

Adsorption of Ce³⁺ and Nd³⁺ by Diglycolic acid functionalised electrospun polystyrene nanofiber from aqueous solution

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Abstract

Highly selective and stable ligands with fast kinetics for rare earth element extraction are not well developed. Durable attachment of ligands to the support would make regeneration possible. Polystyrene nanofiber supports (PS-nF) were prepared using the electrospinning method. Thereafter, PS-nf were chemically modified with diglycolic anhydride (DGA) to produce novel electrospun polystyrene diglycolic acid nanofiber (PS-DGAnf) adsorbents. The immobilisation reaction proceeded via an electrophilic aromatic substitution of the ligand onto the PS nanofiber. The maximum gravimetric loading of DGA on PS nanofiber was 0.827 g g⁻¹. The unmodified and modified nanofibers were characterised by ATR-FTIR, HR-SEM, BET and TGA. After optimising pH, time and concentration, the equilibrium adsorption and binding kinetics of cerium (Ce³⁺) and neodymium (Nd³⁺) ions on the nanofibers surface were examined at pH 6. The adsorption capacity of PS-DGAnf for Ce³⁺ and Nd³⁺ at pH 6.0 was 152.5 mg g⁻¹ (1.09 mmol/g) and 146.2 mg g⁻¹ (1.01 mmol/g) respectively. Selectivity of Ce³⁺ over Ni²⁺, Co²⁺ and Sr³⁺ was also studied at pH 6. The amount of Ce³⁺ adsorbed even in the presence of interfering ions was 100.3 mg g⁻¹, which was only a little lower than 119.4 mg g⁻¹ obtained in a single ion solution. The rapid adsorption kinetics of Ce³⁺ and Nd³⁺ ions were achieved within 15 mins. The desorption and regeneration was carried out with 1 M nitric acid and the developed PS-DGAnf adsorbent could be reused for 4 cycles without any substantial loss to its adsorption abilities.

Keywords	Polystyrene, rare-earth elements; diglycolic acid; adsorption; nanofiber, selectivity
Manuscript category	Functional materials for separation and purification (when necessary)
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Scheme.docx [Figure]

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Table 1.docx [Table]

Table 2.docx [Table]

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Referee suggestion Chemical Engr Journal.docx [e-Component]

Competing interest.docx [e-Component]

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There are no linked research data sets for this submission. The following reason is given:
Data will be made available on request

21st August 2019
4th floor, Chemical Building,
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Dear Editor,

I wish to submit the revised new manuscript titled “**Adsorption of Ce³⁺ and Nd³⁺ by Diglycolic acid functionalised electrospun polystyrene nanofiber from aqueous solution**” for the consideration of the Separation and Purification Technology.

We appreciate your positive comments. We believe that the comments and those from other reviewers have strengthened our manuscript. We have considered the comments and they are now fully incorporated and implemented in the revisions. We have also significantly improved the manuscript based on the suggested comments.

I confirm that this study is original and all sources used are appropriately and transparently acknowledged and cited. This work has not been published elsewhere nor is it currently under consideration for publication anywhere. All the figures and data used in this study were obtained from our laboratory. I acknowledge that the guide for authors was consulted in preparing this manuscript. I also confirm that the manuscript was prepared in compliance with the ethics in publishing policy as described in the guide for authors. Keywords have been provided, references are in correct format of Separation and Purification Technology and manuscript length is in compliance with the guide for authors. The authors have no competing interests to declare.

It is hoped that this research will serve as a good reference tool for researchers in the areas of developing new materials for innovative physico-chemical technique for waste water remediation. The study should be of interest to researchers and scientist in the fields of material science and metal removal strategies in waste water remediation. Moreover, this article will help in better understanding of nanofiber preparation and their applications.

Please address all correspondence concerning this manuscript to me at pereaokola@gmail.com

Thank you for the consideration of this manuscript.

Sincerely,

Omoniyi Pereo

Response to Reviewers' Comments

Manuscript No: SEPPUR_2019_866

Changes made to the original manuscript were highlighted in the revised manuscript.

- Reviewer's comments: black
- Response: blue

We appreciate your positive comments. We believe that the comments and those from other reviewers have strengthened our manuscript. We have considered the comments and they are now fully incorporated and implemented in the revisions. We have also significantly improved the manuscript based on the suggested comments. Please consider the following specific responses to the comments.

Reviewer #1

General Comments:

The authors present the preparation of functionalised polystyrene nanofibers for adsorption of rare earth elements. I believe the subject is interesting and within the scope of the Journal. However, I feel that the results analysis lack scientific quality and should be improved. What is the phenomena that occurs in the reported study? Physical adsorption, ion exchange, ...?

Response :

.....chelating adsorption.....

The following text has been added.“ The REE cations are strong Lewis acids and easily coordinate nucleophiles to form stable complexes and they show a clear tendency towards oxygen donors which is advantageous for their efficient extraction. The derivatives of DGA are used for the selective extraction of REEs from aqueous solutions, because they are recognised as effective and size selective binders of trivalent f-elements [49]. The structural analysis of complexes bearing the DGA ligands shows that REEs bind traditionally in a tridentate fashion, where each metal ion is coordinated by the three oxygen atoms of DGA-type ligands. The lanthanide ions (e.g., La, Nd, Ce) are sterically saturated in their nine-coordinate geometry with three DGA ligands [50]. Therefore, by the right tailoring of chemically similar chelating ligands and their grafting on solid supports, it is possible for functional materials to exhibit selective affinities for smaller or larger ions [51,52].....”.

Specific comments:

Comment 1:

Please explain the meaning of this sentence “The significance of the solution concentration of Ce³⁺ or Nd³⁺ on the adsorption efficiency was examined by testing PS-DGAnf adsorbent in an unlimited supply of metal ions in solution because the REEs being recovered exist in diverse concentrations subject to the sources of metal ions.”

Response :

The statement was corrected to read “...The PS-DGAnf adsorbent functionality with the large number of active sites was investigated for the interaction with Ce³⁺ or Nd³⁺ ions by testing the solution concentration to understand the adsorption capacity...”

Comment 2:

I believe there is no need to show the linearized forms of the isotherms and also that the reference for these equations should not be from 2010 or 2003 as they are much older.

Response :

The linearized forms of isotherms have been removed from the manuscript and the references have been updated to recent studies from 2018 and 2019

Comment 3:

Also, I believe that the use of pseudo kinetic models is outdated as they were developed when the computational capacity that we have today was unavailable. There is no need no use them nowadays. The kinetic data obtained by these models is useless and misleading, because for example, it cannot be used in the design of continuous units. A more appropriate and meaningful analysis should be made.

Response :

Pseudo kinetic models have been removed from the manuscript. Finally, according to the comments of other reviewers we decided to show only the experimental kinetic data and just compared our results to the similar type of functionalized nanofibers found from the literature. “.....The short time required to attain equilibrium shows that the PS-DGAnf has a great potential and very high adsorption efficiency for Ce³⁺ or Nd³⁺ uptake when compared to other adsorbent surface modification using diglycolic-based selective ligands which reported fast metal binding kinetics toward REEs [10,15,57].....”

Comment 4:

Please indicate the volume of solution used and final concentration obtained related with the results presented in Fig 7.

Response :

This is implemented and the volume of solution used and final concentration is now included.

Comment 5:

Also, indicate the initial concentration used to determine the isotherm point with equilibrium concentration of 180 mg/L in Fig 8.

Response :

The initial concentration used to determine the isotherm point with equilibrium concentration of 120 mg/L in Fig 7 is 180 mg/L

Comment 6:

The word absorption appears some times in the text. I believe you mean adsorption.

