

POLYANILINE BASED CERIUM PHOSPHOSILICATE: SYNTHESIS, CHARACTERIZATION AND DIFFUSION MECHANISM OF LA(III) IN AQUEOUS SOLUTIONS.

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ABSTRACT

In this study, a strategy has been provided for the preparation of different organic and inorganic-organic composite materials as ion exchange materials to be used for the removal of heavy metals from waste water. Polyaniline cerium phosphosilicate has been synthesized by incorporation of organic polymer polyaniline into the inorganic precipitate of cerium phosphosilicate. Scanning electron microscope (SEM), X-ray diffraction (XRD), IR and XRF have been used to characterize the structure of the different prepared materials. This new synthesized polyaniline cerium phosphosilicate was applied to remove toxic metal lanthanum La(III) from aqueous solution. The kinetic studies have been done to determine the mechanism of ion exchange system for the prepared inorganic and composite ion exchangers. The effects of different experimental parameters such as initial concentration of heavy metals, particle size, reaction temperature and drying temperature against interaction time were investigated in batch mode. The obtained data correlated well with the particle diffusion mechanism. The activation energy (E_a), activation entropy ΔS^* , and diffusion coefficient D_0 were evaluated. The correlation of these parameters with the ion-exchange characteristics of the material is discussed.

Keywords : kinetics, polyaniline cerium phosphosilicate, adsorption, diffusion, toxic metals

INTRODUCTON

Environmental pollution is one of the important problems that world faces today. Lanthanides are found to be one of these pollutants that its separation from aqueous solution is mostly needed. The amount control of lanthanides in liquid wastes has become an issue of great concern because of their destructive effects on the environment. They are potentially dangerous to human health and also to the environment, for example lanthanum is dumped



in the environment in many different places, mainly by petrol-producing industries. It can also enter the environment when household equipment is thrown away. Lanthanum will gradually accumulate in soils and water soils and this will eventually lead to increasing concentrations in humans, animals and soil particles. With water animals lanthanum causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system. It strongly accumulates in muscles.

Conventional methods employed for the removal of heavy metal ions from wastewater include chemical precipitation, filtration, electrochemical treatment, adsorption, membrane separation, reverse osmosis and ion exchange. Ion exchange treatment is the second most widely used method for metal removal. It can reduce the metal ion concentration to a very low level. The organic ion exchangers are well known for their uniformity, chemical stability and control of their ion exchange properties through synthetic method (Devi et al., 2010). Inorganic ion exchange materials, besides other advantages, are more stable at high temperatures and in radiation fields than the organic (Amphlett and Jones, 1964; Khan et al., 2009; Varshney et al., 2007; Zakaria et al., 2002; El-Naggar et al., 1999). In order to obtain a combination of these advantages and to increase interlayer distance of layered inorganic ion exchangers many organic–inorganic exchangers have been developed earlier by the incorporation of organic monomers in the inorganic matrix (Pandit and Chudasama, 1998; Shpeizer et al., 2010; Ferragina et al., 2010). Efforts have been made to improve the chemical, thermal and mechanical stabilities of ion exchangers and to make them highly selective for certain metal ions. Mardan et al. (1999) prepared silica potassium cobalt hexacyanoferrate composite ion exchanger which has excellent exchange properties of Cs. Alam et al. (2010) prepared polyaniline Ce(IV) molybdate that has high selectivity to Cd(II). Inamuddin and Ismail prepared poly-*o*-methoxyaniline Zr(IV) molybdate that has high selectivity to Cd(II) (Inamuddin and Ismail, 2010). Nabi et al. (2009) prepared acrylonitrile stannic(IV) tungstate that has high selectivity to Pb(II). Cobalt ferrocyanide impregnated organic anion exchanger was found to be highly selective for cesium (Valsala et al., 2009). Khan and Inamuddin (2006) prepared polyaniline Sn(IV) phosphate that was found to be highly selective for Pb(II). polyaniline Sn(IV) tungstoarsenate (Khan et al., 2003) was found to be highly selective for Cd(II). Siddiqui et al. (2007) synthesized a hybrid type of ion exchanger poly (methyl methacrylate) Zr(IV) phosphate that has high selectivity to Pb(II). Polypyrrole thorium(IV) phosphate cation-exchanger was found to be highly selective for pb(II) ion (Khan, 2005).

cerium phosphosilicate as one of heteropolyacid materials is very useful for the removal of La(III) from water streams. cerium phosphosilicate supported on poly aniline (PA) as a matrix material is used to separate La(III) from



liquid wastes. polyaniline has been proposed as a universal binding polymer for practically any inorganic ion exchanger. The use of PA as based organic binding polymer has a number of advantages provided by the relatively easy modification of its physico-chemical properties (hydrophilicity, porosity, mechanical strength). The following pages summarized synthesis, characterization and kinetic studies analysis for the removal of Lanthanum ions from aqueous solutions using this material.

EXPERIMENTAL

Chemicals and Reagents

All chemicals and reagents used in this work were of analytical grade purity and used without further purification. cerium chloride, orthophosphoric acid, sodium metasilicate and potassium persulphate ($K_2S_2O_8$) were obtained from Prolabo (England). Aniline ($C_6H_5NH_2$), nitric acid and hydrochloric acid were purchased from Adwic (Egypt). Ammonia solution 33% was purchased from El Nasr Pharmaceutical chemicals Co. (Egypt). In all experiments, bidistilled water was used for preparation and dilution of solutions. A solution (1M) of cerium chloride and 1 M sodium metasilicate solution was prepared in demineralized water (DMW). Solution of orthophosphoric acid 4 M added drop wise to sodium metasilicate solution with constant stirring. Solutions of 10% (v/v) aniline and 0.1M potassium persulphate were prepared in 1 M HCl.

