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Impregnation of task-specific ionic liquid into a solid support for removal of neodymium and gadolinium ions from aqueous solution

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ABSTRACT

Impregnation of trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, as an ionic liquid, into silica was carried out for removal of neodymium and gadolinium ions from aqueous solution. Silica and the impregnated silica (Cyphos@silica) were characterized using FT-IR, SEM, XRD and TGA. Comparative sorption behavior of silica and Cyphos@silica for sorption of neodymium and gadolinium ions was investigated. The experimental outcome revealed that the impregnation process enhanced the sorption behavior of silica, from 18 to 67% for neodymium ion and from 20 to 89.45% for gadolinium ion. From the kinetic studies, the sorption could be described well by pseudo-second-order model. Langmuir and Freundlich isotherms were performed to determine the best fit equation for the sorption process; the results indicated that the latter surpasses the former. Comparison of the sorption capacity of Cyphos@silica with other materials reported in the literature shows that the former has a comparatively high sorption capacity. Desorption percent of gadolinium and neodymium ions from Cyphos@silica using 1.0 mol/L of HNO_3 was found to be 97.74 and 86.33%, respectively. The desorption studies revealed the reusability of Cyphos@silica for further sorption.

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1. Introduction

Ionic liquids are ionic molecules that contain both organic cations and inorganic or organic anions [1]. They often exist in the liquid state at room temperature [2]. The ionic liquids have become extremely popular compounds in recent separation research due to their unique physicochemical properties. Compared with conventional organic compounds, ionic liquids are characterized by low volatility, low toxicity, high thermal and chemical stability, high polarity, high viscosity, high hydrophobicity and high surface activity due to the presence of both cation and anion species in the same molecule [3,4]. They can be modulated to suit the reaction conditions; therefore, earning the name task-specific ionic liquids [5]. The non-inflammability and non-volatility of ionic liquids provide environment-friendly advantages for using them instead of volatile organic compounds in solvent extraction.

Ionic liquids are used in several applications in different fields, such as waste recycling, nuclear fuel reprocessing, metal extraction, batteries, electrochemical capacitors and electrodeposition of metals [6]. Currently, some types of ionic liquids have been utilized in sorption of pollutants from water and have presented good performances [7,8]. trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, commercially known as Cyphos IL-104, is one of the phosphonium ionic liquids and classified as hydrophobic and highly viscous ionic liquid [9]. It has been used in various applications; it is utilized as carriers for extracting some metal ions such as; Zn^{2+}, Fe^{3+}, Cu^{2+} and Pd^{2+} from chloride media [10–12].

Even though ionic liquids are considered as efficient liquid extractants, several drawbacks such as large consumption, difficult recycling and tedious separation procedures have restricted their applications. To overcome these problems, impregnation of ionic liquids onto solid materials were carried out. Cyphos IL-104 was impregnated onto solid supports like Amberlite XAD-7 and then used for removal of Cr(VI) from potassium chromate aqueous solution [13]. Cyphos IL-104 was used in conjunction with imidazolium ionic liquids on a silica template for Y^{3+} removal and separation of lanthanides, such as Ho^{3+}, Er^{3+} Dy^{3+}, and Yb^{3+} [14].

Separation and recovery of lanthanide elements from radioactive and industrial wastes are important both environmentally and economically. Radioisotope of neodymium is used as burn-up monitors to evaluate the performance of nuclear fuel [15]. Gadolinium oxide is used in the nuclear power as shielding and fluxing devices; it can be mixed directly with uranium to achieve a uniform neutron flux [16]. Further, the lanthanide elements are increasingly used in many electronic devices.

Toxicological investigations revealed that the lanthanides may have significant adverse effects on the living organisms [17]. Accumulation of

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lanthanides in soil, water and the food chain needs to be considered in environmental studies.

Several methods are available for sorption of lanthanide elements, including adsorption, ion exchange, chemical precipitation and evaporation. Impregnation technique is a type of ion selective exchanger based on the solvent extraction. Impregnation process has some potential advantage over solvent extraction such as minimal organic solvent utilization, less waste accumulation, simple operation and low capital cost. The concept of solvent impregnated resin is based on incorporation of extractant into a porous material matrix either by a physical impregnation technique, or introduction of extractant during synthesis of porous matrix. Some considerations must be taken in impregnation process such as; the solubility of extractant in water should be low to prevent the loss of impregnated extractant during the extraction process, the extractant should have an appropriate viscosity so that the extractant can easily penetrate into the pores of the matrix, and the impregnation process should not damage the chemical and physical structure of the support material. This work focused on removal of neodymium (light lanthanide element) and gadolinium (heavy lanthanide element) ions from aqueous solution using solvent impregnated resin, Cyphos IL-104 impregnated on silica.

2. Experimental

2.1. Materials

Phosphonium ionic liquid, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate, commercially known as Cyphos IL-104, was purchased from Fluka. Gadolinium and neodymium nitrates ($Nd(NO_3)_3.6H_2O$ and $Gd(NO_3)_3.6H_2O$) were obtained from Merck. Silica gel, grade 62, (60–200) mesh, 150 A°, was obtained from Sigma-Aldrich. NH_4OH and HCl were purchased from Winlab Company. All chemicals and reagents were of analytical grade and were used without further purification.

2.2. Impregnation of Cyphos IL-104 onto silica

Cyphos IL-104 was impregnated on silica in presence of ethanol as follow; 2 mL of Cyphos IL-104 was added to 4 g of silica to obtain 1:2 ratio, 50% loading percent, then few drops of ethanol were added to the mixture, stirring overnight to obtain a homogeneous mixture, the product, Cyphos@silica, was filtered and washed with distilled water to ensure complete elimination of solvent, then dried in an air oven at 333 ± 1 K overnight.

2.3. Evidences of the impregnation process

The impregnation of Cyphos IL-104 on silica can be evidenced by two proofs; (1) silica was impregnated by different loading percent of Cyphos IL-104, and then weighed before and after the impregnation process. The experimental data illustrated that the weight of impregnated silica increased by increasing the loading percent. These results prove that Cyphos IL-104 was impregnated into silica. (2) Another evidence for the impregnation process is illustrated by testing silica, without extractant, for sorption of neodymium and gadolinium ions; the percent uptake was determined and found to be only 18–20%. While after the impregnation process, the percent uptake increased to be >67% for the two ions. This evidence also revealed that the impregnation process is successfully done.