Response :

The word absorption has been corrected all through the manuscript

Reviewer #2

General Comments:

Reviewer #2: I like to recommend this article for major revision. The authors need to address the following comments.:

Specific comments:

Comment 1:

Typo: Diglycolamic acid (p-3)

Response :

It has been corrected to read diglycolic amic acid

Comment 2:

What is the quantitative loading of DGA functionalities on the surface of PS nanofiber? It is very important to know.

Response :

The quantitative loading of DGA functionalities on the surface of PS nanofiber was determined from the TGA results "...The amount of DGA adsorbed onto the PS nanofiber was gravimetrically determined by TGA and was estimated to be 0.827 g g⁻¹."

Comment 3:

What are the sources of REE salt, nitrates?

Response :

"..The sources of the salts are.... neodymium(III) nitrate hexahydrate (99.9%), cerium(III) nitrate hexahydrate (99.99%).... from Sigma-Aldrich (South Africa)"

Comment 4:

Were the samples acidified (2% HNO₃) for ICP analysis?

Response :

Yes, 2% HNO₃ was used for ICP analysis."The metal ion concentration in solution before and after the adsorption experiments was acidified with 2% HNO₃ and determined by Inductively Coupled Plasma-Optical Emission Spectroscopy....."

Comment 5:

What is the chemistry of regeneration when it fibers are washed with 1M HNO₃?

Response :

“.....Regeneration was carried out with 1 M HNO₃ to desorb the metal ions taken up on the adsorbent for reuse without disrupting the ligand attached. It was considered that the desorption by HNO₃ is caused by ion exchange reaction between protons and adsorbed ions and this stripping agent was earlier tested for ligand stability to confirm whether the functional fibers can withstand it's short term contact.....”

Comment 6:

For selectivity study with Ce, why Co, Sr and were employed? What is the real world scenario, does Ce need to be separated from those elements in reality?

Response :

The potential source of REE are secondary materials and elements from low grade ores (Ancylite) and scrap, geothermal fluids, fly ash from coal combustion and the waste electrical and electronic equipment and radioactive waste therefore, in the recovery process of rare earth selective separation of dilute rare earth metal ions from solutions containing high concentrations of base metal ions is required.

“.....Much attention for potential source of REE has been directed towards identifying and leveraging new or recycled sources of REE such as electronics waste, coal fly ash, brines, and various industrial wastes to meet surging demand [58–60].”

Comment 7:

What is reason of the ratio of 100 mg/L REE solution with 0.0075 g nanofiber?

Response :

“We chose 100 mg/L because it is a compromise between high concentration and low concentration. In higher concentration level precipitations of REE becomes a problem. We chose 100 mg/L because that value is in the middle of the adsorption isotherm curve.

Comment 8:

The fiber diameter of 400-900 nm is very high compared to conventional electrospun fibers, the authors need to work on the electrospinning parameters to lower the diameter. I think 17 cm is too high, the authors should have tried the distance in the range of 10 cm, to get reasonably low fiber diameter.

Response :

Fiber diameter used for this study is in the range of 392 nm. Several collector distances were also investigated for polystyrene but not shown in this study.

”..... a morphological transformation of the beaded fibres to more cylindrical fibres with average fibre diameters ranging from 350 nm to 900 nm at a higher concentrations were obtained as presented in Fig 1 and the fiber diameter further used for this study was in the range of 392 nm.....”

Comment 9:

I do not see that XRD peak becomes ‘sharper’ upon functionalization of the nanofiber, in fact, there is no scientific reason for such phenomena. The authors should remove the XRD from the manuscript.

Response :

This has been implemented and the XRD has been removed from the manuscript.

Comment 10:

N₂ adsorption-desorption plot is not type IV, it is close to type V.

Response :

This has been implemented and changed to type V
.....” The nitrogen adsorption–desorption isotherm for the PS-DGAnf may be assigned to a type V isotherm”.....

Comment 11:

Page-16: “The uptake of metals below pH 2 was unimportant, because the energetics and kinetics was in favour of proton attachment to the adsorption sites ” –What do the authors mean by that?

Response :

This was reconsidered and re-written. “.....The uptake of metals below pH 2 was limited due to proton attachment to the adsorption sites because under acidic conditions, the surface of PS-DGAnf was covered with H⁺ ions which were in competition with the Ce³⁺ and Nd³⁺ ions adsorption upon the surface of the adsorbent.....”

Comment 12:

In fig 7, why there is a broken trend in pH dependency at pH=2 and 4 for Nd and Ce ? Please explain.

Response :

This was due to analytical challenges.

Comment 13:

Please pH dependency relating to the complexation of Nd and Ce with DGA.

Response :

“.....The dependence of Ce³⁺ and Nd³⁺ adsorption on the increasing pH of the solution suggested that the carboxylic groups progressively formed carboxylate functions that can bind metal cations by chelation [34].”

Comment 14:

Fig-8, make x and y axis consistent. If X axis (eq concentration) is mg/L, then Y-axis (adsorbed amount) should mg/g.

Response :

This has been implemented everywhere on the manuscript

Comment 15:

Please calculate and report distribution coefficient (K_d , mL/g) as a functional of initial concentration. it is very important and most of the papers report it.

Response :

This has been implemented.

“.....Fig. 8. Dependence of distribution coefficient (K_d) on initial concentration of Ce^{3+} or Nd^{3+} in the equilibrium adsorption study.....”

Comment 16:

I do not understand table 4, what is difference between the selectivity of single, mix and $S(Ce/M)$? Selectivity is the preference of adsorption of one species (REE) over other (metals), so it must be greater than 1. Why the numbers in the first two rows are less than 1?? The authors need to recalculate the rewrite the this table.

Response :

Table 3 has been corrected.

“..... the numbers in the first two rows are not the selectivity. They are the adsorption capacity of ions in single and mixture of different ions.....” $S(Ce/M)$ is the selectivity only. “.....Selectivity coefficient (S) (Ce/Co , Ni or Sr)”.....

Comment 17:

The comparison in table 2 is incomplete. For Nd adsorption, they must include Journal of Environmental Chemical Engineering 5 (2017) 4684–4692, where the Nd adsorption capacity was reported as 335.5 mg/g, which is higher than their findings.

Response :

This has been implemented. Journal of Environmental Chemical Engineering 5 (2017) 4684–4692 was added

Reviewer #3

General Comments:

Reviewer #3: From a scientific viewpoint, the paper is competent. However, the data fitting part is inadequate. If my concerns can be addressed successfully in a revision, then I believe

the paper should be published. My major concerns are as follows:

Specific comments:

Comment 1:

Highlights: Mentions adsorption capacity for Ce but not Nd.

Response :

This has been implemented. “.....• The adsorption capacity of PS-DGAnf for Ce³⁺ and Nd³⁺ was as high as 152.5 and 146.2 mg/g respectively.....”

Comment 2:

P3, fast adsorption equilibrium

This should read fast adsorption kinetics.

Response :

This has been implemented. “.....fast adsorption kinetics.....”

Comment 3:

P4, kinetics mechanism

Kinetic analysis was done using empirical pseudo first and second order equations, they are just a curve fitting tool that cannot reveal the true nature of the kinetics mechanism.

Response :

Pseudo kinetic models have been removed from the manuscript according to this comment and those of other reviewers. The authors decided to show only the experimental kinetic data and just compare our results to similar type of functionalized nanofibers found from the literature.

