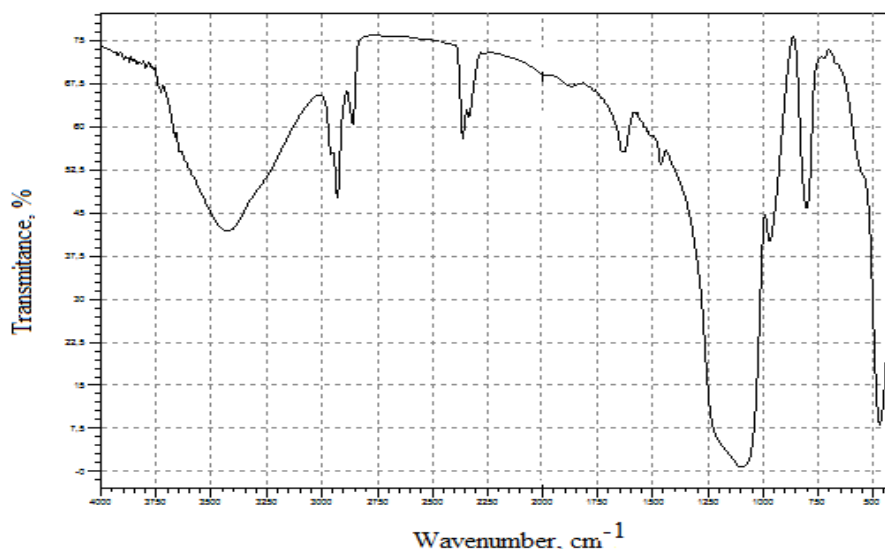

Fig. 4. FTIR spectrum of the Silica impregnated with Cyphos IL-101

2007

In the subsequent studies, experiments were performed in the solution pH of 8, because after the treatment process the waters could be directly discharged without a supplementary step of pH adjustment.
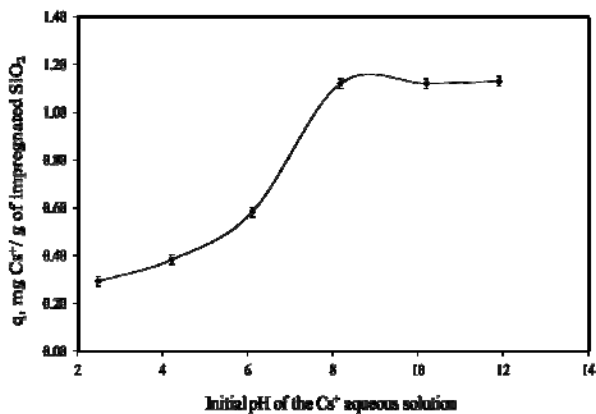

Fig. 5. Effect of pH on the adsorption capacity of the impregnated SiO_2 with IL

3.3. Effect of the S:L ratio on Cs^+ adsorption process

The experimental data regarding the dependence of the adsorption capacity of the impregnated SiO_2 in the removal process of Cs^+ from aqueous solutions versus the S:L ratio, are presented in Fig. 6.
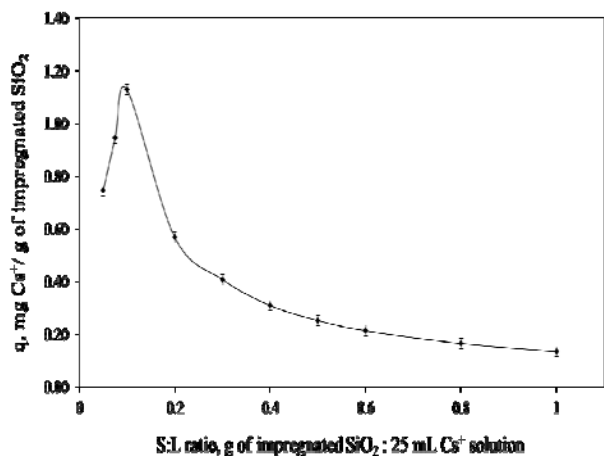

Fig. 6. Effect of S:L ratio on the adsorption capacity of the impregnated SiO_2 with IL

From Fig. 6 it can be observed that the increasing of the amount of the impregnated SiO_2 used in the removal process of Cs^+ from aqueous solutions lead to the increasing of the Cs^+ uptake in the first step and then lead to a decreasing, because the adsorption capacity is related to the amount of the adsorbent used in the removal process.