2.4. Loss of the impregnated extractant

Cyphos IL-104 may be released into the liquid phase during the sorption process due to the mechanical force and the dissolution effect. Cyphos@silica was subjected to further washing by water to determine the loss of impregnated extractant. 1 g of Cyphos@silica was consecutively rinsed with 20 mL of water in every washing step; the results revealed that after several times of rinsing, no significant loss of the impregnated Cyphos IL-104 was observed. This is due to the low solubility of Cyphos IL-104 in water.

2.5. Characterization of Cyphos@silica

Silica was characterized before and after the impregnation process using different analytical techniques such as; FT-IR, SEM, XRD and TGA.

IR spectra of the samples were recorded on a Model 2000 FT-IR, Perkin Elmer Co., USA. The sample was thoroughly mixed with KBr; then the mixture was ground and pressed with a hydraulic press at about 5 tons to obtain a disc of standard diameter. The spectrum was measured and recorded at a wavelength range of 400–4000 cm^{-1}.

The morphology of silica, Cyphos@silica and Cyphos@silica-Ln was investigated using Scanning Electron Microscopy, SEM, Philips XL 30 model, Netherlands. The sample was washed, dried and mounting on support.

X-ray diffraction spectra of silica before and after impregnation were made using X-ray powder diffractometer (Philips Analytical PW-1710) equipped with Cu Kα radiation at a scanning speed of 2°/min from 10° to 90° operated at voltage 40 kV and applied potential current 30 mA.

A thermogravimetric analysis of Cyphos@silica was carried out using a Shimadzu TGA thermal analyzer of type DTA-TGA-50, Japan, at a heating rate of 20 °C/min, using 5–10 mg of sample. The experiments were performed under a 100 mL/min nitrogen flow.

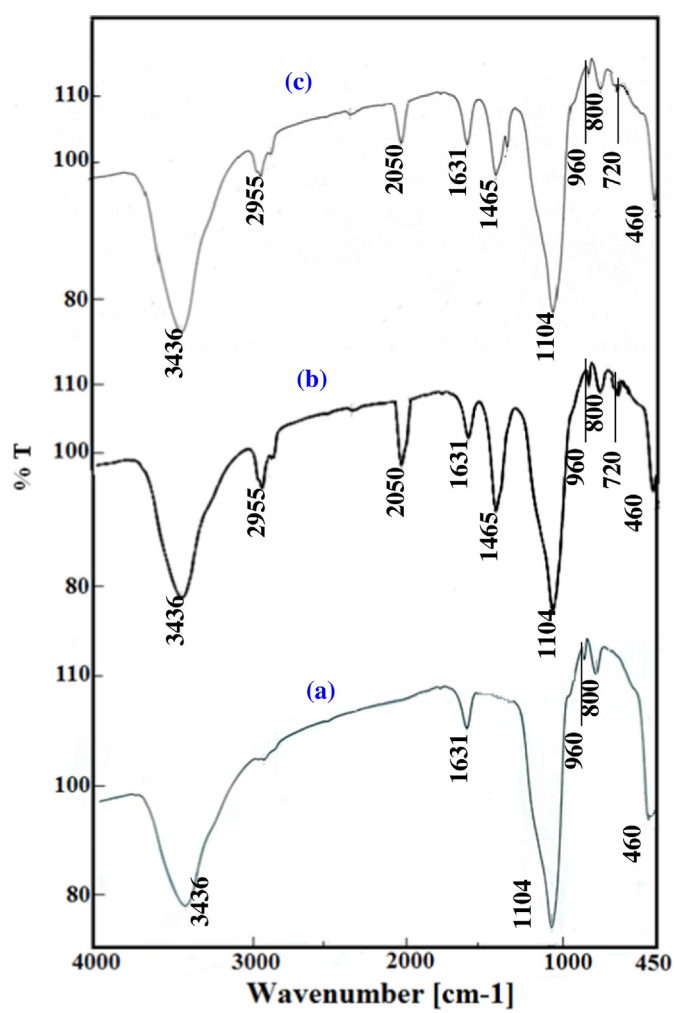


Fig. 1. FT-IR spectra of (a) silica (b) Cyphos@silica and (c) Cyphos@silica-Ln.

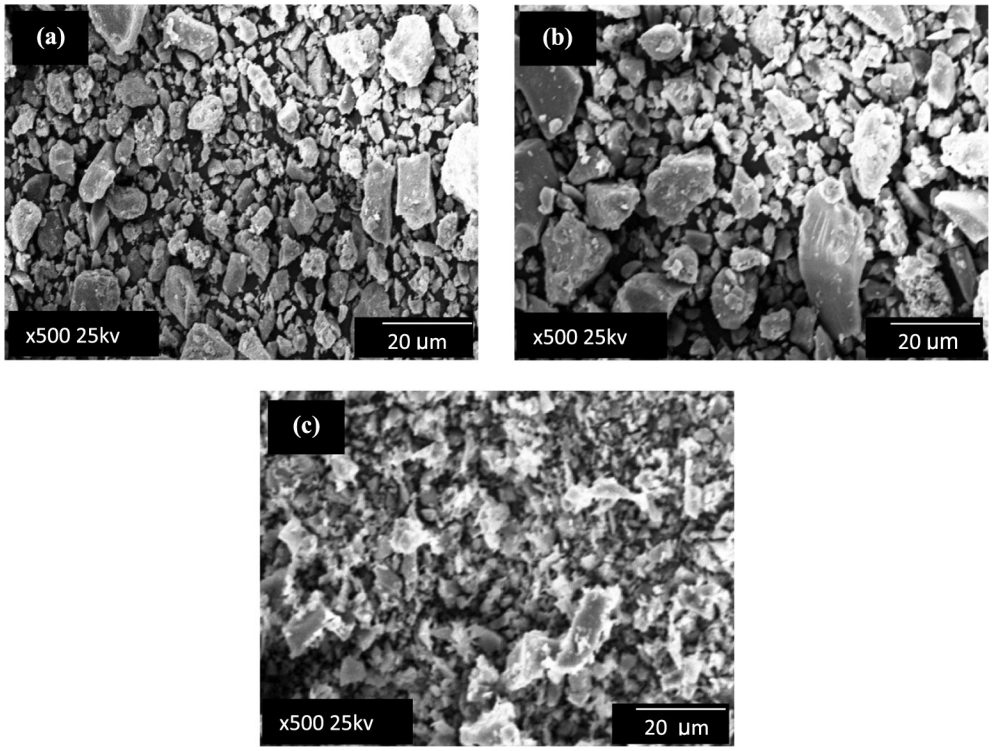


Fig. 2. SEM images of (a) silica (b) Cyphos@silica and (c) Cyphos@silica-Ln.