“.....The short time required to attain equilibrium shows that the PS-DGAnf has a great potential and very high adsorption efficiency for Ce³⁺ or Nd³⁺ uptake when compared to other adsorbent surface modification using diglycolic-based selective ligands which reported fast metal binding kinetics toward REEs [10,15,57].....”

Comment 4:

P6, PS electrospun nanofibers were cut into square shapes weighing 0.109 g

What is the size of the adsorbent samples?

Response :

“.....PS electrospun nanofibers were cut into 5cm by 5cm square shapes weighing 0.109 g”

Comment 5:

P8, linearized isotherm equations

The use of linearized isotherm equations for parameter estimation has been criticized in the literature (see, for example, Soil Sci. Soc. Am. J. 71 (2007) 1796–1806). The authors should either justify why linear regression should be used in their data analysis or apply nonlinear regression to their data analysis.

Response :

“Authors know the limitations of the linearized Langmuir equations, but because it explains quite well the data, we used it because of its simplicity and for direct comparisons to other sorbents previously published using these equations.

.....” The sorption properties of the nanofiber adsorbents for Ce^{3+} or Nd^{3+} were matched to the sorption capacities of alternative or commercial sorbents also fitted by the Langmuir model which are typically adopted in the studies of adsorbents for the extraction of REEs.....”

Comment 6:

P9, linearized kinetic equations

The above comment on the use of linear regression for parameter estimation applies to the analysis of kinetic data as well. Additionally, the weaknesses of the pseudo first order and second order kinetic equations are well documented in the literature. Some examples include Ind. Eng. Chem. Res. 57 (2018) 2705-2709; J. Soils Sediments 10 (2010) 838-844; J. Colloid Interface Sci. 448 (2015) 437-450; Chem. Eng. J. 306 (2016) 1138-1142; Sep. Purif. Technol. 136 (2014) 303-308. If the authors insist on using the two empirical kinetic equations in their data fitting and analysis, they should at least mention some of the problems associated with these two kinetic equations and provide justification for their use in the present paper.

Response :

“As mentioned earlier, pseudo kinetic models have been removed from the manuscript. Finally, we decided to show only the experimental kinetic data and compared just our results to the similar type of functionalized nanofibers found from the literature.”

Comment 7:

P16, uniform porosity to be 8.86 nm in the range of 1 to 18 nm; average pore diameter was 13.2 nm with a uniform porosity in the range of 6 to 23 nm

The term porosity by definition means void volume divided by adsorbent volume which is dimensionless. It should not be used to indicate pore diameter.

Response :

This has been implemented. The term porosity was removed. “.....The average pore diameter between the as-made nanofibers was measured to be 8.86 nm in the range of 1 to 18 nm. The measured PS-DGAnf average pore diameter was 13.2 nm in the range of 6 to 23 nm.....”

Comment 8:

P19, The correlation coefficient R^2 values for the Langmuir equation were 0.9999 or 0.9916 for Ce^{3+} or Nd^{3+} respectively, therefore the equilibrium adsorption capacity demonstrates that monolayer adsorption can best describe the metal adsorption as defined by the Langmuir isotherm model.

Excellent fit of the Langmuir isotherm does not confirm the presence of monolayer adsorption. The Langmuir equation is just a curve fitting tool. One cannot deduce the mechanism of adsorption by examining the R² value.

Response :

This has been implemented and corrected. “....which indicated that the Langmuir isotherm was better fitted to the experimental data than the Freundlich model and could better explain the Ce³⁺ or Nd³⁺ adsorption process.”

Comment 9:

P21, The rate-limiting step assumes that the PS-DGANf surface is homogenous and contains the reactive groups which bind the metal ions, with the operating sorption mechanism being chemisorption, which involves valence forces sharing or exchanging electrons among metal ions.

As mentioned above, the pseudo reaction kinetic equations are just an empirical curve fitting tool. A good fit does not reveal the actual uptake mechanism. There is no evidence presented in the paper to confirm that the rate limiting step is chemisorption. The PS-DGANf is a highly porous adsorbent, mass transfer processes such as surface or pore diffusion could well be the rate limiting step. The ability of a model to fit experimental data is not sufficient to validate the underlying dominant mechanism. Mechanism studies should be supported by analytical techniques, such as XPS, FTIR and SEM.

Response :

This is noted and has been corrected.

....“The N₂ BET adsorption–desorption characterisation indicated a porous structure for the adsorbent and the surface area was large enough to result in a high adsorption rate compared to the pristine nanofiber adsorption (not shown)”....

....“ Ogata et al [16] clarified the adsorption mechanism of immobilized diglycolic amic acid ligands by showing that adsorbents with diglycolic amic acid ligands adsorb REE ions via three oxygen atoms and that the tridentate chelation conferred high selectivity for REE ions.”....

.....“The evidence provided by FTIR data showed that strong adsorption is likely involved in the interactions of Ce³⁺ or Nd³⁺ with multiple carbonyl groups on the nanofiber. Hence, the Ce³⁺ and Nd³⁺ adsorption tended to be homogeneous and showed monolayer coverage, because of the strong interactions between the surface functional groups of PS-DGANf and Ce³⁺ and Nd³⁺ which is also consistent with the much higher K_d value (Fig. 8).”.....

Comment 10:

Fig. 7 caption, adsorbent dosage should be given as adsorbent mass/solution volume.

Response :

This has been implemented. “....adsorbent dosage - 0.0075 g/10 mL.....”

Comment 11:

Fig. 8, the equilibrium data points are connected by straight lines. The authors should calculate the isotherm fits using the best estimates of the isotherm parameters and show the calculated curves in Fig. 8.

Response :

This has been implemented. Based on other reviewers comments, only the isotherm parameters are shown

Comment 12:

Fig. 9a, Linear fits of the Langmuir isotherm for both Ce and Nd show 4 data points. Fig. 9b, Linear fits of the Freundlich isotherm for both Ce and Nd show 6 data points. The equilibrium data for both Ce and Nd in Fig. 8 show 7 data points. Why did the authors reduce the number of data points in the fittings of the Langmuir and Freundlich isotherms?

Response :

Only the isotherm parameters were used for comparison. The isotherms plots has been removed from the manuscript based on other reviewers comment

Comment 13:

Fig. 10, the kinetic data points are connected by straight lines. The authors should calculate the kinetic equation fits using the best estimates of the kinetic parameters and show the calculated curves in Fig. 10.

Response :

As stated earlier, Pseudo kinetic models have been removed from the manuscript and authors only showed the experimental kinetic data and just compared our results other similar type of functionalized nanofibers found from the literature.

Comment 14:

Fig. 10 caption, adsorbent dosage should be given as adsorbent mass/solution volume.

Response :

This has been implemented. “.....adsorbent dosage - 0.0075 g/10 mL.....”

Comment 15:

Fig. 11a, Linear fits of the pseudo first order kinetic equation show 7 data points. The kinetic data in Fig. 10 show 11 data points. Why did the authors use fewer data points in Fig. 11a?

Response :

The pseudo order kinetics models has been removed from the manuscript.

Comment 16:

Fig. 12 caption, adsorbent dosage should be given as adsorbent mass/solution volume.

Response :

This has been implemented. “.....adsorbent dosage - 0.0075 g/10 mL.....”

Comment 17:

Table 1, the adsorption capacity parameter for the Langmuir isotherm should be q_m .

Response :

This has been implemented to “..... q_m ...”