The optimum S:L ratio used for the further experiments is 0.1 g of impregnated SiO_2 for 25 mL of Cs^+ aqueous solutions.

3.4. Kinetic studies

Preliminary investigations regarding the effect of stirring time on the adsorption capacity of the impregnated SiO_2 (Fig. 7) indicate that the process is quite rapid and the equilibrium between the adsorbent and adsorbate is achieved in 120 min. The data showed that the amount of the sorbed Cs^+ increases with the increase in temperature. This indicates an endothermic nature of the process and the required time to reach equilibrium remained practically unaffected.
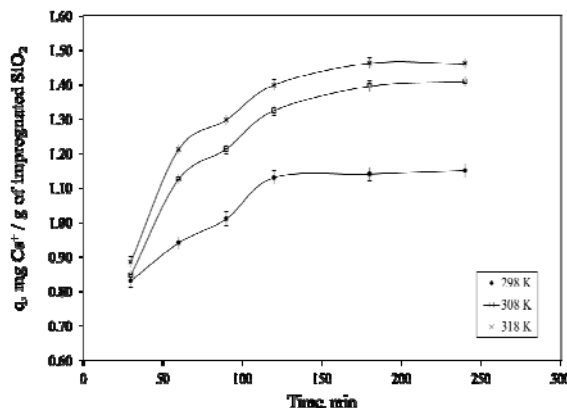

Fig. 7. Effect of stirring time on the adsorption capacity of the impregnated SiO_2 with IL

To describe the changes in the sorption of metal ions with time, pseudo-first-order, pseudo-second-order and intraparticle diffusion models were tested (Abd El-Latif and Elkady, 2011; Mahmoud, 2011; Nilchi et al., 2011; Xu et al, 2010; Volchek et. al., 2011). The pseudo-first-order kinetic model is defined by Eq. (2).

$$ln(q_e - q_t) = ln\, q_t - k_1 t \qquad (2)$$

where q_e and q_t are the amount of the Cs^+ adsorbed onto the impregnated SiO_2 with IL (mg/g) at equilibrium and at time t, respectively. t is the contact time (min), k_1 is the pseudo-first-order adsorption rate constant (min^{-1}).

The values of the adsorption rate constant (k_1) were determined from the $ln(q_e-q_t)$ in terms of t (Fig. 8). The linear form of the pseudo-second order model is defined by Eq. (3).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where: q_e and q_t are the amount of the Cs^+ adsorbed onto the the impregnated SiO_2 with IL (mg/g) at equilibrium and at time t, respectively. t is the contact time (min), k_2 is the pseudo-second-order adsorption rate constant (g/mg·min). The value q_e and k_2 are determined from the slope and intercept of t/q_t versus t (Fig. 9).
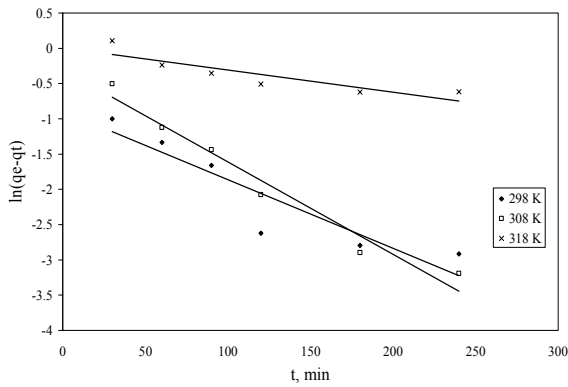
Fig. 8. Pseudo first order kinetic plots for Cs⁺ adsorption onto SiO₂ impregnated with IL

Intra-particle diffusion model: The adsorption of Cs⁺ ions onto impregnated SiO₂ may be controlled via external film diffusion at earlier stages and later by the particle diffusion. The possibility of intra-particle diffusion resistance was identified by using the following intra-particle diffusion model (Eq. 4).

$$q_t = k_{dif} t^{1/2} + C \qquad (4)$$

where: K_{dif} is the intra-particle diffusion rate constant (mg/(g·h$^{1/2}$)) and C is the intercept. The values of q_t versus $t^{1/2}$ and the rate constant K_{dif} are directly evaluated from the slope of the regression line (Fig. 10).