2.6. Sorption investigations

Sorption tests of neodymium and gadolinium ions by Cyphos@silica were carried out in the batch system. The batch sorption experiments were conducted to obtain the data for estimating the kinetics, equilibrium and thermodynamic parameters.

2.6.1. Effect of pH

The effect of initial pH on the sorption of neodymium and gadolinium ions with an initial concentration of 200 mg/L was studied at pH range 2–6. The batch experiments were conducted in 50 mL glass bottles containing 0.1 g of Cyphos@silica and 10 mL of neodymium and/or gadolinium ion solutions. The test bottles were shaken overnight at a speed of 250 rpm and room temperature. The liquid and the solid phase were centrifuged at 6000 rpm, then the concentration of ions in the aqueous phase was determined using Shimadzu UV–visible spectrophotometer model UV-160 A, Japan, with a photometric accuracy of ±0.008 Abs at 1.0 Abs, the determination process was carried out at wave length of 650 nm with a wavelength accuracy of ±0.5 nm and arsenazo (III) was used as a reagent. The percent uptake of the ions by Cyphos@silica and the distribution coefficient, K_d, of the metal ions between the aqueous and the solid phases can be calculated from the following equations.

$$\%\text{Uptake} = \frac{C_o - C_e}{C_o} x100 \quad (1)$$

$$K_d = \frac{C_o\text{-}C_e}{C_e} x \frac{V}{m} \quad (2)$$

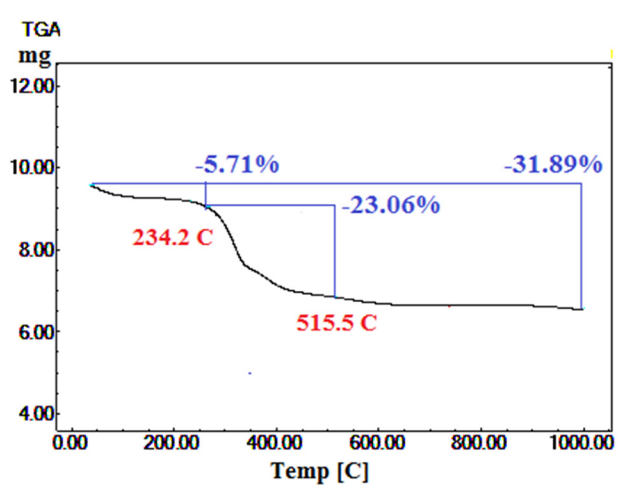


Fig. 3. TGA of Cyphos@silica.

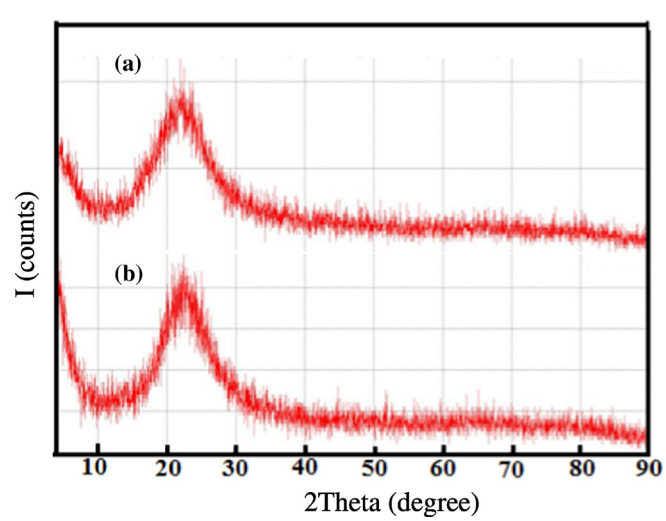


Fig. 4. XRD pattern for (a) silica and (b) Cyphos@silica.

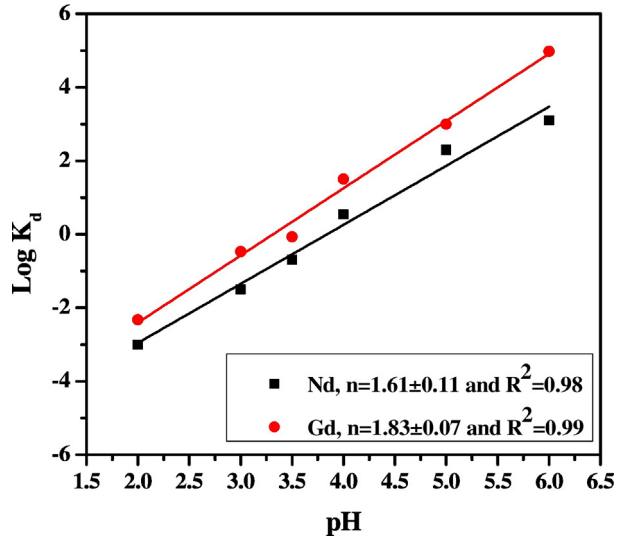


Fig. 5. Plot of log K_d against pH for sorption of neodymium and gadolinium ions onto Cyphos@silica.