Adsorption of Ce³⁺ and Nd³⁺ by Diglycolic acid functionalised electrospun polystyrene nanofiber from aqueous solution

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Highlights

ABSTRACT

Highly selective and stable ligands with fast kinetics for rare earth element extraction are not well developed. Durable attachment of ligands to the support would make regeneration possible. Polystyrene nanofiber supports (PS-nF) were prepared using the electrospinning method. Thereafter, PS-nf were chemically modified with diglycolic anhydride (DGA) to produce novel electrospun polystyrene diglycolic acid nanofiber (PS-DGAnf) adsorbents. The immobilisation reaction proceeded via an electrophilic aromatic substitution of the ligand onto the PS nanofiber. The maximum gravimetric loading of DGA on PS nanofiber was 0.827 g g⁻¹. The unmodified and modified nanofibers were characterised by ATR-FTIR, HR-SEM, BET and TGA. After optimising pH, time and concentration, the equilibrium adsorption and binding kinetics of cerium (Ce³⁺) and neodymium (Nd³⁺) ions on the nanofibers surface were examined at pH 6. The adsorption capacity of PS-DGAnf for Ce³⁺ and Nd³⁺ at pH 6.0 was 152.5 mg g⁻¹ (1.09 mmol/g) and 146.2 mg g⁻¹ (1.01 mmol/g) respectively. Selectivity of Ce³⁺ over Ni²⁺, Co²⁺ and Sr³⁺ was also studied

at pH 6. The amount of Ce^{3+} adsorbed even in the presence of interfering ions was 100.3 mg g^{-1} , which was only a little lower than 119.4 mg g^{-1} obtained in a single ion solution. The rapid adsorption kinetics of Ce^{3+} and Nd^{3+} ions were achieved within 15 mins. The desorption and regeneration was carried out with 1 M nitric acid and the developed PS-DGAnf adsorbent could be reused for 4 cycles without any substantial loss to its adsorption abilities.

Keywords: Polystyrene, rare-earth elements; diglycolic acid; adsorption; nanofiber, selectivity

Graphical abstract

1 INTRODUCTION

Rare earth elements (REEs) have received increased consideration in recent decades, due to their distinctive properties and diverse applications in modern technologies, particularly in the nuclear fuel control, metallurgy, and ceramic industry [1,2]. Significant amounts of cerium and cerium oxide concentrates are used in glass-polishing applications and many cerium compounds have found important uses in biomedical applications [3] while neodymium, being the first triad of the lanthanide group, is illustrative for most of the valued REEs which are used in steel modifiers, optical filters, electronics components, superalloys, hydrogen storage and artistic glasses. Several hydrometallurgical techniques exist for the recovery and separation of REEs from aqueous solutions and these include adsorption, precipitation, ion exchange and solvent extraction [2,4,5], but disadvantages, such as the huge volume of chemical reagents needed, sludge generation, poor selectivity, and ineffective recovery from low metal concentrations [6], make obtaining the requisite rare earth metal purity very difficult.

The use of adsorbents and resins for removing or extracting rare earth metals from aqueous solutions was reported [7,8], and ligands comprising of the glycolamic acid group have been developed for REE removal. Results have indicated selectivity for the removal and recovery of REEs [9]. Diglycolic amic acid is comparable to diglycolic acid and well suited as task specific ligands capable of the removal of lanthanides [10], due to an etheric oxygen atom and two carbonyl groups

as functional groups. Rare earth elements recovery using this ligand is now being reported [11,12]. In all these studies, ligands comprising of glycol amic acid exhibited very selective and effective extraction of REEs from mixtures of other diverse metals. Adsorbents comprising of glycol amic acid were utilised for scandium (Sc) separation and reported to preferentially extract Sc from a mixture [6]. Modification of *Escherichia Coli* (E. coli) through the succinylation of E. coli amine groups with the diglycolic amic acid ligand indicated high affinity to REEs [13]. Elastic diglycolic amic acid modified chitosan sponges were applied as adsorbents for the removal of REEs and reported to have fast adsorption kinetics [14]. The need for suitable supports in designing a practical adsorbent for the recovery of REE are being investigated and some research on the adsorption of REEs using diglycolic amic acid immobilised using different support was published with varied results [15,16].

Nanofibers have high interfiber porosity with excellent interconnectivity, high surface area to volume ratios, layer thinness, low basis weight, controllable thickness of the electrospun scaffold, good structural stability as well as being cost effective, which make them promising materials [17]. Nanofibers can be functionalised with suitable ligands in a viable and cost effective manner [18] and these functionalised nanofibers can provide an effective, high surface area support which could be useful for waste water treatment and purification [19]. Electrospinning is a feasible technique that can be used to fabricate nanofibers of diameters in the range of 40–500 nm with the use of electrostatic forces [20,21]. Electrospun nanofibers are produced from numerous natural or synthetic polymers, or some blends or hybrids of both types of polymers [22]. Polystyrene (PS) is a versatile synthetic polymer support, due to the large number of ligands that can be covalently bound to it [23]. Because of its outstanding physical and reactive properties, chemical resistance, ease of electrospinning, good mechanical properties and low cost, PS is well studied, but it cannot efficiently adsorb individual metal ions [24].

In this study, the surface of PS nanofibers were modified chemically using diglycolic acid chelating ligands and its effectiveness in aqueous solutions for the recovery of Ce^{3+} or Nd^{3+} was assessed by performing batch adsorption studies. The dependence of factors including contact time, pH and equilibrium concentration on Ce^{3+} and Nd^{3+} adsorption efficiency as well as selectivity was studied.

The desorption of REEs from the loaded PS-DGAnf and the regeneration of the functional fibres using nitric acid was determined.

2 EXPERIMENTAL

2.1 Materials

Polystyrene ($M_w \sim 192,000$), diglycolic anhydride (90%), neodymium(III) nitrate hexahydrate (99.9%), cerium(III) nitrate hexahydrate (99.99%), N,N-dimethylformamide (DMF) ($\geq 99.8\%$), methanol ($\geq 99.9\%$), acetic acid (100%), tetrahydrofuran (THF) ($\geq 99.0\%$), HNO_3 (69%), NaOH (99.9%), strontium nitrate ($> 99.0\%$) were all purchased from Sigma-Aldrich (South Africa), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (98%), and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (97.5%) were purchased from Merck Chemicals. Deionised water was used throughout this work. All the reagent grade chemicals were used without any further purification.

2.2 Electrospinning

Electrospinning was performed using an infusion pump (Harvard Apparatus 33 Twin Syringe Pump) and applied voltages were driven by a high voltage power supply. The PS was dissolved in a 10 mL dimethylformamide and tetrahydrofuran (DMF:THF) (4:1 v/v) solvent system. The mixture was agitated by a magnetic stirrer for 12 h to achieve a consistent and homogenous solution. The attained viscous PS solution was thereafter loaded into a 10 mL glass syringe, and mounted on the programmable infusion pump. The electrospinning procedure was carried out under ambient conditions, and nanofibers were collected on aluminium foil as a non-woven nanofiber mat. The fibre diameter was evaluated using Image J[®] software. For this study, PS concentration was investigated, at varied concentration of 10, 15, 20, 25 or 30 wt % PS polymer in DMF:THF (4:1 v/v) with flow rate (1 mL/h), collector distance (17 cm) and applied voltage (20 kV) as fixed parameters. The applied flow rate was also changed from 0.2, 0.4, 0.8 to 1.0 mL/h using a fixed voltage of 20 kV, 15 wt. % PS polymer in DMF:THF (4:1 v/v) solution concentrations and a fixed tip to collector distance of 17 cm.