Synthesis of cerium phosphosilicate (CePSi)

A precipitate of cerium phosphosilicate was prepared by adding 1 M cerium chloride solution to an aqueous solution of 1M sodium metasilicate along with 4M solution of Orthophosphoric acid in a volume ratio of 2:2:1 at 65 ± 1 °C. The white precipitate was obtained when the pH of the mixture was adjusted to 4.5 by adding aqueous ammonia with constant stirring. The supernatant liquid was decanted and the gel was rewashed with bidistilled water in order to remove fine adherent particles then filtered by using a centrifugation (about 10^4 rpm). The excess acid was removed by washing with DMW and the material was dried in an air oven at 50 ± 1 °C. The dried product was immersed in DMW to obtain small granules. The material was converted to H -form by treating with 0.01 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and then dried at 50 ± 1 °C. Several particles size of material was obtained by sieving and kept in desiccators.



Synthesis of polyaniline

Polyaniline gel was prepared by mixing equal volume of 10% aniline and 0.1M potassium persulphate with continuous stirring by a magnetic stirrer. Green colored polyaniline gel was obtained by keeping the solution below 10 °C for half an hour.

Synthesis of polyaniline cerium phosphosilicate (PACePSi)

The fresh gel of polyaniline was added to the fresh white precipitate of cerium phosphosilicate that previously obtained and mixed thoroughly with constant stirring. The resultant green color gel was kept for 24 h at room temperature (25 ± 1 °C) for digestion. The supernatant liquid was decanted and the gel was rewashed with bidistilled water in order to remove fine adherent particles and was filtered by using a centrifugation (about 10^4 rpm). The hybrid material was dried in an air oven at 50 °C. The dried product was immersed in DMW to obtain small granules. It was converted to H -form by treating with 0.01 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and then dried at 50 °C. Several particles sizes of material were obtained by sieving and kept in desiccators.

Instruments and characterization of materials

The IR spectra of the materials were measured by IR spectrometer using KBr disc technique. The spectra were scanned over the wave length range 400-4000 cm^{-1} using BOMEM FTIR model MB 147, Canada. Measurements of powder X-ray diffraction patterns were carried out using Shimadzu X-ray diffractometer, XD- DI Shimadzu, Japan, with a nickel filter and Cu- K_α radiation tube. Samples were very lightly ground and mounted on a flat sample plate at room temperature. Microphotographs of the prepared materials were obtained by the scanning electron microscope (SEM) at various magnifications, JSM- 6510LA, Jeol, Japan. Measurements of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a Shimadzu DT-60 thermal analyzer, Shimadzu, Japan. The sample heated from ambient temperature up to 1000°C at heating rate of 20°C /min. The La(III) concentrations were measured using UV spectrophotometer and inductively coupled plasma spectrometer (ICPs), Shimadzu, Japan.

All samples and chemicals used in this work were weighted using an analytical balance of AE Adam type having maximum sensitivity of 10^5 g and accuracy ± 0.001 /y. For the equilibrium experiments, a good mixing for the two phases of solid and solution were achieved using thermostatic shaker



water bath of the type Clifton, Nickel-Electro LTD, Weston-S-MARE SOMEREST (England).

All the pH values of different solutions were measured using an Adwa digital pH meter research model AD1030 (Romania) with accuracy of ± 0.02 units. The pH meter scale was calibrated using two standard buffer solutions within the pH range of the measured solution before each experiment. The deviation in the readings was in the range of ± 0.01 at the laboratory temperature 25 ± 1 °C.

IR spectra

It is evident from the FTIR studies of the ‘organic–inorganic’ composite cation-exchanger polyaniline cerium phosphosilicate in H^+ -form (Fig. 1) that the material shows the presence of external water molecules in addition to –OH groups and the metal oxygen bond. In the spectrum of the material, a strong and broad band around 3374 cm^{-1} is found which can be ascribed to –OH stretching frequency. The band appearing at 620 cm^{-1} may correspond to metal metal oxide linkage of Ce–O, while the bands at 534 cm^{-1} and 1066 cm^{-1} are due to the presence of phosphate and silicate groups respectively. It can be detected that peaks at 1562 and 1299 cm^{-1} corresponding to C=C and N–C stretching vibrations respectively. These characteristic bands of PACePSi (Fig. 1) indicating the binding of inorganic precipitate with organic polymer and formation of inorganic–organic composite PACePSi. This indicates that the PACePSi contains considerable amount of aniline.

X-ray diffraction patterns

X-ray powdered diffraction patterns of PACePSi is given in Fig. 2, same shows some prominent peaks together with a number of low intensity peaks which suggests crystalline nature of the prepared materials. The XRD patterns of prepared samples show the same peak positions with different intensities. It was found that the morphology of the exchanger got changed after binding the solids of CePSi with the matrix of polyaniline. The prepared sample of the inorganic-organic composite PACePSi shows XRD reflections at 29, 32, 38, 42, 45, 47, 65 and 78 from which it can be seen that the composite material PACePSi is crystalline. The X-ray diffraction pattern of the composite material PACePSi shows that the intensity of the peaks at 27, 31 and 42 (2θ) decreased while the region of the characteristic peak of the prepared composite material was different than the other samples, which indicates that the crystal structure has changed. This shift can be probably attributed to the completely reaction of hydrous oxide with polyaniline forming new composite material with total difference than inorganic materials. This result was confirming with the data observed in SEM, IR and the efficiency of the samples towards the studied ions.