The values of the constants, together with the regression coefficients (R^2) obtained in all the cases are summarized in Table 1.
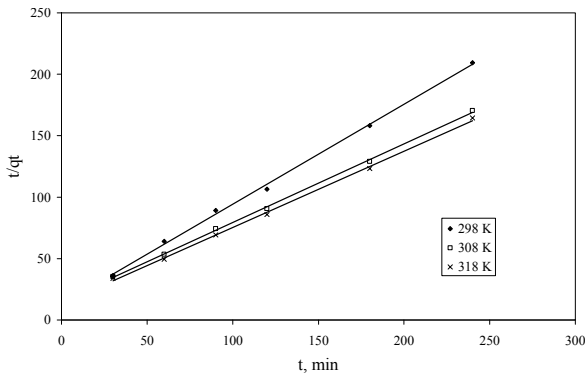

Fig. 9. Pseudo second order kinetic plots for Cs⁺ adsorption onto SiO₂ impregnated with IL

In case of the pseudo first order the correlation coefficient is lower and a considerable deviation between the experimental and calculated q_e values occurred (Table 1), this confirm that it is not

appropriate to use the pseudo-first order kinetic model to predict the sorption kinetics of the Cs⁺ ions adsorption onto the impregnated SiO₂ with IL.

The kinetic plot of the pseudo second order model presented in Fig. 9 is linear, and the correlation coefficient (R^2), suggests a strong correlation between the parameters and also explain that the Cs⁺ ions adsorption onto the impregnated SiO₂ follows pseudo-second order kinetic model and the adsorption process has the profile of chemisorption.
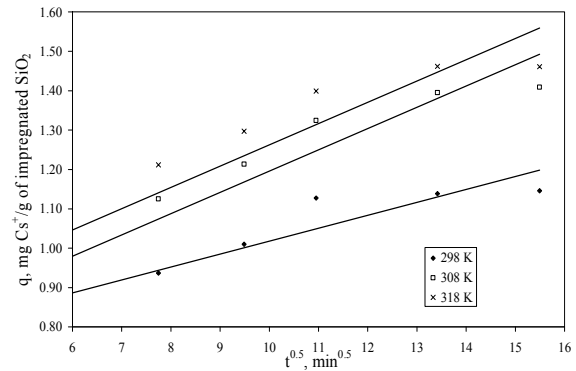

Fig. 10. The intra-particle diffusion kinetic plot for adsorption of Cs⁺ onto impregnated SiO₂ with IL

The rate constant of adsorption (k_2) increased as the temperature increased. This was due to the fact that a higher temperature resulted in a faster diffusion of cesium ions towards the surface and inside the pore of the impregnated SiO₂ (Volchek et al., 2011). From Table 1, it can be shown that the theoretically predicted equilibrium adsorption capacity was close to the experimentally determined value. As seen in Table 1, which shows the K_{dif} values and coefficient constant, the intra-particle diffusion model cannot be the dominating mechanism for the adsorption of the Cs⁺ from aqueous solution by the impregnated SiO₂ with IL.

The values of the rate constants from the pseudo-second-order model can be used to calculate the activation energy of the adsorption process by Arhenius Eq. (5).

$$ln(k_2) = ln(A) - \frac{E}{RT} \qquad (5)$$

where k_2 is the pseudo-second-order rate constant of sorption (g/(min·mg)), A the Arrhenius constant which is a temperature independent factor (min·g/mg), E is the activation energy of sorption (kJ/mol) and T is the absolute temperature (K).