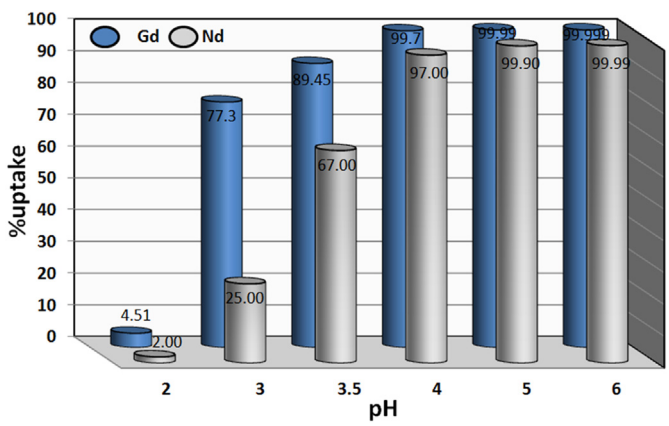


Fig. 6. Effect of pH on sorption of neodymium and gadolinium ions onto Cyphos@silica.

where C_o and C_e are the initial and equilibrium concentrations of the tested ions, mg/L, respectively. K_d is the distribution coefficient, mL/g, V is the volume of sample, in mL, and m is the weight (g) of sorbent.

The charge of sorbed metal ions can be determined from the following equation [18].

$$\text{Log } K_d = \text{Log } K_{ex} \left[\text{R-H}^+\right]^n + n\ \text{pH} \tag{3}$$

where K_{ex} is the equilibrium constant, R-H^+ refers to Cyphos@silica and n is an integer number refers to the charge of the sorbed ion.

2.6.2. Effect of contact time and temperature

A batch technique was followed to determine the amount sorbed of metal ions at different times and temperatures; 0.1 g of Cyphos@silica was shaken with 10 mL of 200 mg/L of Nd^{3+} and/or Gd^{3+} ions at different temperatures (298, 303, 313 and 323 K). The pH was maintained at the optimum value as indicated above. After an overnight standing, the mixtures were centrifuged and the amount of metal ions sorbed was determined as the following.

$$q_t = (C_o - C_t) x \frac{V}{m} \tag{4}$$

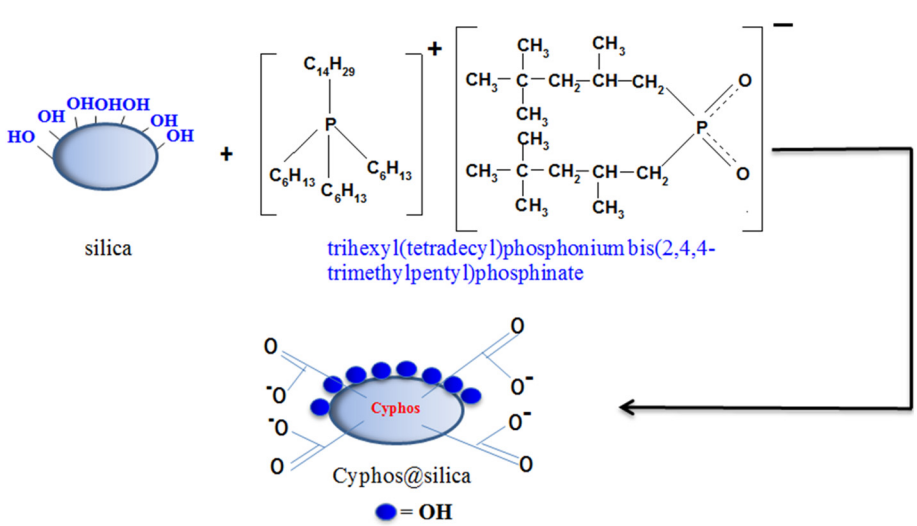
where q_t is the quantity sorbed of metal ion at time t, mg/g, C_t is the concentration of metal ions at time t, mg/L.

2.6.3. Effect of metal ion concentration at different temperatures

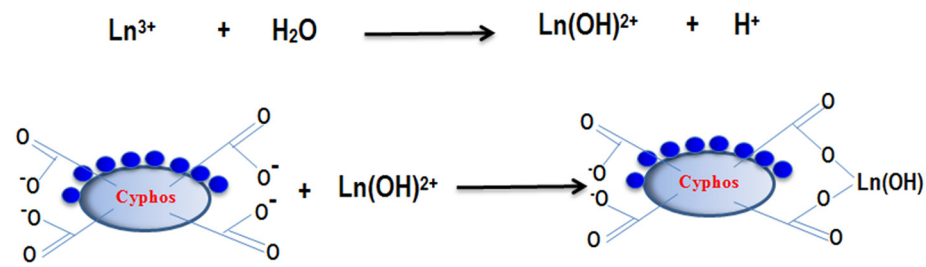
Effect of metal ion concentration on the sorption process was investigated by transferring 0.1 g of Cyphos@silica into a series of 50 mL glass bottles containing 10 mL of different concentrations of the metal ions (in the range of 50–200 mg/L) adjusted to the optimum pH value and different temperatures (278–323 K). The mixtures were shaken on a thermostatic shaker for the equilibrium time. The amount of metal ions sorbed at equilibrium, q_e, can be calculated from Eq. (4) by using C_e instead of C_t.

2.7. Desorption investigations

Desorption of neodymium and gadolinium ions from Cyphos@silica was studied by a batch system at room temperature using different molarities of HNO_3, 0.2, 0.5 and 1.0 mol/L, as well as distilled water. A series of 50 mL bottles each containing 0.05 g of loaded Cyphos@silica by neodymium and/or gadolinium ions and 10 mL of distilled water was shaken for 180 min, then the two phases were separated and the concentration of neodymium and gadolinium ions was determined in the supernatant (C_a). These steps were repeated using different molarities of HNO_3 instead of the distilled water. The percent of desorption,



Scheme 1. Proposed impregnation of Cyphos IL-104 onto silica.



Scheme 2. Proposed sorption mechanism of the metal ions onto Cyphos@silica.

%D, was calculated using the following equation.

$$\%D = \frac{C_a}{C_s} x100 \quad (5)$$

where C_s is the concentration of metal ions in the solid phase, mg/L, that can be calculated from C_o - C_e, and C_a is the concentration of metal ions in the aqueous phase.