2.3 Surface modification of PS nanofibers

The experiments were undertaken according to previously reported chemical grafting procedures [25–27]. The reaction is an acid-catalysed process using acetic acid. First, a suitable amount of

diglycolic anhydride was added to 10 mL of 5 % (v/v) aqueous acetic acid solution in 40 mL methanol (99.9%) and the reaction mixture was mechanically stirred for 30 min. To functionalise the synthesised electrospun PS with DGA, fibre mats were inserted into the stirred solution and the temperature was slowly raised to 43 °C under reflux with further constant stirring for 4 h (Scheme 1).

Scheme 1 - Modification of PS nanofiber with DGA chelating ligand

Typically, PS electrospun nanofibers were cut into 5cm by 5cm square shapes weighing 0.109 g and immersed in a mixture of different ligand concentration range of 1 to 4 g diglycolic anhydride in 10 mL of 5 % (v/v) aqueous solution of acetic acid in 40 mL methanol (99.9%) and shaken for 4 hours at 43 °C in a beaker. PS nanofibers were tested at different reaction times between 1 to 4 h in 3 g of diglycolic anhydride containing solution under the same conditions and after the reactions, the PS-DGAnf samples were washed in deionised water to remove the residual salts and any unreacted ligand and the fibres were air-dried overnight. Stability experiments were performed to determine if the optimised material (PS-DGAnf) obtained can withstand short term contact with 1M HNO₃ as regenerant for 1 h to mimic the conditions that would be used for batch desorption experiments. The fibre samples were then washed with deionised water and air dried. The modification reaction was carried out using triplicate samples for each considered parameter.

2.4 Analytical methods

Thermo Scientific-Nicolet iS10 Fourier Transform Infrared Spectrophotometer (FT-IR) equipped with diamond Attenuated Total Reflectance (ATR) was used to record spectra in the range of 4000 – 650 cm⁻¹ to assess and identify the specific functional groups on the nanofiber surfaces before and after modification. The morphology of the nanofibers was investigated using the Zeiss Gemini Auriga high resolution scanning electron microscope (HRSEM) fitted with a CDU-lead detector using 25 kV with tungsten filament. Nanofiber diameters were evaluated using Image J® analysis software. The nitrogen adsorption/desorption (Brunauer-Emmett-Teller (BET)) isotherms was assessed by using a Micromeritics Tristar porosity and surface area analyser fitted

with a Micromeritics flowprep o6o sample degas system and was measured at -196 °C. Thermal behaviour of the fibres and stability of the immobilised ligands were investigated by thermogravimetric analyser (TGA) using STA 6000 (Perkin-Elmer Instrument Model, USA) under nitrogen. The metal ion concentration in solution before and after the adsorption experiments was [acidified with 2% HNO₃](#), and determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The instrument used for determining the metal ion concentrations was a Varian Radial ICP-OES coupled with a High Matrix Introduction (HMI) accessory.

2.5 Batch Adsorption

The surface-modified adsorbents PS-DGANf were applied in batch studies to investigate their performance in the removal of two rare earth metals (Ce³⁺ and Nd³⁺) from solution. For each REE, 0.0075 g of PS-DGANf was immersed in a vial of the single metal ion solution containing 10 mL of Ce³⁺ or Nd³⁺ (100 mg/L) respectively. The pH was adjusted in the range 1 to 6 by using NaOH or HNO₃. It was then shaken for a period of 2 h using an agitation speed of 200 rpm until equilibration was reached and the solution was then filtered with 20-25 µm filters (Whatman® qualitative filter paper, Grade 4) before analysis. The ICP OES was used for the determination of the REEs concentration in the aqueous stock, and in extracted solutions. The changes between the initial and final concentration of the solutions were considered to be the concentration of metal ion adsorbed. Initial concentration was changed from 60 to 180 mg/L at pH 6.0 for studying the adsorption isotherms of Ce³⁺ or Nd³⁺ on the surface of functionalised PS-DGANf. Contact times were changed from 1 to 60 min at pH 6.0 to evaluate the efficiency of the adsorption kinetics. The initial and final readings were then calculated using Eq. (1).

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

For aqueous phase adsorption, it is a practice to calculate distribution coefficient (K_d) [28] defined using Eq. (2),

$$K_d = \frac{C_0 - C_e}{C_e} \left(\frac{V}{m} \right) \quad (2)$$

where: q_e is the metal ions adsorbed by the nanofiber adsorbent (mg g^{-1}). M and V are adsorbent weight and solution volume while C_o and C_e are the initial and final equilibrium solution concentrations of metal ions. To confirm the actual concentration of working solutions, negative controls (with no adsorbent) were concurrently carried out to determine the metal ion loss during the adsorption due to the glassware. The experiments were generally carried out at $22 \pm 1^\circ\text{C}$ and the entire batch experiments were performed in duplicate.

2.6 Desorption and reusability studies

To examine the feasibility of regenerating PS-DGAnf, desorption studies were performed using 1 M HNO_3 for 1h. The regenerated PS-DGAnf were then washed about 3 times in 10 mL portions of ultrapure water and dried on a filter using vacuum suction before reuse. The regenerated nanofiber mats were dried at 40°C overnight. This regeneration was repeated three times under the same adsorption and desorption conditions to determine how many regeneration cycles were possible. The desorption efficiency was calculated using Eq. (3).

$$D_E = \frac{c \times v}{q \times m} \times 100 \% \quad (3)$$

where C (mg/L) is the concentration of adsorbates in the desorption solution, q (mg g^{-1}) is the amount of adsorbate adsorbed on the nanofiber before the desorption experiment, V is the volume of the desorption solution, and m (mg) the amount of the adsorbent used in the desorption experiments.

2.7 Selective adsorption of Ce(III) and Nd(III) onto PS-DGAnf.

The metal selectivity of PS-DGAnf was examined in 15 mL plastic vials containing 10 mL of aqueous solution of various metal ions (Ce^{3+} , Co^{2+} , Ni^{2+} and Sr^{2+}) using equal concentrations of 100 mg/L each and the nanofiber adsorbent (0.0075 g) was immersed into the solution. The fibre samples in the vials were equilibrated in a shaker operated at 200 rpm for 1 h in pH 6.0. The concentration of the various metal ions initially in solution and after adsorption was determined. The amount of metal ions absorbed on the nanofiber sample at adsorption equilibrium (q_e , mg g^{-1}) was calculated according to Eq. (1), and the selective coefficient of $K_{\text{REE}/\text{M}}$ was calculated using Eq. (4)

$$K^{REE_M} = \frac{q_{REE} * C_M}{q_M * C_{REE}} \quad (4)$$

where q_{cREE} and q_{eM} was the amount of REE ion and metal ions adsorbed onto PS-DGAnf at equilibrium.

3 RESULTS AND DISCUSSION

3.1 Electrospinning

The electrospinning effects on the solution polymer concentration and flow rate on the morphology and fibre diameter of polystyrene nanofibers were studied. The fibres produced at the low polymer weight percentage of 10 wt% showed that the bead-on-string morphology turned into blobs of polymer but by increasing the concentration of PS in solution, a morphological transformation of the beaded fibres to more cylindrical fibres with average fibre diameters ranging from 350 nm to 900 nm at a higher concentrations were obtained as presented in Fig 1 and the fiber diameter further used for this study was in the range of 392 nm. The fibre diameter increased due to a raise in polymer concentration and to insufficient stretching or elongation of the ejected jets with higher viscosity of the electrospinning solution. The beads on strings and bead formation in the electrospinning process was ascribed to lower viscosity, higher surface tension, and the low polymer concentration of the polymer solution [18,29].