Table 1. Kinetic parameters for Cs⁺ ions adsorption onto imregnated SiO₂ with IL

Temp., K	q_{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion model		
		k_1 (min^{-1})	q_{calc} (mg/g)	R^2	k_2 (g/(mg·h))	q_{calc} (mg/g)	R^2	K_{dif} (mg/(g·h$^{1/2}$))	C	R^2
298	1.2	0.0097	0.412	0.8523	0.0266	1.23	0.9982	0.0328	0.6899	0.8744
308	1.45	0.0135	0.795	0.9548	0.0293	1.56	0.9993	0.054	0.6553	0.8726
318	2	0.0031	1.006	0.7759	0.0506	1.61	0.9986	0.054	0.7223	0.8181

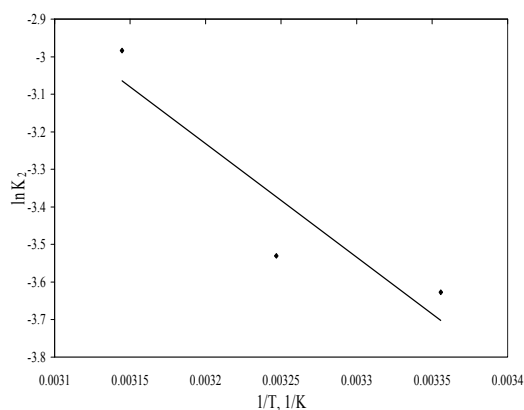The activation energy was calculated from the slope of the plots lnk_2 versus 1/T (Fig. 11).

Fig. 11. Arhenius plot of Cs^+ adsorption onto impregnated SiO_2 with IL

In this study the activation energy values were found to be 25.13 (kJ/mol). The magnitude of activation energy can give information on whether the adsorption process is physical or chemical. The activation energy of physisorption is normally not more than 4.2 (kJ/mol) (Ramesh et al., 2007). Hence, the values of activation energy found in this study suggest that the adsorption of Cs^+ onto the studied materials is a chemical adsorption.

3.5. Thermodynamic studies

In general, the experimental conditions such as metal ion concentration and temperature have strong effects on the equilibrium distribution coefficient value (K_d); so it can be used as a comparative measure to the efficiency of various adsorbents. Equilibrium distribution coefficient value (K_d) is the amount of removed Cs^+ ions per gram of adsorbent divided by their concentration in the liquid phase (Eq. 6).

$$K_d = \frac{q_e}{C_e} \qquad (6)$$

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Thermodynamic parameters such as Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) can be estimated using equilibrium constant changing with temperature. The Gibbs free energy change of the adsorption reaction is given by Eq. (7) (Abd El-Rahman et al., 2006; Ramesh et al., 2007).

$$\Delta G^o = -RT \ln K_d \qquad (7)$$

where R is universal gas constant (8.314 J·mol/K), T is absolute temperature (K) and K_d is the distribution coefficient.

Relation between $\Delta G°$, $\Delta H°$ and $\Delta S°$ can be expressed by Eqs. (8, 9):

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (9)$$

where values of $\Delta H°$ and $\Delta S°$ can be determined from the slope and intercept of the plot between lnK_d versus 1/T.

The thermodynamic parameters were determined from the slope and intercept of the plot of lnK_d versus 1/T (Fig. 12). The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are given in Table 2.

The positive values of $\Delta G°$ suggests the existence of an energy barrier and that the reaction is non-spontaneous process. The positive values of $\Delta H°$ indicate the endothermic nature for the diffusion process. The decreasing values of $\Delta G°$ imply a greater driving force to the adsorption process. The values of $\Delta H°$ are high enough to ensure the strong interaction between the Cs^+ and the impregnated SiO_2 with IL. The positive values of $\Delta S°$ indicate an increased randomness at the solid-solution interface during the adsorption process. (Abd El-Rahman et al., 2006; Ramesh et al., 2007) The increasing of the adsorption capacities of the impregnated SiO_2 with Cyphos IL-101 at higher temperatures may be due to the pore size enlargement and/or activation of the adsorbent surface.
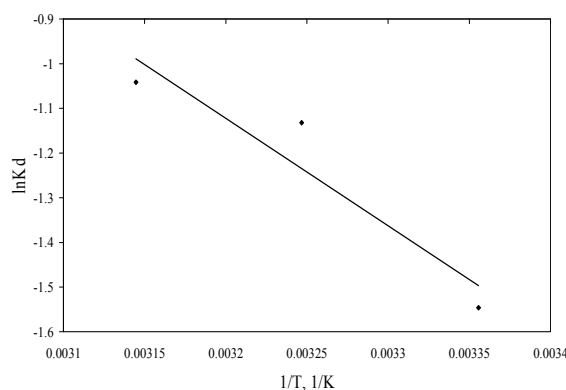