3. Results and discussion

3.1. Characterization of silica before and after impregnation

FT-IR spectra of silica, Fig. 1(a), show absorption bands of SiO_2 at 1104, 960, 800 and 460 cm^{-1} [3], the band at 1104 cm^{-1} is asymmetric Si–O–Si [19]. These characteristic bands are also observed in both the impregnated silica (Cyphos@silica) and the impregnated silica loaded with the sorbed ions (Cyphos@silica-Ln), Fig. 1(b) and 1(c), respectively. In the case of Cyphos@silica, the peaks at 720 and 1465 cm^{-1} correspond to P—C stretching, while the absorption band at 2955 cm^{-1} is characteristic to C—H stretching of CH_3 group [20]. Phosphonate stretching shows a vibrational band at 2050 cm^{-1} [21]. These results indicated that Cyphos IL-104 was successfully impregnated into silica to obtain Cyphos@silica, Fig. 1(b). The IR spectrum of Cyphos@silica after sorption of lanthanide ions, Cyphos@silica-Ln shows similar vibrational bands, Fig. 1(c), the change in the intensity or position of the peaks by the uptake of ions on the impregnated material was observed. The two bands at 3436 cm^{-1} and 1631 cm^{-1} in the three figures are due to the stretching vibration of O—H bond of the silanol group (Si–OH) which is caused by the sorbed water molecules on the surface of silica [22].

Fig. 2(a–c) illustrates the morphology of silica, Cyphos@silica and Cyphos@silica-Ln. When Cyphos IL-104 was impregnated in silica, it was not observed on the surface of silica, this revealed that Cyphos IL-104 did not coat the surface of silica, but sorbed on the inner surface (pores) of silica through coulomb interactions, Fig. 2(b), this avoided the loss of extractant from the surface of silica. The figure shows that Cyphos@silica material is quite porous, which facilitates the sorption of neodymium and gadolinium ions from aqueous solutions. Cyphos@silica is composed of particles of different sizes, the particle size of range 2–10 μm. The significant particles have a size of 2 μm. Fig. 2(c) illustrates some aggregates of silica particles after sorption of lanthanide ions.

The thermal stability of Cyphos@silica was investigated by thermogravimetric analysis, Fig. 3. The curve showed that degradation process occurred between 234.2 and 515.5 °C. There are three distinct weight loss stages; the first weight loss stage, 5.74% was associated with the water removal. The second step, 23.06%, was probably due to the thermal degradation of Cyphos IL-104 within silica matrix at 515.5 °C. The third one is 31.89%, due to thermal decomposition of the ionic liquid.

X-ray diffraction patterns of silica and Cyphos@silica are shown in Fig. 4. The broad diffraction peak at $2\theta = 23.6°$, is characteristic for silica, which is associated with amorphous silica. The absence of sharp peaks indicates that silica is predominantly an amorphous solid, as described by Velmurugan [23]. The figure illustrates that the impregnation of silica with Cyphos IL-104 has not any observed effect on the amorphous silica.

3.2. Effect of pH

The effect of pH of medium is an important factor that often affects the removal of the sorbate from the solution. In aqueous solution, the hydrolysis of trivalent lanthanide ions occurs and different species can be presented, such as Ln^{3+}, $Ln(OH)^{2+}$, $Ln(OH)_2^+$, $Ln(OH)_3$ and $Ln(OH)_4^-$ [19, 24]. Thus, as pH increases, hydrolysis precipitation most probably would start due to the formation of different hydrocomplexes in aqueous solution. According to Eq. (3), the plot of log K_d against pH gives a straight line with a slope equal to n which corresponding to the charge of sorbed metal ions, Fig. 5. The value of n was found to be 1.83 and 1.61 for gadolinium and neodymium ions, respectively; therefore, neodymium and gadolinium ions are sorbed as divalent cations, $Ln(OH)^{2+}$, the mechanism of sorption is illustrated by scheme 2. Fig. 6 shows the effect of pH on the removal of neodymium and gadolinium ions from aqueous solution using Cyphos@silica within a range of pH 2–6 at room temperature. At low pH

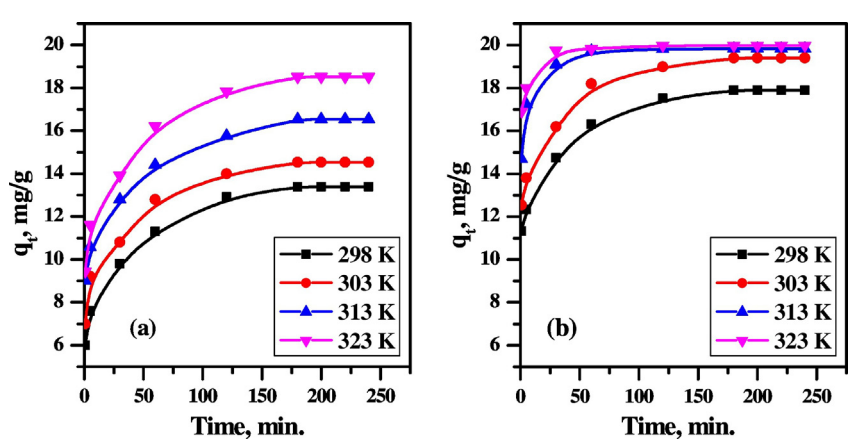


Fig. 7. Effect of contact time on sorption of (a) neodymium and (b) gadolinium ions onto Cyphos@silica at different temperatures.

Table 1
The kinetic parameters of pseudo-first-order model for sorption of Gd^{3+} and Nd^{3+} ions onto Cyphos@silica at different temperatures.