Different flow rates were also investigated at 0.2, 0.4, 0.8 and 1.0 mL/h using fixed polymer concentration of 15 wt %; applied electrostatic potential of 20 kV and collection distance of 20 cm. The effect of flow rate on fibre diameter for polystyrene (PS) showed a decrease of fibre diameter (500 to 350 nm) from 0.2 mL/h up to an optimum of 0.8 mL/h flow rate, but there was an increase in fibre diameter when the flow rate was increased to 1.0 mL/h as depicted in Figure 1(b). The fibres produced at the high flow rate of 1.0 mL/h showed the bead-on-string morphology and an increased fibre diameter while too low flow rate (0.2 mL/h) of the spinning solution caused obstructions to the needle nozzles when hanging droplets appeared on the tip of the needle and dried up, thus sealing the nozzle with the solidified polymer residue. The optimal solution flow rate used for fabricating PS nanofibers was determined to be 0.8 mL/h and 15 wt % PS

concentrations in DMF:THF (4:1 v/v) were suitable for fabricating a nanofiber with well-defined structure.

Fig 1. Trend of the effect of (a) solution concentration (b) flow rate on the fibre diameter

3.2 Surface modification and morphology of PS-DGAnf

To examine and confirm the effective synthesis of PS-DGAnf, various characterisation techniques were used. The as-made and modified PS-DGAnf obtained after DGA functionalising at different reaction times of 2, 3, and 4 h was studied by HRSEM and shown in Fig. 2. The PS nanofiber mats obtained are very similar with uniform surface morphology to that of the as-made PS fibres. However, there is a slight increase in fibre diameter from 392 nm to 462 nm, 475 nm and 485 nm respectively with increased DGA reaction time during fibre modification. The smooth fibre structures were not altered due to DGA attachment, and 3 h was selected because this afforded sufficient time for the modification without denaturing the nanofiber.

Fig 2. SEM micrograph a) pristine PS b) PS-DGAnf at 2 h c) PS-DGAnf at 3 h d) PS-DGAnf at 4 h (DGA conc - 3 g; initial fibre weight - 0.109 g)

The effect of the ligand concentration on the modification of PS-DGAnf was investigated and showed smooth fibres with no beads or beads-on-strings prior to modification and afterwards but an increase in fibre diameter from 392 nm to 456 and 481 nm respectively for 2 and 3 g ligand concentration. 3 g was selected as the characteristic FTIR bands and peaks for DGA were already present as shown in Fig 3 (b). Increasing DGA concentration may result in a waste of ligands and anchoring of the ligand showed no morphological changes or damage to the PS nanofibers after the functionalisation steps. The known poor mechanical characteristics of PS adsorbents may make them susceptible to impairment [30] but as revealed from the HRSEM, the fibres remained

smooth and still retained their fibre structure up to 4 h of functionalisation time. Physical examination showed no mechanical damage to the fibre.

3.3 Characterisation of PS-DGAnf

The effective functionalisation of PS nanofiber with the diglycolic acid moiety was confirmed by FT-IR spectroscopy. As depicted in Fig. 3, the FTIR spectrum in Fig 3a identified aromatic C-H bond stretching vibrations at 1601; 1493; 1453 cm^{-1} , deformation of the aromatic ring CH_2 and C=C at 1026 cm^{-1} ; 756 cm^{-1} which confirmed the presence of the main characteristic peaks of PS. Fig 3b depicts the FTIR spectrum of the two C=O groups of DGA band at 1800 -1700 cm^{-1} that is related to the stretching vibrations. The bands due to the scissoring vibrations of CH_2 groups are observed in the 1425 cm^{-1} range.

Fig 3. FTIR spectra of a) Pristine PS, b) DGA and c) PS-DGAnf (time - 240 mins; PS fibre weight - 0.109 g; temp - 43 °C; 5 mL acetic acid; 40 mL 99% methanol) d) regenerated-PS-DGAnf (Vol - 10 mL; time - 1 h; rpm - 240; Conc - 1.0M of HNO_3)

Fig 3c depicts the spectra of the functionalised nanofibers and the presence of C=O groups on the PS polymer matrix. The carbonyl ($-\text{C}=\text{O}$) group stretching vibration peak at 1737 cm^{-1} , 1128 cm^{-1} and 1227 cm^{-1} confirmed the successful functionalisation of PS nanofiber with DGA while the $-\text{CH}_2$ bending peak at 1454 cm^{-1} of the polymer support confirmed the presence of PS backbone structure. The PS-DGAnf spectra exhibited a very strong peak at 1737 cm^{-1} that is representative of the C-O stretch. The adsorption band at 1227 cm^{-1} could possibly be allotted to the asymmetric stretching of the C-O and C-C bonds attached to the carbonyl carbon while the band at 1128 cm^{-1} may be due to vibrations relating to the two carbons and oxygen attached to the chain. PS-DGAnf was shaken in 1.0 M of HNO_3 for 1 h to mimic the conditions utilised for batch desorption testing. As shown in Fig 3d, the peak positions and shapes were consistent with Fig 3c (PS-DGAnf) after the nitric acid regeneration test. These results indicate that the chemical modification and structure of the PS-DGAnf were not adversely affected by any chemical destruction or degradation up to 1.0 M nitric acid after 1 h exposure.

The TGA thermograms weight loss curve of electrospun PS nanofiber showed that PS nanofibers (Fig. 4) only started losing their thermal stability at temperatures around 215 °C and were completely pyrolysed at 487 °C in two steps. However, the PS-DGAnf TGA thermograms showed loss of a small amount of mass at 80-100 °C due to the solvent used because oxygen-containing functional groups of DGA resulted in water adsorption and thus, some mass loss below 100 °C was expected. The second weight loss between 215 and 350 °C, corresponded to CO₂, CO, and steam released from the labile oxygen containing functional groups. The additional mass loss between 405 and 498 °C was ascribed to the degradation of more stable oxygen functionalities which was an indication of the independent decomposition of components (PS nanofiber; DGA functionalities) in the modified nanofiber adsorbent.

Fig 4. (a) TGA profile (b) TGA derivatives of pristine PS and PS-DGAnf

The TGA results showed good attachment of DGA onto PS. Thus, the TGA result confirmed that the surface of PS-DGAnf was successfully functionalised with DGA. PS and PS-DGAnf reached a char value of about 40.5 wt. % at 500 °C. [The amount of DGA adsorbed onto the PS nanofiber was gravimetrically determined by TGA and was estimated to be 0.827 g g⁻¹.](#) This deduction was made from the TGA profile as shown in Figure 4 using the mass of ligand immobilised per gram of PS-DGAnf. The N₂ BET adsorption–desorption characterisation in Fig 5a depicts the N₂ adsorption–desorption isotherm for PS, showing a substantial uptake of nitrogen because of the capillary condensation in the range of 0.6 to 0.99 at relative pressure (P/P_o) which is indicative of multiform distribution of the interfiber pores. The BET surface area of PS-DGAnf (67.3 m²/g) was higher than that of the pristine PS (41.3 m²/g).

Fig 5. N₂ adsorption–desorption isotherm for (a) PS and (b) PS-DGAnf. (Inset) Pore size distribution of PS and PS-DGAnf

Figure 5b shows that PS-DGANf has a hysteresis loop at relative pressure which is >0.8 . This hysteresis loop Type H₁ which is associated with porous materials that consist of compacts or agglomerates in fairly regular array and of approximately uniform spheres [31]. The average pore diameter between the as-made nanofibers was measured to be 8.86 nm in the range of 1 to 18 nm. The measured PS-DGANf average pore diameter was 13.2 nm in the range of 6 to 23 nm. The average pore size between fibres of surface modified PS-DGANf was higher than that of untreated nanofiber and could be associated with crosslinking between ligand and the nanofiber matrix and the creation of mesopores between adjacent nanofibers. The nitrogen adsorption–desorption isotherm for the PS-DGANf may be assigned to a type V isotherm [32] and the porous structure and large specific surface area showed that the PS-DGANf will have prospective applicability in adsorption or separation.