Fig. 12. Effect of temperature on the adsorption of Cs^+ onto impregnated SiO_2 with IL

Table 2. Thermodynamic parameters for Cs^+ adsorption onto impregnated SiO_2 with IL

$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol·K)	ΔG^o (kJ/mol)			R^2
		298 (K)	303(K)	308 (K)	
20.014	54.7	3.7134	3.1664	2.6194	0.9963

3.6. Equilibrium studies

To optimize the design of an adsorption system for the removal of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. In this concern various isotherm equations have been used to describe the equilibrium nature of adsorption processes in heterogeneous systems. The adsorption isotherm of Cs^+ removal by impregnated SiO_2 is presented in Fig. 13.

The adsorption capacity increased with the increasing equilibrium concentration of Cs^+ and approached a constant value at the highest equilibrium concentration. The adsorption equilibrium data were correlated with the well-known Freundlich and Langmuir isotherms (Gallardo et al., 2008; Negrea et al., 2013; Nilchi et al., 2011).

The Freundlich isotherm in its linear form can be expressed by Eq. (10) (Freundlich, 1907).

$$ln\, q_e = ln\, K_F + \frac{1}{n} ln\, C_e \qquad (10)$$

where q_e is the amount of Cs^+ adsorbed per gram of adsorbent, i.e., metal uptake (mg/g), and C_e is the equilibrium concentration of adsorbate in the bulk solution after adsorption (mg/L). K and $1/n$ are characteristic constants that can be related to the relative adsorption capacity of the adsorbent mg/g) and the intensity of the adsorption, respectively.

The logarithmic plot of q_e against C_e should result in a straight line that allows computations of $1/n$ and K_F from the slope and intercept, respectively (Fig. 14).
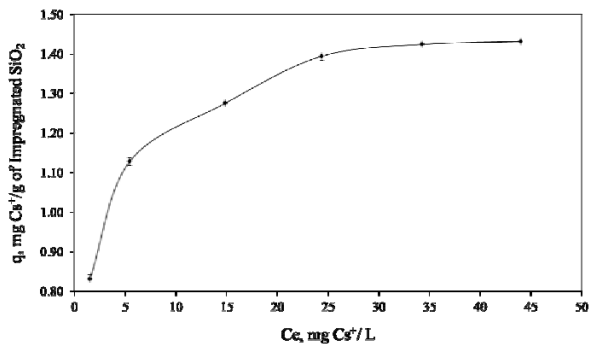

Fig. 13. Adsorption isotherm of Cs^+ onto impregnated SiO_2

The linear form of the Langmuir isotherm can be expressed by Eq. 11) (Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \qquad (11)$$

where q_m is the measure of the monolayer sorption capacity (mg/g) and K_L denotes the Langmuir isotherm constant related to the affinity between adsorbent and the adsorbate (L/mg).

The rest of the terms have their usual meanings as described above. The values of q_m and

K_L can be determined by plotting C_e/q_e versus C_e (Fig. 15).

The calculated parameters, as well as the correlation coefficients (R^2) for Cs^+ removal through adsorption onto impregnated SiO_2 with the studied IL are presented in Table 3.