Temp, K	Gd^{3+}				Nd^{3+}			
	k_1, min^{-1}	q_e, exp., mg/g	q_e, cal., mg/g	R^2	k_1, min^{-1}	q_e, exp., mg/g	q_e, cal., mg/g	R^2
298	0.023	17.89 ± 0.08	6.49 ± 0.01	0.99	0.022	13.40 ± 0.02	7.12 ± 0.04	0.99
303	0.024	19.40 ± 0.05	6.35 ± 0.04	0.98	0.021	14.52 ± 0.01	6.76 ± 0.03	0.97
313	0.046	19.84 ± 0.07	3.41 ± 0.14	0.95	0.018	16.94 ± 0.02	6.77 ± 0.02	0.97
323	0.053	19.98 ± 0.08	2.36 ± 0.20	0.82	0.020	18.52 ± 0.03	8.53 ± 0.03	0.99

values, the hydrogen ions in the acidic solution compete for the lanthanide ions so, the sorption is low at low pH value, and by increasing pH value the sorption increases. At pH 3.5, the percent uptake of neodymium and gadolinium ions are 67 and 89.45%, respectively, and the percent uptake at pH 6 is 99.99% for both cations. Higher pH values, >6, have not been studied to avoid the precipitation of the lanthanide ions. The optimum pH value was desired at pH 3.5. A Comparative sorption behavior of silica and Cyphos@silica for sorption of neodymium and gadolinium ions was investigated at the optimum pH. The experimental outcome revealed that the impregnation process enhanced the sorption behavior of silica, from 18 to 67% for neodymium ion and from 20 to 89.45% for gadolinium ion. It is well known that the radii of Ln(III) ions decrease regularly from La(III) to Lu(III), hence, the ionic radius of gadolinium is smaller than that of neodymium ion, therefore, gadolinium ion can be sorbed easily than neodymium ion, i.e. the uptake of gadolinium is greater than that of neodymium ion.

3.3. Mechanism of sorption

Scheme 1 illustrates the mechanism of the impregnation process of Cyphos IL-104 onto silica, and Scheme 2 shows the proposed mechanism of sorption of the metal ions by the impregnated silica, Cyphos@silica. Cyphos IL-104 has an appropriate viscosity so that it can easily penetrate into the pores of the support material. Therefore, the impregnation process was carried out by incorporating of Cyphos IL-104 into the pores of silica, this method is known as a physical impregnation technique [19]. Cyphos IL-104 molecule contains both cation and anion as illustrated in Scheme 1, the negative charge on Cyphos@silica is considered as the active sites; therefore, it attracts the sorbed cations as illustrated in Schem2. As mentioned above, that the lanthanide ions were sorbed as divalent cations, hydrolysis of the lanthanide ions to produce $Ln(OH)^{2+}$ which is sorbed by Cyphos@silica is outlined by the proposed mechanism in Scheme 2.

3.4. Kinetic studies

The time dependence graph of neodymium and gadolinium uptake at different temperatures is shown in Fig. 7, which presents the plots of amount of ions sorbed, q_t, versus contact time. Initially, the sorption of ions is fast and becomes slower near the equilibrium at which the values of amount sorbed at room temperature were found to be 13.4 mg/g and 17.89 mg/g for neodymium and gadolinium ions, respectively. The amount of ions sorbed increased by increasing the temperature; this increase indicates the endothermic nature of the sorption process of neodymium and gadolinium ions onto Cyphos@silica at 298, 303, 313 and 323 K. Some kinetic models were used including pseudo-first-order and pseudo-second-order models.

3.4.1. Pseudo-first-order model

Pseudo-first-order model was investigated by applying Lagergren equation as follows [25]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{6}$$

where k_1 is the sorption rate constant and t is the time, min.

Plot of log (q_e _ q_t) versus t gives straight lines for pseudo-first order kinetics (the figure was omitted), which allows computation of the sorption rate constant, k_1, from the slope, while the values of amount sorbed, q_e, were calculated at different temperatures from the intercept. The values of k_1 and $q_{e,}$ are presented in Table 1. This table illustrates that there is a difference between the calculated and the experimental values of q_e, this indicates that the pseudo-first order kinetic model is not applicable for the sorption of both neodymium and gadolinium ions by Cyphos@silica.

3.4.2. Pseudo-second-order model

Pseudo second-order rate model is expressed as [26]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\,t \tag{7}$$

The plot of t/q_t against t at different temperatures gives straight lines, Fig. 8, from the slope and the intercept one can determine the calculated quantity sorbed of the lanthanide ions and the rate constant, k_2, respectively. The values of $q_{e\ Cal.}$ are more close to the experimental values, $q_{e\ exp.,}$ and a high correlation coefficient was obtained

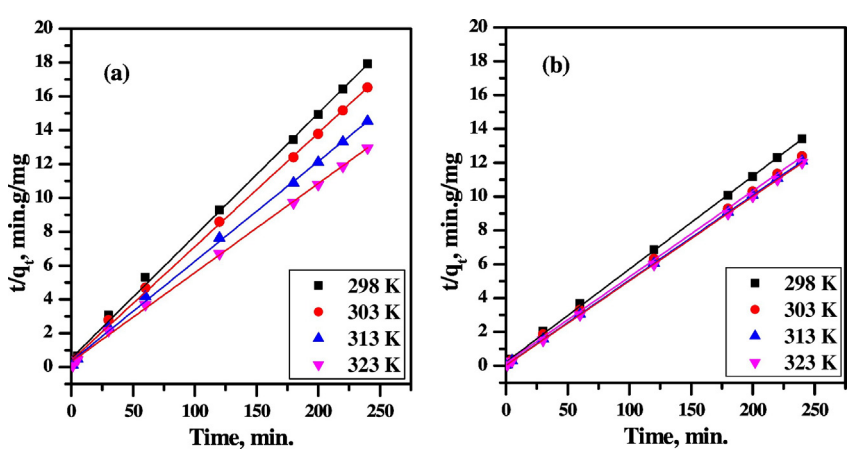


Fig. 8. Plot of pseudo-second-order equation for sorption of (a) neodymium and. (b) gadolinium ions onto Cyphos@silica at different temperatures.

Table 2
The kinetic parameters of pseudo-second-order model for sorption of Gd^{3+} and Nd^{3+} ions onto Cyphos@silica at different temperatures.