3.4 Batch adsorption studies

The feasibility of PS-DGANf as adsorbent was demonstrated for the removal of rare earth metals, (Ce^{3+} and Nd^{3+}) from solution. The removal and extraction effectiveness can be studied by using several factors as described below. The pH experiment was manually adjusted to a pH ranging between 1 to 6 with 0.1 M HNO_3 or NaOH solution. In previous studies, precipitation was noticeable at a higher pH than 6 [33] due to the speciation of REEs. Therefore, this study was limited to a maximum pH of 6.

Fig 6. Dependence of Nd^{3+} and Ce^{3+} adsorption on pH of solution using PS-DGANf (contact time - 120 min; Ce^{3+} or Nd^{3+} concentration - 100 mg/L; adsorbent dosage - 0.0075 g/10 mL)

Fig 6 displays an initial low adsorption capacity of Ce^{3+} at very low pH values, since the active sites on PS-DGANf are mostly protonated. But as the pH increases, the H^+ ions concentration decreased leading to less protonation and increased vacant sites available for metal ion adsorption. Nd^{3+} adsorption improved after pH 4 and increased rapidly up to pH 6 while Ce^{3+} adsorption started from pH 3 and increased gradually up to pH 6. The adsorption reached the maximum amount of

44.42 or 79.86 mg g⁻¹ for Ce³⁺ or Nd³⁺ at pH 6, respectively. The pH of 6 was used to monitor the adsorption for Ce³⁺ or Nd³⁺ from synthetic aqueous solutions for subsequent adsorption studies in order to avoid metal hydroxide formation. The dependence of Ce³⁺ and Nd³⁺ adsorption on the increasing pH of the solution suggested that the carboxylic groups progressively formed carboxylate functions that can bind metal cations by chelation [34].

The PS-DGAnf adsorbent functionality with the large number of active sites was investigated for the interaction with Ce³⁺ or Nd³⁺ ions by testing the solution concentration to understand the adsorption capacity. The different initial concentrations of the metal ions investigated ranged from 60 to 180 mg/L while other factors, such as equilibration time, pH and adsorbent quantity, were kept constant. At a concentration of metal ion of 100 mg/L, there were sufficient sites for all the available metal ions, and on increasing the concentration, there was an increased adsorption up to 140 mg/L indicating enhanced capacity. The attained results indicated that binding efficiency increased together with increased metal ion concentrations up to 140 mg/L until the equilibrium was reached. As shown in Fig. 7, the equilibrium was reached at metal ion concentrations of between 140 and 180.0 mg/L because of the saturation of the available ligand binding sites present on the PS-DGAnf. This increase in uptake with a rise in concentration may be associated with the large surface area and the numerous vacant binding sites upon inter fibrous pores of the nanofibers. The high uptake capacities observed was mainly due to the specific interaction between the metal ion and the functional groups on the nanofiber surface since only a negligible amount of the target metal ions was adsorbed by pristine PS nanofibers (not shown). The maximum adsorption capacities of Ce³⁺ or Nd³⁺ ions on the PS-DGAnf were 152.0 or 144.0 mg g⁻¹ respectively indicating that the available sites were fully occupied.

Fig 7. Adsorption isotherm models fitted to experimental adsorption of (a) Ce³⁺ (b) Nd³⁺ onto PS-DGAnf (contact time - 90 min; initial concentrations - 60 to 180 mg/L; pH - 6; adsorbent dosage - 0.0075 g /10 mL)

The adsorption isotherms were analysed by using Langmuir and Freundlich models [35,36] to interpret and elucidate the experimental data and matching parameters associated with the models are illustrated in Table 1. The maximum Langmuir adsorption capacities (q_e) for Ce^{3+} or Nd^{3+} were 152.5 mg g^{-1} (1.09 mmol/g) or 146.2 mg g^{-1} (1.01 mmol/g) respectively. This number is very close to the measured values of 152.1 mg g^{-1} (1.09 mmol/g) for Ce^{3+} ; and 144.0 mg g^{-1} (0.998 mmol/g) for Nd^{3+} at the C_e of 140 mg/L , indicating the dependability of q_e value.

Table 1. Parameters obtained from the plot of Langmuir and Freundlich isotherms for Ce^{3+} or Nd^{3+} adsorption using PS-DGAnf.

The correlation coefficient R^2 values for the Langmuir equation were 0.999 or 0.992 for Ce^{3+} or Nd^{3+} respectively which indicated that the Langmuir isotherm was better fitted to the experimental data than the Freundlich model and could better explain the Ce^{3+} or Nd^{3+} adsorption process. The Langmuir advocates 3 major situations such that (i) there is no inter-action between the monolayer of molecules (ii) the intermolecular attractive forces among the adsorbate molecules in the solution and the monolayer decreases significantly with distance, and (iii) the sorption of adsorbate molecules in neighbouring sites do not influence or impact the adsorption of other molecules in other adsorbing site [37], therefore, the Langmuir isotherm model suggest homogeneous binding sites on the surface of PS-DGAnf.

The evidence provided by FTIR data showed that strong adsorption is likely involved in the interactions of Ce^{3+} or Nd^{3+} with multiple carbonyl groups on the nanofiber. Hence, the Ce^{3+} and Nd^{3+} adsorption tended to be homogeneous and showed monolayer coverage, because of the strong interactions between the surface functional groups of PS-DGAnf and Ce^{3+} and Nd^{3+} which is also consistent with the much higher K_d value (Fig. 8). The sorption properties of the nanofiber adsorbents for Ce^{3+} or Nd^{3+} were matched to the sorption capacities of alternative or commercial sorbents also fitted by the Langmuir model which are typically adopted in the studies of adsorbents for the extraction of REEs. Due to the different bulk and surface properties, it was difficult to

perform a fair comparison. However, the data in Table 2 still provided useful information especially on the order of magnitude of removal of the metal ions.

Table 2. Sorption capacities of different sorbents in comparison to PS-DGAnf

The adsorption capacity (q_e) value of PS-DGAnf is competitive with and outperforms other adsorbents when compared with the previously reported adsorbents. Even though some materials such as phosphoric acid functionalised adsorbents [43], calcium alginate–poly glutamic acid [42], Chitosan/Polyvinyl Alcohol/3-mercaptopropyltrimethoxysilane beads [45] or impregnated alginate microcapsules [44] showed considerably higher sorption levels than those achieved with PS-DGAnf, their modification and synthesis was more complex. These new nanofiber adsorbents have improved sorption capacities and rapid kinetics (Section 3.5) when compared to other similar conventional adsorbents, and were made using a simple, one-step grafting procedure to obtain the functionalised adsorbents. Ogata et al [16] clarified the adsorption mechanism of immobilized diglycolic amic acid ligands by showing that adsorbents with diglycolic amic acid ligands adsorb REE ions via three oxygen atoms and that the tridentate chelation conferred high selectivity for REE ions.