Table 3. Parameters of Freundlich and Langmuir isotherms for Cs^+ ions adsorption onto imoregnated SiO_2

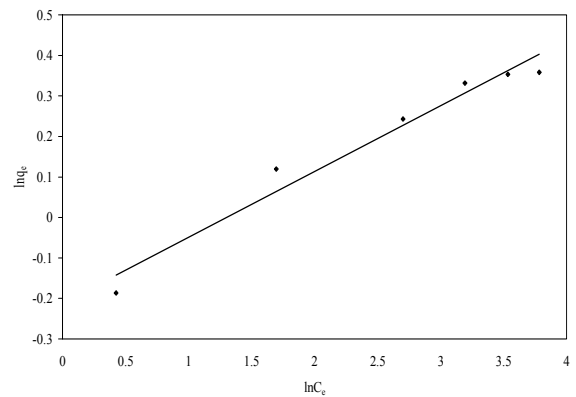| $q_{m, exp}$ (mg/g)	Freundlich isotherm			Langmuir isotherm		
	K_F (mg/g)	$1/n$	R^2	K_L (L/mg)	$q_{m, calc}$ (mg/g)	R^2
1.43	0.81	0.1623	0.9641	0.597	1.48	0.9994

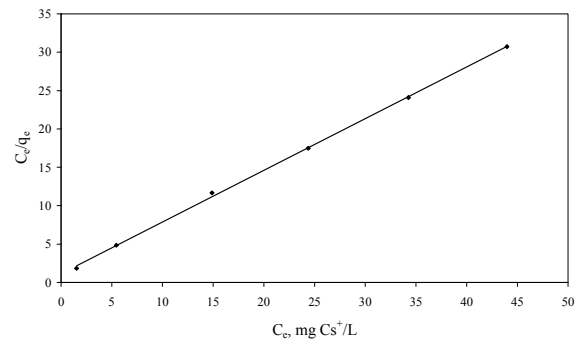**Fig. 14.** Freundlich plot for Cs^+ adsorption onto impregnated SiO_2 with IL

Fig. 15. Langmuir plot for Cs^+ adsorption onto impregnated SiO_2 with IL

The Freundlich plots (Fig. 14) have a lower regression coefficient suggesting a restriction on the use of Freundlich isotherm. The constants K_F and $1/n$ computed from the linear plot are presented in Table 3. The constant K_F can be defined as an adsorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration. The slope $1/n$ is a measure of the adsorption intensity or surface heterogeneity. For $1/n = 1$, the partition between the two phases is independent on the concentration. The situation $1/n < 1$ is the most common and correspond to a normal L-type Langmuir isotherm, whilst $1/n > 1$ is indicative of a cooperative adsorption which involves strong interactions between the molecules of adsorbate. Values of $1/n < 1$ show favourable adsorption of Cs^+ ions onto the impregnated SiO_2. The Langmuir model

effectively describes the sorption data with correlation coefficient close to 1. Thus the isotherm follows the sorption process in the entire concentration range studied. Moreover the maximum adsorption capacity obtained from the Langmuir plot is very close to that experimentally obtained.

The dimensionless constant, called separation factor (R_L) can be used to describe the essential characteristics of a Langmuir isotherm (Eq. 12).

$$R_L = \frac{1}{1 + K_L \cdot C_0} \qquad (12)$$

where the terms have their meanings as stated above.

In fact, the separation factor is a measure of the adsorbent capacity used. Its value decreases with increasing "K_L" as well as initial concentration. R_L values can be related to the equilibrium isotherm as follows: unfavourable, $R_L > 1$; linear, $R_L = 1$; favourable $0 < R_L < 1$; and irreversible, $R_L = 0$ (Gallardo et al., 2008; Nilchi et al., 2011)

The values were calculated for the entire concentration range studied and the results are found to lie in between 0 and 1, in all the cases, demonstrating a favorable sorption process.

The adsorption capacities (q_m) of different adsorbent for adsorption of Cs^+ ions are compared in table 4. It may be seen that the impregnated SiO_2 with Cyphos IL 101 exhibits a good adsorption capacity in the removal process of Cs^+ from aqueous solutions, compared with other studied materials.

Table 4. Adsorption capacity of various adsorbents in the removal process of Cs^+ from aqueous solutions

Adsorbent	*q_m, mg/g*	*Reference*
Nano-zirconium vanadate	9.1	Abd El-Latif and Elkady, 2011
Resorcinol-formaldehyde RF	5.56	Hassan and Adu-Wusu, 2005
Ceiling tiles	0.2128	Miah et al., 2010
Vermiculite	0.646	Haladi et al., 2009
SiO_2 impregnated with Cyphos IL-101	1.48	Present work

4. Conclusions

In this work the adsorption properties of Silica impregnated with Cyphos Il-101, have been studied in the removal process of Cs^+ from aqueous solutions. The experiments showed that adsorption depend by the pH, the maximum adsorption capacity being achieved at an initial pH of solution 8.