Temp, K	Gd^{3+}				Nd^{3+}			
	k_2,g/mgmin	q_e, exp., mg/g	q_e, cal., mg/g	R^2	k_2,g/mg·min	q_e, exp., mg/g	q_e, cal., mg/g	R^2
298	0.013	17.89 ± 0.08	18.18 ± 0.04	0.999	0.010	13.40 ± 0.02	13.81 ± 0.01	0.997
303	0.014	19.40 ± 0.05	19.23 ± 0.03	0.999	0.011	14.52 ± 0.01	14.88 ± 0.01	0.998
313	0.067	19.84 ± 0.07	19.60 ± 0.05	0.999	0.010	16.94 ± 0.02	16.94 ± 0.01	0.998
323	0.121	19.98 ± 0.08	20.00 ± 0.03	0.999	0.009	18.52 ± 0.03	19.01 ± 0.01	0.998

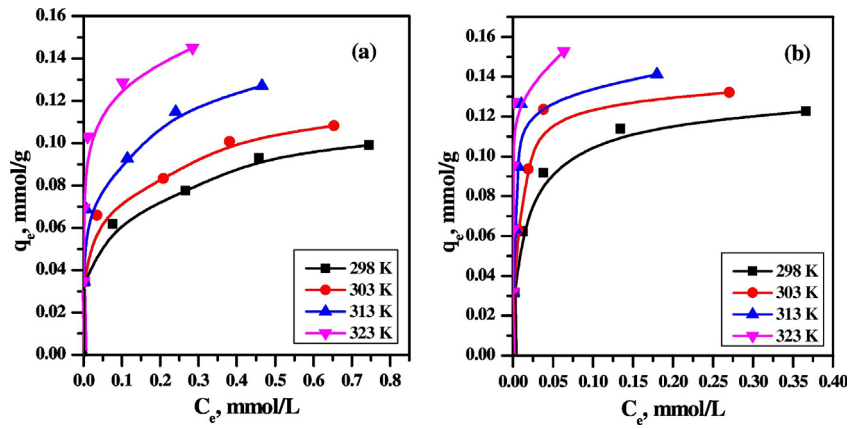


Fig. 9. Isotherm plot for sorption of (a) neodymium and (b) gadolinium ions onto Cyphos@silica at different temperatures.

($R^2 > 0.99$), as illustrated in Table 2. Therefore, the pseudo-second-order mechanism is predominant for the sorption process and that the overall rate constant appears to be controlled by the chemisorption process [27, 28].

3.5. Sorption isotherm studies

Sorption isotherm describes the relationship between the amount of metal ions sorbed on the sorbent and the concentration of the dissolved ions in the liquid phase at equilibrium, as illustrated in Fig. 9. In this work, the effect of initial neodymium and gadolinium ions concentration in the aqueous phase on the amount of the lanthanide ions sorbed by Cyphos@silica at different temperatures was studied. The quantity of lanthanide ions sorbed at equilibrium, q_e, increased by increasing the initial concentration of the ions. Various theoretical models could be applied to experimental data in order to find a model which adequately describes equilibrium results, such as Langmuir and Freundlich models.

3.5.1. Langmuir isotherm

Langmuir model assumes that the sorption process occurs on a structurally homogeneous sorbent, all the sorption sites are energetically identical and monolayer coverage of the sorption surfaces is obtained [29]. Langmuir sorption isotherm is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{bQ} + \frac{1}{Q} C_e \tag{8}$$

Q and b are Langmuir constants and related to the sorption capacity and the energy of sorption, respectively. The linear plot of C_e/q_e versus C_e shows high correlation coefficient, $R^2 \geq 0.99$, this indicates that the sorption of both neodymium and gadolinium ions obeys to Langmuir model, Fig. 10. The values of the monolayer capacity, Q, at different temperatures were determined from the slope, as can be seen in Table 3, the sorption capacity of neodymium and gadolinium ions onto Cyphos@silica and the energy of sorption increased with temperature. The increase

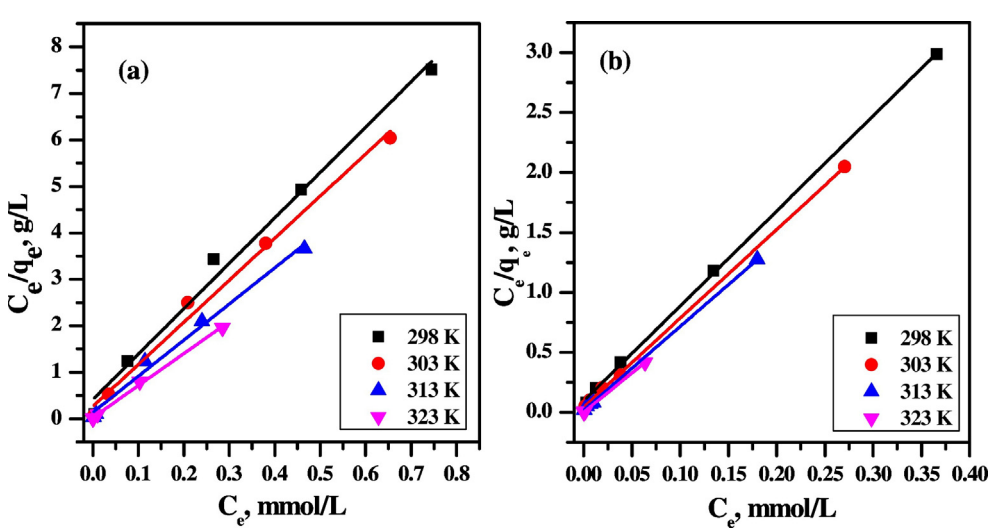


Fig. 10. Langmuir isotherm plot for sorption of (a) neodymium and (b) gadolinium ions onto Cyphos@silica at different temperatures.

Table 3
Langmuir parameters for sorption of Gd^{3+} and Nd^{3+} ions at different temperatures.

Temp, K	Gd^{3+}			Nd^{3+}		
	Q, mmol/g	b, L/mmol	R^2	Q, mmol/g	b, L/mmol	R^2
298	0.126	82	0.999	0.102	23	0.987
303	0.135	161	0.999	0.110	34	0.989
313	0.143	360	0.999	0.129	56	0.988
323	0.154	2129	0.999	0.145	267	0.997

Table 4
Freundlich parameters for sorption of Gd^{3+} and Nd^{3+} ions at different temperatures.