Scanning electron microscopy (SEM) studies

A scanning electron microscopy (SEM) study was performed to examine the surface morphology of the composite. SEM photographs of PACePSi (Fig. 3), indicates the binding of inorganic material with organic polymer, i.e. polyaniline. The SEM pictures showed that the surface morphology of composite material is totally different from their individual inorganic and organic components. The morphology of the composite material is essentially different due to the binding of polyaniline with cerium phosphosilicate. It has been revealed that PACePSi after binding shows smaller sized crystals morphology. This result was agreement with the results of IR and X-ray analysis.

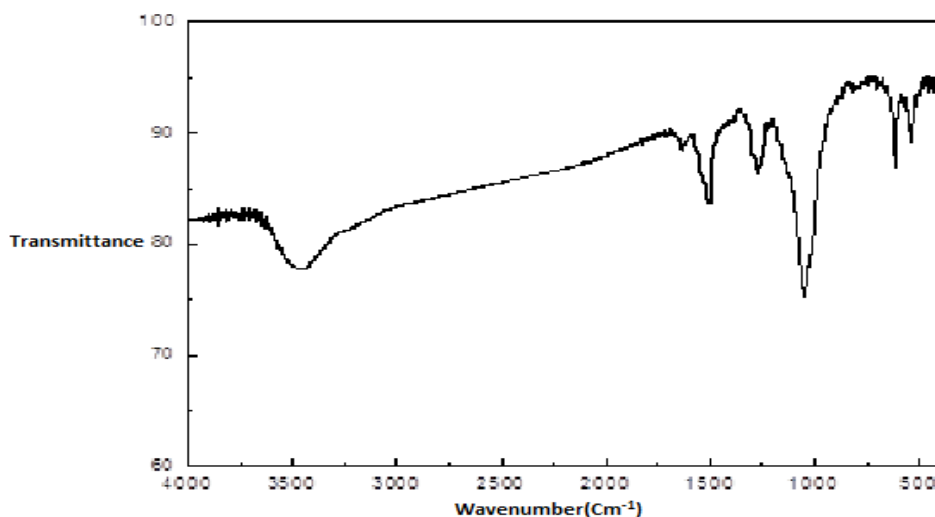


Fig. 1 FTIR spectrum of a prepared PACePsi composite material.

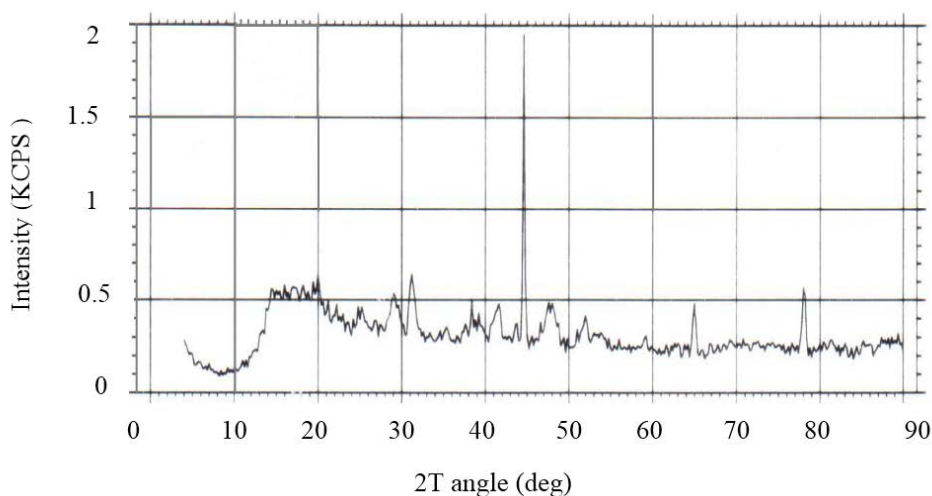


Fig. 2 XRD pattern of PACePsi

Chemical stability

The chemical stability of the prepared samples of both inorganic CePSi and composite PACePSi exchangers was studied in water, acid (HNO₃ and HCl) and base (NaOH) at different concentrations [0.1,1,2,3,4and 5M], by mixing 50 mg of each of the prepared sample and 50 ml of the desired solution with intermittent shaking for 24 hours at 25±1 °C as given in Tables (1).

Table 1 Chemical stability of CePSi and PACePSi in various solvent systems.

Solvent Concentration, M	Amount dissolved (mg/l)							
	HNO ₃		HCl		HNO ₃		H ₂ O	
	CePSi	PACePSi	CePSi	PACePSi	CePSi	PACePSi	CePSi	PACePSi
0.1	11.60	17.20	5.60	7.60	1.60	2.00	not detected	not detected
1.0	31.20	38.80	22.00	27.60	2.40	2.80	-	-
2.0	42.00	49.20	29.60	35.60	4.40	5.20	-	-
3.0	61.20	69.60	34.00	42.80	6.40	7.60	-	-
4.0	78.80	90.00	39.20	49.60	10.00	12.40	-	-
5.0	91.60	118.80	46.40	97.20	12.00	16.40	-	-

It can be seen From Tables (1) that both inorganic CePSi and composite PACePSi materials have good chemical stability. As the results indicated that the materials were resistant to 5 M HNO₃ and 5 M HCl. The solubility in the HNO₃ was higher than in the HCl and very feeble dissolution was observed in the alkaline medium. It was observed that the solubility of composite is slightly increased than the inorganic material, due to the presence of polyaniline which can dissolve into the solution. Despite the increased solubility of PACePSi than CePSi, it showed high mechanical and granular properties [Khan and Alam, 2003].