The kinetic studies revealed that the adsorption process of Cs^+ onto impregnated SiO_2 with the studied IL followed the pseudo-second order kinetic model, suggesting the chemisorptions profile of the adsorption process.

The equilibrium data were fitted with the Langmuir and Freundlich isotherms, the best correlation being obtained by the Langmuir one. The

maximum sorption capacity obtained by the impregnated SiO_2 with Cyphos IL-101 is 1.48 mg Cs^+ / g of adsorbent.

The proposed method for Cs^+ removal from aqueous solutions, by using as adsorbent the impregnated SiO_2 with Cyphos IL-101, is an efficient one because combine the advantages of the ionic liquids with those of the solid support. In this way for the removal of Cs^+ from aqueous solution is used a smaller amount of the ionic liquid and there is no risk of loss of the extractant in the aqueous phase.

The entire results showed that the obtained new impregnated material represents an efficient adsorbent in the removal process of Cs^+ ions from aqueous solutions compared with other materials studied in the literature. The experimental results can be easily used to scale up the studies from the laboratory scale.

References

Abd El-Latif M.M., Elkady M.M., (2011), Kinetics study and thermodynamic behaviour for removing cesium, cobalt and nickel ions from aqueous solution using nano-zirconiuim vanadate ion exchange, *Desalination,* **271**, 41-54.

Abd El-Rahman K.M., El-Sourougy M.R., Abdel-Monem N.M, Ismail I.M., (2006), Modeling the sorption kinetics of cesium and strontium ions on Zeolite A, *Journal of Nuclear Radiochemical Sciences,* **7**, 21-27.

Abdel Rahman R.O., Ibrahium H.A., Hung Y.T., (2011), Liquid radioactive wastes treatment, *Water,* **3**, 551-565.

Cholico-Gonzalez D., Avila-Rodriguez M., Cote G., Chagnes A., (2013), Chemical properties of trihexyl(tetradecyl)phosphonium chloride and bis(2,4,4-trimethylpentyl)phosphinic acid mixtures: Interaction study by FT-IR and NMR spectroscopies, *Journal of Molecular Liquids*, **187**, 165-170.

El-Kamash A.M., (2008), Evaluation of zeolite A for the sorptive removal of Cs^+ and Sr^{2+} ions from aqueous solutions using batch and fixed bed columns operations, *Journal of Hazardous Materials,* **151**, 432-445.

Freundlich H., (1907), Über die adsorption in lösungen, *Journal of Physical Chemistry,* **57**, 385-470.

Gallardo V., Navarro R., Saucedo I., Avila M., Guibal E., (2008), Zinc(II) extraction from hydrochloric acid solutions using Amberlite XAD7 impregnated with Chyphos IL101 (tetradecyl(trihexyl) phosphonium chloride), *Separation Science & Technology*, **43**, 2434-2459.

Guo L., Liu Y., Zhang C., Chen J., (2011), Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr(VI) transport, *Journal of Membrane Science*, **372**, 314 - 321.

Haladi N., Kananpanah S., Abolghasemi H., (2009), Equilibrium and thermodynamic studies of cesium adsorption on natural Vermiculite and optimization of

the operation conditions, *Iranian Journal of Chemistry and Chemical Engineering*, **28**, 29-36.

Hassan N.M., Adu-Wusu K., (2005), Cesium removal from Hanford tank waste solution using resorcinol-formaldehyde resin, *Solvent Extraction and Ion Exchange, 23*, 375-389.

Kalidhasan S., Kumar A.S.K., Rajesh V., Rajesh N., (2012), An efficient ultrasound assisted approach for the impregnation of room temperature ionic liquid onto Dowex 1x8 resin matrix and its application toward the enhanced adsorption of Cr(VI), *Journal of Hazardous Materials*, **213-214**, 249.