Temp, K	Gd^{3+}			Nd^{3+}		
	1/n	K, mmol/g	R^2	1/n	K, mmol/g	R^2
298	0.275	0.189	0.906	0.198	0.105	0.994
303	0.282	0.244	0.808	0.202	0.119	0.984
313	0.259	0.285	0.702	0.203	0.152	0.913
323	0.206	0.336	0.734	0.154	0.189	0.958

in sorption capacity with temperature suggested that the active sites available for the sorption increased with temperature. Another reason may be attributed to the change in the pore size and enhanced rate of intra-particle diffusion of solute, as diffusion is an endothermic process [27].

3.5.2. Freundlich isotherm

Freundlich model can be applied to sorption on heterogeneous surface and multilayer sorption; it is expressed by the following equation [29]:

$$\log q_e = \frac{1}{n} \log C_e + \log k \tag{9}$$

n and k are the Freundlich constants. The value of 1/n gives an indication of the adequacy and intensity of the sorbent/sorbate system and k is a constant indicative of the relative sorption capacity of the sorbent. The plot of log q_e versus log C_e, Fig. 11, gives straight lines; from the slope and the intercept, Freundlich parameters can be calculated. As can be seen in Table 4, the value of 1/n at all studied temperatures is less than unity, indicating a concentration-dependent sorption for both ions onto Cyphos@silica. The correlation coefficient (R^2) is less than that of Langmuir model; therefore, Langmuir isotherm is more applicable for sorption of neodymium and gadolinium ions by Cyphos@silica.

3.6. Comparison of sorption capacity of neodymium and gadolinium ions onto Cyphos@silica and different sorbents

Comparison of the monolayer capacity of neodymium and gadolinium ions onto Cyphos@silica with other sorbents obtained in the literature is listed in Table 5. It can be seen that Cyphos@silica has much higher sorption capacity than many other sorbents, especially for gadolinium ions, It shows that Cyphos@silica can be considered as a promising material for removal of neodymium and gadolinium ions from aqueous solution.

Table 5
Comparison of sorption capacities of neodymium and gadolinium ions on different sorbents.

Sorbents	Experimental conditions	Capacity, mmol/g		References
		Nd^{3+}	Gd^{3+}	
Cyphos@silica	pH = 4.0	0.102	0.126	Present work
Silica gel modified with diglycol amic acid	pH = 1.0	0.112	0.136	[30]
By-pass cement dust	pH = 7.0	0.093	0.112	[31]
Dried parachlorella	pH = 7.0	0.045	0.004	[32]
Carbonized parachlorella 350 °C	pH = 4.0	0.019	0.007	[32]
Iron–Titanium mixed oxide	pH = 4.6	1.26	0.80	[33]
esterified alfalfa	pH = 5.0	0.055	0.055	[34]
Activated carbon	pH = 4.0	0.424	NR[a]	[35]
Resorcinol formaldehyde polymeric resin	pH = 4.0	0.40	NR[a]	[36]
Aliquat-336 impregnated onto Amberlite XAD-4	pH = 5.5	NR[a]	0.028	[37]

[a] NR refers to not reported.

3.7. Desorption of neodymium and gadolinium ions from Cyphos@silica

The possibility of desorption of neodymium and gadolinium ions from Cyphos@silica was studied in a batch system using distilled water and different molarities of HNO_3 (0.2, 0.5 and 1.0 mol/L). The results illustrated that the distilled water has no effect and cannot be used for the desorption process. Desorption percent of gadolinium ions from Cyphos@silica was found to be 71.60, 72.40 and 97.74% using 0.2, 0.5 and 1.0 mol/L of HNO_3, respectively, while for neodymium ions the desorption percent was 76.12, 79.50 and 86.33%, respectively. After the regeneration process, Cyphos@silica was evaluated for further sorption of neodymium and gadolinium ions, the results revealed that Cyphos@silica can be regenerated and reused for further sorption.

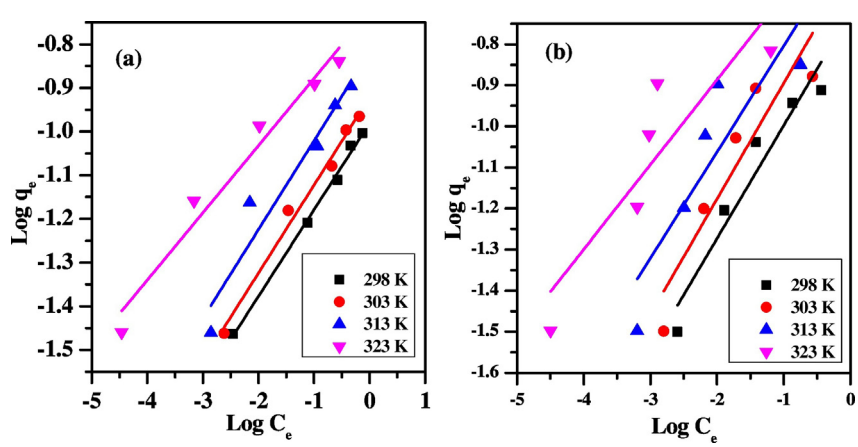


Fig. 11. Freundlich isotherm plot for sorption of (a) neodymium and (b) gadolinium ions onto Cyphos@silica at different temperatures.

4. Conclusion

Modification of silica by impregnation of Cyphos IL-104, as ionic liquid, in silica was successfully carried out and used for removal of neodymium and gadolinium ions from aqueous solutions. The impregnation process enhanced the percent uptake of neodymium and gadolinium ions from 18 to 67% and from 20 to 89.45%, respectively. For evaluating the impregnation process of Cyphos IL-104 onto silica, the loss of extractant from the solid support was tested; the results indicated that no significant loss of the impregnated Cyphos IL-104 was observed. These results give advantage to the used material, as well as the comparison of the sorption capacity of Cyphos@silica for Nd^{3+} and Gd^{3+} ions with the state of the art in the literature revealed that Cyphos@silica has comparatively high sorption capacity. The sorption process is controlled by pseudo-second-order mechanism. Langmuir isotherm was more applicable than Freundlich model. Desorption investigations indicated that neodymium and gadolinium ions can be desorbed from Cyphos@silica using 1.0 mol/L of HNO_3, the desorption percent was found to be 97.74 and 86.33% for gadolinium and neodymium, respectively, the results revealed the reusability of Cyphos@silica for further sorption.

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