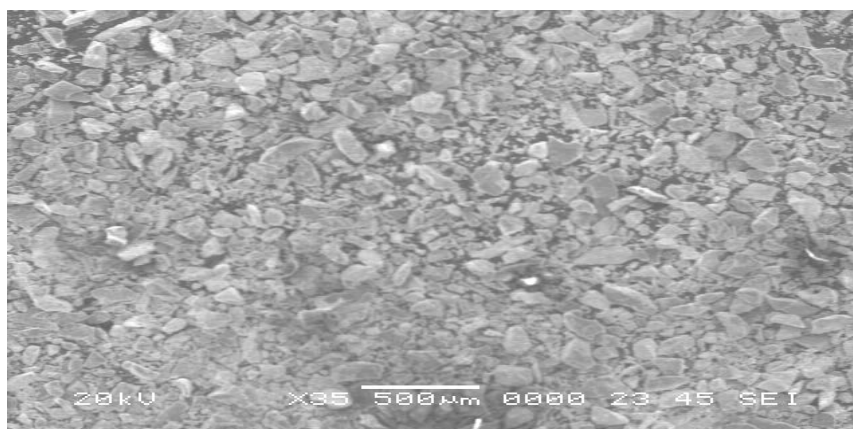


Fig. 3 Scanning electron microphotograph (SEM) of chemically prepared polyaniline cerium phosphosilicate at the magnification of 35×.

pH Titration

(Fig. 4) is showing the pH-titration curves for CeSi, CePSi and the pH-titration curve of the PACePSi shows only one inflection point indicating that the PACePSi behaves as monofunctional. The pH-titration curve (Fig. 4) shows slow increase when the added NaOH was increased from 0 – 2 ml and rapid increase when NaOH was increased from 2 – 6 ml. This composite exchanger may be a strong acid cation-exchanger because the pH-titration curve usually showed a step edge at 6 ml added of NaOH. This means that the H^+ ions on the hybrid cation-exchanger were depleted and replaced with Na^+ ions at that point and the number of H^+ sites was equivalent to the same amount of NaOH, i.e. the strong acidic groups Na^+ form. Thus, theoretical ion-exchange capacity of this hybrid cation-exchanger may be considered as 6 ml. After that point, in the region when more NaOH added, the equilibrium pH further increases but (H^+) of the composite cation-exchanger are completely converted to the more slowly. This slow increase of pH-titration curve after 6ml added of NaOH implies due to surface precipitation other than conventional ion exchange or surface adsorption. Similar behavior has been noticed in the PH titration curves of both inorganic exchangers CeSi and CePSi , however in these cases the capacity of both exchangers were found to be less than in the case of composite exchanger , this may be an indicator for the less number of H^+ ions in both inorganic exchangers that may be replaced by Na^+ ions

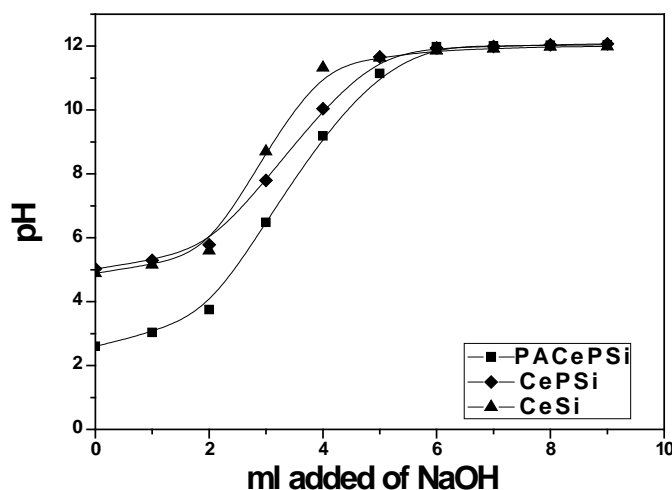


Fig. 4 The pH-titration curve of CeSi, CePSi, PACePSi with 0.1M NaOH.

RESULTS AND DISCUSSION

Kinetic Studies

Unlike the kinetics studies techniques in homogeneous media, fine powders and most of the surface processes, the ion exchange kinetics can be controlled by rates of actual chemical reactions; however many ion exchange interactions do not involve any direct chemical reactions, hence the overall process will be controlled by the slow step (rate determining step) in the ion exchange reaction which is diffusion of the liquid surrounding the particle of the exchanger (film diffusion control) or diffusion inside the exchanger particles itself (particle diffusion mechanism) (Rudolf and A. Clearfield, 1989; Inezed, 1957), in that case the process will be controlled solely by the diffusion which, is defined by the material structure. The kinetic approaches are very specific for ion exchange materials as it is being used to identify the sorption rate of the ion exchanger considering the initial concentrations of the adsorbed ions, particle sizes of the adsorbent, reaction temperature and drying temperatures. Basis that we can identify the rate of sorption of La(III) onto PACePSi and represent the corresponding kinetic model of the sorption process.

Effect of initial concentration and contact time

The effect of the initial ion concentration on the La(III) sorption onto PACePSi was performed at concentrations of 200, 500 and 900 PPM at 25 ± 1 °C, the results were shown in Fig. 5. It is clear that the sorption amount of La(III) increase with increasing the initial ion concentration, and the amount of La(III) sorbed by composite is greater than that of La(III) sorbed by inorganic adsorbent. Also, the amount of La(III) sorbed sharply increased for each adsorbent with time in the initial stage (0–240 min range), and then gradually increased to reach at equilibrium in approximately 330 min. A further increase in contact time had a negligible effect on the amount of ion sorption. According to these results, the agitation time was fixed at 6 h for the rest of the batch experiments to make sure that the equilibrium was reached. From the data presented in Fig. 6, at the concentration studied, the rate of exchange is independent on the metal ion concentration. So, this is the evident that the conditions set in this thesis are particle diffusion mechanism.