Langmuir I., (1918), The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal of the American 333 Chemists' Society,* **40**, 1361-1403.

Lemus J., Palomar J., Gilarranz L., Rodriquez J., (2011), Characterization of supported ionic liquid phase (SILP) materials prepared from different supports, *Adsorption*, **17**, 561-571.

Liu Y., Zhu L., Sun X., Chen J., Luo F., (2009), Silica materials doped with bifunctional ionic liquid extractants for Yttrium extraction, *Industrial & Engineering Chemistry Reearch*, **48**, 7308-7313.

Luo H., Dai S., Bonnesen P.V., (2004), Solvent extraction of Sr^{2+} and Cs$^+$ based on room-temperature ionic liquids containing monoaza-substituted crown ethers, *Analytical Chemistry, 76*, 2773-2779.

Mahmoud M.E., (2011), Surface loaded 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM$^+$Tf$_2$N$^-$] hydrophobic ionic liquid on nano-Silica sorbents for removal of lead from water samples, *Desalination, 266*, 119-127.

Miah M.Y., Volchek K., Kuang W., Tezel F.H., (2010), Kinetic and equilibrium studies of cesium adsorption on ceiling tiles from aqueous solutions, *Journal of Hazardous Materials, 183*, 712-717.

Negrea A., Ciopec M., Lupa L. Negrea P. Gabor A., (2013a), Influence of the solid support base impregnated with IL on the soprtion of various radionuclides from aqueous solutions, *AWERProcedia Advances in Applied Science*, **1**, 241-250.

Negrea A., Ciopec M., Davidescu C.M., Muntean C., Negrea P., Lupa L., (2013b), Kinetic, equilibrium and thermodynamic studies of Cesium removal from aqueous solutions using Amberjet UP1400 and Amberlite IR120 resins, *Environmental Engineering and Management Journal*, **12**, 991-998.

Nilchi A., Saberi R., Moradi M., Azizpour H., Zarghami R., (2011), Adsorption of caesium on copper hexacyanoferrate-PAN composite ion exchanger from aqueous solution, *Chemical Engineering Journal*, **172**, 572-580.

Plinio I., (2003), Infrared spectroscopy of sol-gel derived silica-based films: a spectra-microstructure overview, *Journal of Non-Crystalline Solids*, **316**, 309-319.

Ramesh A., Hasegawa H., Maki T., Ueda K., (2007), Adsorption of inorganic and organic arsenic from aqueous solution by polymeric Al/Fe modified montmorillonite, *Separation and Purification Technology*, **56**, 90-100.

Sun X.. Li Y., Chen J., Ma J., (2009), Solvent impregnated resin prepared using task-specific ionic liquids for rare earth separation, *Journal of Rare Earth, 27*, 932-936.

Volchek K., Miah M.Y., Kuang W., DeMaleki Z., Tezel F.H., (2011) Adsorption of cesium on cement mortar 370 from aqueous solutions, *Journal of Hazardous materials,* **194**, 331-337.

Xu C., Shen X., Chen Q., Gao H., (2009), Investigation on the extraction of strontium ions from aqueous phase using crown ether-ionic liquid systems, *Science in China Series B: Chemistry,* **52**, 1858-1864.

Xu C., Yuan L., Shen X., Zhai M., (2010), Efficient removal of cesium ions from aqueous solution using a calyx crown ether in ionic liquids: mechanism and radiation effect, *Dalton Transactions*, **39**, 3897-3902.

Zhang A., Hu Q., (2010), Adsorption of cesium and some typical coexistent elements onto a modified macroporous silica-based supramolecular recognition material, *Chemical Engineering Journal, 159*, 58-66.

Zhao H., Xia S., Ma P., (2005), Review. Use of ionic liquids as "green" solvents for extractions, *Journal of Chemical Technology and Biotechnology*, **80**, 1089-1096.

Zhu L., Guo L., Zhang Z., Chen J., Zhang S., (2012), The preparation of supported ionic liquids (SILs) and their application in rare metals separation, *Science in China, Chemistry*, **55**, 1479-1486.