The increase in the uptake capacity of the adsorbent material with increasing the initial ion concentration may be due to higher probability of collision between each investigated ion and the adsorbent particles. The variation in the extent of sorption may also be due to the fact that initially all sites on the surface of adsorbent were vacant and the metal ion concentration gradient was relatively high. Consequently, the extent of La(III) ion uptake decreases

significantly with the increase of contact time, depending on the decrease in the number of vacant sites on the surface of adsorbent material.

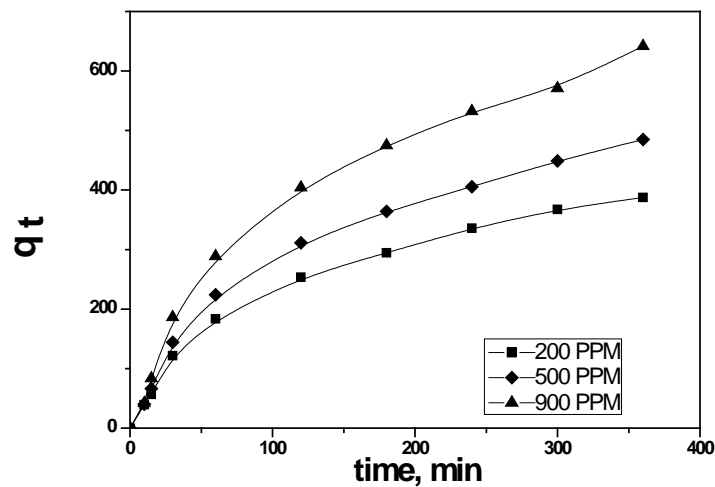


Fig. 5 Effect of initial ion concentration and contact time on the amount sorbed of La(III) onto CePSi at V/m 100 and 25 ± 1 °C.

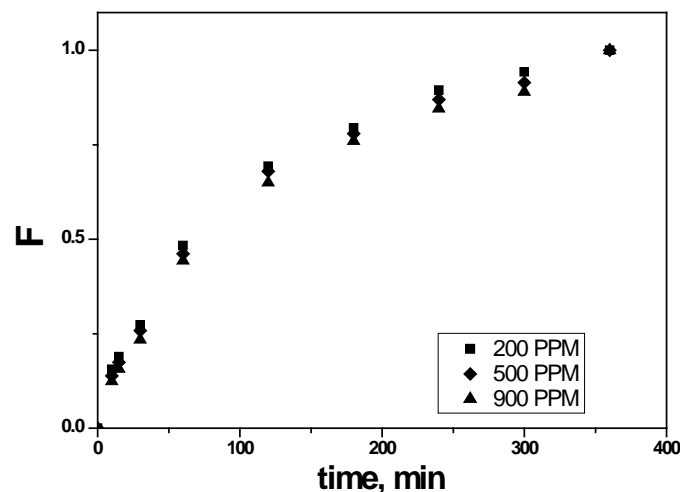


Fig.6 Plots of F versus time for sorption of La(III) onto PACePSi at different initial ion concentration, V/m 100 and 25 ± 1 °C.

Effect of particle size

The effect of particle diameters of composite PACePSi exchanger on the rate of exchange of La(III) ions was studied and the data are given in Fig. 7 as relation between F and Bt against time. The adsorbent diameters are the averages of the mesh sizes for the consecutive sieves that allowed the particles to pass through and retained the particles. Figure 7 show that straight lines passing through the origin are obtained for Bt and t relations for La(III) ions on PACePSi which is a further proof of a particle diffusion mechanism. The same trend was reported by others (Amphlett, 1964; Guibal et al., 1998; El-

Naggar et al., 1999; Zakaria et al., 2009). It is clear that the exchange of La(III) ions on PACePSi significantly affected by the particle sizes. The rate and extent of sorption, for a constant mass of the adsorbent, is proportional to the specific surface area, which is higher for small particles indicates the sorption process of La(III) into adsorbents is in agreement with the fundamental theory of particle diffusion mechanism as shown in Fig 7. This can also be taken as a further proof of particle diffusion mechanism (Vinter et al., 1970; Reichenberg, 1953; Abe, 1987).

The average values of diffusion coefficients (D_i) of La(III) ions on PACePSi of different particle diameters are calculated from Fig. 7 and given in Table (2). It was found that, D_i values have generally increased with increasing the particle size as shown in Table (2).

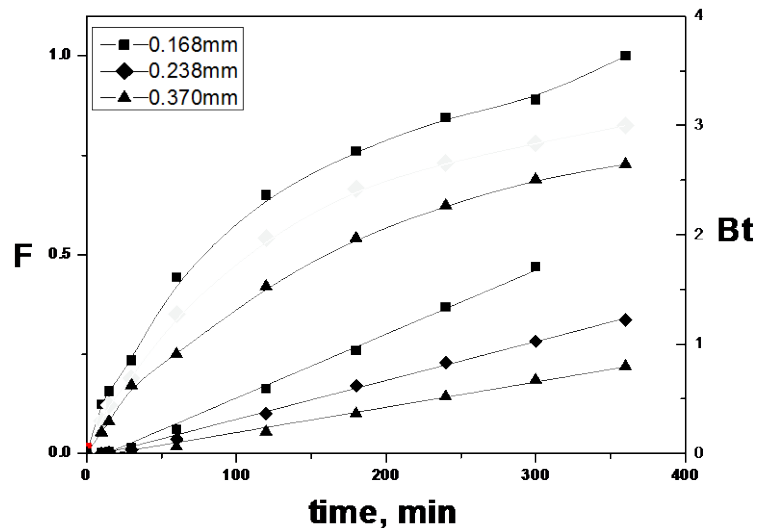


Fig. 7 Plots of F and Bt versus time for sorption of La(III) onto PACePSi at different particular sizes, V/m 100 and 25 ± 1 °C.

Table 2 Values of diffusion coefficient of La(III) on different particle diameters both PACePSi and CePSi at 25 ± 1 °C.

Particle diameter (± 0.02 mm)	$D_i, \text{cm}^2 \text{s}^{-1} \times 10^{10}$
	PACePSi
0.168	6.966
0.238	12.015
0.370	13.364

Effect of contact time and reaction temperature

Figure 8 shows plots of F and Bt for sorption of La(III) ion from aqueous solutions onto PACePSi, at initial metal ion concentration 900PPM and at different reaction temperatures 25, 45 and 65 ± 1 $^{\circ}\text{C}$ as a function of contact time. The figures show a high initial rate of removal within the first 240 minutes of contact (over 80% removed) followed by a slower subsequent removal rate that gradually approached an equilibrium conditions in 6 h. The plots of F and Bt for sorption of La(III) ion onto PACePSi shows straight lines passing through the origin were obtained in all cases studied, which confirmed the particle diffusion mechanism. The effect of varying reaction temperatures 25, 45 and 65 ± 1 $^{\circ}\text{C}$ on the rate of exchange of La(III) onto PACePSi are investigated and showed that, the rate of exchange reactions of La(III) were increased with increasing the reaction temperatures from 25 to 65 ± 1 $^{\circ}\text{C}$ where the mobility of the counter ions increased with increasing the reaction temperatures (Mathew and Tandon, 1975).

The entropy change (ΔS^*) depends normally on the extent of hydration of exchangeable and exchanging ions along with any change in water structure around the ions that may occur when they pass through the channel of the exchanger particles. The ΔS^* values for La(III)/PACePSi at 25 $^{\circ}\text{C}$ were found -743.44 J/mol K. The negative values of entropy change shows no significant structure change occurs in the absorbent structure which support the higher stability and hence the least steric difference of the system.

Effect of drying temperature

Figures 8-10 show the rate of exchange of La(III) (900PPM) decrease with increasing the drying temperature of PACePSi from 50 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ and 400 ± 1 $^{\circ}\text{C}$, respectively at different reaction temperature 25, 45 and 65 ± 1 $^{\circ}\text{C}$ as a relation between F and Bt against time.

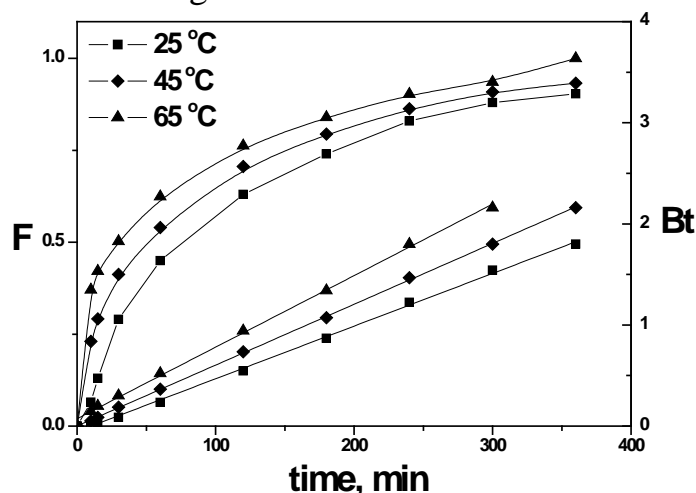


Fig. 8 Plots of F and Bt versus time for sorption of La(III) onto PACePSi at V/m 100 and at different reaction temperatures.

The thermodynamic parameters for the the La(III)/H⁺ exchange systems on PACePSi was calculated at different temperatures and summarized in Table 3.

Table 3 Thermodynamic parameters of La(III)/H⁺ system on PACePSi at different reaction temperatures.

Exchange System	Drying temp. °C	Particle diameter, mm	Reaction temp. °K	Di cm ² s ⁻¹ x10 ¹⁰	D _o cm ² s ⁻¹ x10 ⁹	E _a kJmol ⁻¹	Δs* Jmol ⁻¹ k ⁻¹
La(III)/H ⁺	50 °C	0.168±0.02	298	6.97	2.43	3.09	-743.44
			318	8.53	2.75		-742.2
			338	9.78	2.94		-742.23

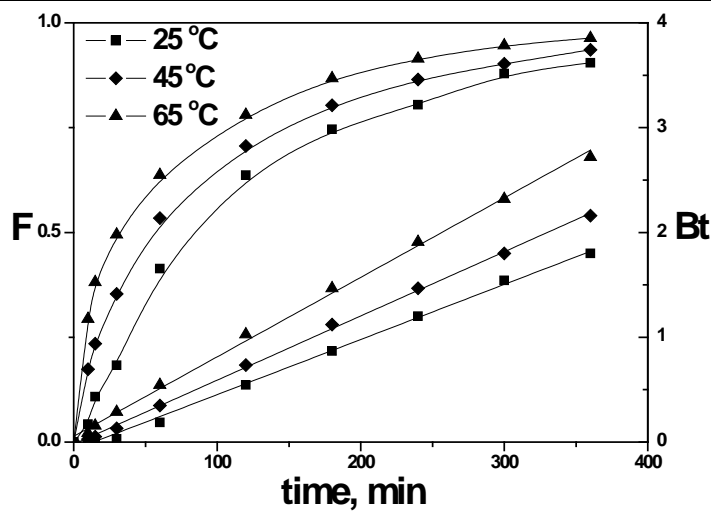


Fig. 9 Plots of F and Bt versus time for sorption of La(III) onto PACePSi (dried at 200±1 °C) at V/m 100 and at different reaction temperatures.

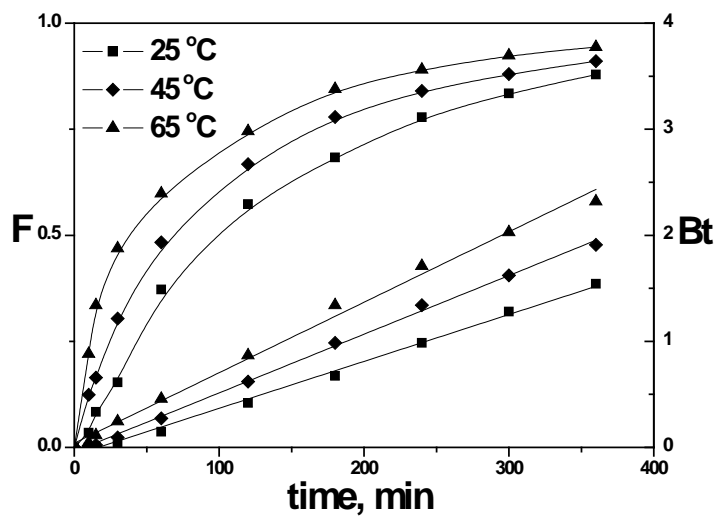


Fig. 10 Plots of F and Bt versus time for sorption of La(III) onto PACePSi (dried at 400±1 °C) at V/m 100 and at different reaction temperatures.

The figures show a high rate of removal of La(III) onto PACePSi dried at 50 °C. The sorption rate was decreased with increase the drying temperature from 50 up to 400 °C. Where by increasing drying temperature the active sites in PACePSi are removed and destroyed. The water content in PACePSi were decreased and removed with increasing drying temperature.

From these Figures, the values of D_i were calculated and summarized in Tables 4. Tables 4 show an appreciable decrease of self-diffusion of La(III) ions on PACePSi with increasing the drying temperature from 50 to 400±1°C. The reduction in the D_i values for La(III) ions with increasing the drying temperature of PACePSi from 50 °C to 400±1 °C may be attributed to the lower pore sizes and porosity for the dried exchanger (Mathew et al., 1987; Mathew and Tandon, 1977). The lower porosity means less free water inside the exchanger particles which hinders the diffusion of ions (Misak and El-Naggar, 1989).

The values of diffusion coefficient (D_i), energy of activation (E_a) and entropy of activation (ΔS^*) for La(III) at different reaction temperature 25, 45, 65±1 °C, on PACePSi are given in Tables 4. The activation energy of cation diffusion process represented in Table 4 reflects the ease with which cations can be pass through the exchanger particles. The relatively small activation energies (E_a) given in Tables 4 for La(III) ions sorption on PACePSi suggest that the rate of exchange is particle diffusion. These values of activation energy are relatively small compared to the other organic and inorganic exchangers which confirm the particle diffusion mechanism. In general, Tables 4 show that negative values of ΔS^* have been reported for La(III) ions PACePSi. The entropy change normally depends on the extent of hydration of the exchangeable and exchanging ions along with any change in water structure around ions that may occur when they pass through the channels of exchanger particles. The obtained negative values for the entropy of activation suggest that upon the exchange of La(III) ions on PACePSi , no significant structure change occurs in the adsorbent structure in both instances which support the higher stability and hence the least steric difference of the system. experimentally studied and the obtained data were analyzed. Based on the values of activation energy (E_a), activation entropy ΔS^* , and diffusion coefficient D_0 , particle diffusion mechanism was found to best correlate the rate kinetic data of both adsorbent. The magnitudes of the particle diffusion coefficients of adsorbent was found to be $6.966 \times 10^{10} \text{ cm}^2\text{s}^{-1}$ while the values of E_a obtained is $<4.47 \text{ kJ/mol}$, indicating a diffusion-controlled process and based on negative ΔS^* values, no significant structure change occurs in the adsorbent structure in both instances which support the higher stability and hence the least steric difference of the system.

Table 4 Thermodynamic parameters for the diffusion of La(III) on PACePSi heated at 50, 200 and 400 °C at different reaction temperatures.

Exchange system	Drying temperature °C	Reaction temperature °C	$D_i \times 10^{10}$	$D_o \times 10^9$	E_a	ΔS^*
			cm^2s^{-1}	cm^2s^{-1}	kJmol^{-1}	$\text{Jmol}^{-1}\text{k}^{-1}$
La(III)/H ⁺	50	25	6.97	2.43	3.09	-743.44
		45	8.53	2.75		-742.20
		65	9.78	2.94		-742.23
	200	25	6.274	2.38	3.31	-743.88
		45	7.300	2.55		-743.91
		65	9.041	2.93		-742.30
	400	25	5.272	2.35	3.70	-744.18
		45	6.596	2.68		-742.80
		65	7.920	2.96		-742.10

Conclusion

Polyaniline cerium-phosphosilicate was chemically prepared, characterized using SEM, XRD and IR, also pH titration curve was drawn for all prepared materials and it was found that PACePSi behaves as monofunctional, chemical stability has been investigated for both inorganic CePSi and composite PACePSi exchangers showing that both materials have good chemical stability as the materials were resistant to 5 M HNO₃ and 5 M HCl. The composite material PACePSi was tested as adsorbent material for the removal of Lanthanum ions from aqueous solutions. The kinetics studies were done for ion exchange system and the obtained data were analyzed. Based on the values of activation energy (E_a), activation entropy ΔS^* , and diffusion coefficient D_0 , particle diffusion mechanism was found to best correlate the rate kinetic data. The magnitude of the particle diffusion coefficients was found to be $6.966 \times 10^{10} \text{ cm}^2\text{s}^{-1}$ while the value of E_a obtained are $<3.7 \text{ kJ/mol}$, indicating a diffusion-controlled process and based on negative ΔS^* values, no significant structure change occurs in the adsorbent structure which support the higher stability and hence the least steric difference of the system.

References

- **Alam, Z., Inamuddin, Nabi, S.A.**, 2010 . Desalination, 250,515.
- **Amphlett, C.B., Jones, P.J.**, 1964. Journal of Inorganic and Nuclear Chemistry 26 (10), 1759.
- **Amphlett, C.B.**, 1964 . Inorganic Ion Exchangers , McGraw-Hill, New York.
- **Abe, M., P.A. Williams and M.J. Hudson**, 1987 . In Recent Developments in Ion Exchange, eds. Elsevier, London, 227.
- **Devi, P.S.R., Joshi, S., Verma, R., Lali, A.M., Gantayet, L.M.**, 2010. Radiation Physics and Chemistry 79 (1), 41.
- **El-Naggar, I.M., Zakaria, E.S., Shady, S.A., Aly, H.F.**, 1999. Solid State Ionics 122 (1–4), 65.
- **El-Naggar, I.M., Zakaria, E.S., Abou-Mesalam, M.M., and Aly, H.F.**, 1999 . Czechoslovak J. of physics., 49 Suppl. S1
- **Ferragina, C., Rocco, R.D., Giannoccaro, P., Petrilli, L.**, 2010. Materials Research Bulletin 45 (1), 34.
- **Guibal, E., Milot, C., Tobin, J.M.**, 1998 . Ind. Eng. Chem. Res., 37, 1454.
- **Inamuddin, Ismail, Y.A.**, 2010. Desalination 250 (2), 523.
- **Inezed, J.**, 1957 . "Analytical Application of ion exchangers" Pergman Press, New York
- **Khan, A.A., Inamuddin**, 2006. Reactive and Functional Polymers 66 (12), 1649.
- **Khan, A.A., Inamuddin, Alam, M.M.**, 2005. Reactive and Functional Polymers 63 (2), 119.
- **Khan, A.A., Alam, M.M., Mohammad, F.**, 2003. Electrochimica Acta 48 (17), 2463.
- **Mardan, A., Ajaz, R., Mehmood, A., Raza, S.M., Ghaffar, Abdul**, 1999. Separation and Purification Technology 16 (2), 147.
- **Mathew, J., and Tandon, S.N., J.** 1975 . Radioanal. Chem., 72(2), 315.
- **Mathew, J., and Tandon, S.N., Can. J.** 1977 . Chem., 55, 3857.
- **Mathew, J., Singh, N.J., Gupta, C.B., and Tandon, S.N., Indian J.** 1987 . Chem., 16,524.
- **Misak, N.Z., and El-Naggar, I.M.**, 1989 . Reactive Polymer, 10, 67.
- **Nabi, S.A., Naushad, Mu., Bushra, R.**, 2009. Chemical Engineering Journal 152 (1), 80.
- **Reichenberg, D., J. Am.** 1953 . Chem. Soc., 75,589.
- **Rudolf, P.R., and Clearfield, A.**, 1989 . Inorg. Chem., 28 ,1706.



- **Shpeizer, B.G., Bakhmoutov, V.I., Zhang, P., Prosvirin, A.V., Dunbar, K.R., Thommes, M., Clearfield, A., 2010.** Colloids and Surfaces 357 (1-3), 105.
- **Siddiqui, W.A., Khan, S.A., Inamuddin, 2007.** Colloids and Surfaces 295 (1–3), 193.
- **Varshney, K.G., Rafiquee, M.Z.A., Somya, A., 2007.** Colloids and Surfaces 301 (1–3), 224.
- **Vinter, I.K., Boichinova, E.S., and Denisova, N.A., Zh. 1970 .** Prikl. Khim. (Leningrad)., 43,1678.
- **Zakaria, E.S., Ali, I.M., El-Naggar, I.M., 2002.** Colloids and Surfaces 210 (1), 33.
- **Zakaria, E.S., Ali, I.M., Aly, 2009 .** H.F., J. Colloid. Interf. Sci., 338-346.

متراكب البولى أنيلين سيريوم فوسفوسليكات : تحضير و توصيف و ميكانيكية الانتشار لأيونات اللانثانيوم الثلاثي فى المحاليل المائية

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فى هذه الدراسة تم تحضير المتراكب بولى أنيلين سيريوم فوسفوسليكات كماده تبادل أيونى لاستخدامها فى إزالة أيونات اللانثانيوم من المحاليل المائية. تم عمل توصيف للماده باستخدام SEM, XRD, IR. تم قياس الثبات الكيميائى لمواد البحث ووجد أنها تملك ثبات كيميائى جيد فى أحماض النيتريك والهيدروكلوريك. تم عمل الدراسات الحركيه لنظام التبادل الأيونى باستخدام المتراكب بولى أنيلين سيريوم فوسفوسليكات ودراسه تأثير العوامل المختلفه مثل تركيز أيونات اللانثانيوم فى المحلول، حجم جزئ المبادل الأيونى، درجة حرارة التفاعل ودرجة الحرارة التى تم تجفيف المبادل الأيونى عندها ، وبتحليل نتائج هذه الدراسه وجد ان المتراكب بولى أنيلين سيريوم فوسفوسليكات يتبع ميكانيكية الانتشار الجزيئى اتناء عملية التبادل الأيونى.