The REE cations are strong Lewis acids and easily coordinate nucleophiles to form stable complexes and they show a clear tendency towards oxygen donors which is advantageous for their efficient extraction. The derivatives of DGA are used for the selective extraction of REEs from aqueous solutions, because they are recognised as effective and size selective binders of trivalent f-elements [49]. The structural analysis of complexes bearing the DGA ligands shows that REEs bind traditionally in a tridentate fashion, where each metal ion is coordinated by the three oxygen atoms of DGA-type ligands. The lanthanide ions (e.g., La, Nd, Ce) are sterically saturated in their nine-coordinate geometry with three DGA ligands [50]. Therefore, by the right tailoring of chemically similar chelating ligands and their grafting on solid supports, it is possible for functional materials to exhibit selective affinities for smaller or larger ions [51,52].

The distribution coefficient values as a function of initial concentration is shown in Fig. 8 and the values are between ca. 10251 to 3000 mL/g and 10400 to 3300 mL/g for Ce^{3+} or Nd^{3+} , respectively. The high values of K_d represents more effective adsorbent for the separation of REEs [53]. For the PS-DGAnf studied, the K_d value is attributed to the chelation mechanism of diglycolic amic acid and the distribution coefficient values for Ce^{3+} or Nd^{3+} are higher or showed similar values to several studies reported in literature [10,54–56]. Demir et al, [28] reported a high K_d value ca. 30,000 mL/g for Nd at higher pH using carboxylic acid functionalized porous aromatic frameworks though the value dropped to below 20 at a lower pH. Roosen and Binnemans [46] also reported high K_d values for Nd(III) and Dy(III) at about 10000 mL/g with DTPA chitosan-based sorbents which dropped below 1000 mL/g at pH 2.

Fig. 8. Dependence of distribution coefficient (K_d) on initial concentration of Ce^{3+} or Nd^{3+} in the equilibrium adsorption study.

3.5 Effect of contact time

Another important parameter investigated was contact time which could be used for evaluating the adsorption kinetics. The result showed that the adsorption rate increased sharply within the first minute before the rate of adsorption slowed down gradually to attain the maximum equilibrium within 10 mins for Ce^{3+} and 20 min for Nd^{3+} ions as represented in Fig. 9. The fast adsorption rate during the first 10 min was associated with the high number of vacant surface sites of the nanofiber adsorbent available during the adsorption of the metal ions. Within the first 20 min, the amount adsorbed reached 119.4 mg g^{-1} Ce^{3+} and 108.4 mg g^{-1} Nd^{3+} of the available concentration of metal ions present in the solution. Hence, a contact time of 20 min was adequate to reach equilibrium for PS-DGAnf.

The high adsorption rate was attributed to low diffusional constraints as well as the high surface area and numerous binding sites of PS-DGAnf. After 20 mins, no further adsorption occurred on the adsorbent due to limited supply of metal ions in solution as more than 90 % of the adsorbate was removed from solution. The short time required to attain equilibrium shows that the PS-

DGANf has a great potential and very high adsorption efficiency for Ce^{3+} or Nd^{3+} uptake when compared to other adsorbent surface modification using diglycolic-based selective ligands which reported fast metal binding kinetics toward REEs [10,15,57].

Fig 9. The effect of contact in the time removal efficiency of (a) Ce^{3+} (b) Nd^{3+} from aqueous solution by PS-DGANf (Ce^{3+} or Nd^{3+} concentration - 100 mg/L; pH - 6; adsorbent dosage - 0.0075 g /10 mL)

3.6 Desorption and reusability studies

The regeneration and desorption cycle of an adsorbent is crucial and essential for its possible practical application. The reusability of PS-DGANf for Ce^{3+} or Nd^{3+} was studied by evaluating four consecutive cycles using 1 M HNO_3 solution as regenerant and the results are depicted in Fig 10. The nanofibers retained high uptake capacity after the third and the fourth cycles of adsorption-desorption. PS-DGANf maintained up to 92 % capacity for the removal of Nd^{3+} after 4 cycles and was able to maintain capacity for Ce^{3+} uptake up to 96.7 % of the initial concentration after four adsorption-desorption cycles. The key objective of the regeneration and desorption procedure was to reinstate the adsorption capacity of the used adsorbent and to recover valued metal ions existing in the adsorbed phase. These results compare favourably to the study by Galhoum et al. (2017) [34] which used nitric acid (0.5 M solution) as regenerant to desorb Nd^{3+} from loaded sorbents. Regeneration was carried out with 1 M HNO_3 to desorb the metal ions taken up on the adsorbent for reuse without disrupting the ligand attached. It was considered that the desorption by HNO_3 is caused by ion exchange reaction between protons and adsorbed ions and this stripping agent was earlier tested for ligand stability to confirm whether the functional fibers can withstand its short term contact.

Fig 10. Desorption efficiency for Ce^{3+} or Nd^{3+} from PS-DGANf for three cycles of adsorption-desorption (initial concentration - 100 mg/L; adsorbent dosage - 0.0075 g/10 mL; stripping agent - 1 M HNO_3 ; desorption time - 60 min).

3.7 Selective adsorption

To investigate the selectivity of the PS-DGANf toward Ce^{3+} , the selective adsorption study was carried out in an aqueous solution containing mixed ions of Ce^{3+} , Co^{2+} , Ni^{2+} and Sr^{2+} . Similarly, the adsorption of the different metal ions in solutions of single ions using PS-DGANf was also evaluated. The amount of every single metal ion sorbed onto the PS-DGANf was calculated and the results are summarised in Table 3. The amount of Ce^{3+} adsorbed despite the existence of competing ions was 100.3 mg g^{-1} , which was only slightly lower (119.4 mg g^{-1}) than what was obtained in the single ion solution. The selectivity was attributed to the low amount of competing adsorption of other different metal ions such as Co^{2+} , Ni^{2+} and Sr^{2+} present in solution which is suggested to have led to a small alteration in the Ce^{3+} adsorption equilibrium. The high selective adsorption coefficient revealed that the PS-DGANf showed much higher selectivity toward Ce^{3+} in the modelled solution than to the other metals investigated. The PS-DGANf depicted better adsorption selectivity toward Ce^{3+} over other metal ions which may be related to the chelating bonding orbital and the ion radius of the different metal ions. The N_2 BET adsorption–desorption characterisation indicated a porous structure for the adsorbent and the surface area was large enough to result in a high adsorption rate compared to the pristine nanofiber adsorption (not shown). The high selectivity for the rare earth elements was therefore attributed to chelation by the tridentate diglycolic acid framework. PS-DGANf containing diglycolic acid exhibit higher extraction of trivalent lanthanides such as Ce^{3+} compared to divalent metal ions and this finding solves the first major challenge for the REE industry, which is the separation of REEs from base metals [61]. The co-existence in solution of selected metal ions did not significantly interfere with the adsorption of REEs binding to PS-DGANf as can be deduced from the high selectivity coefficient.

Table 3. Selectivity coefficients (S) and adsorption capacities of diverse metal ions in solution using PS-DGANf (Contact time - 200 rpm for 1 h; concentration - 100 mg/L; pH - 6; solution pH 6; adsorbent dosage - 0.0075 g /10 mL)

Ce³⁺ was selected for the experiments because both dynamic and equilibrium experiments indicated that the nanofiber adsorbents had very comparable sorption properties and capacities for the two REEs (Ce³⁺ and Nd³⁺) signifying that a selective separation between different REEs may be challenging at the metal-binding equilibrium due to their close sorption capacities as shown previously in Table 1. Their individual differences were therefore not large enough and would therefore require more enrichment steps to achieve metal separation between these two REEs. The selective separation and extraction of dilute rare earth metal ions from solutions containing higher concentrations of base metal ions is necessary in the recovery process of rare earth elements from low grade ores and scrap. This adsorbent, PS-DGAnf can therefore be useful for the recovery and separation of REEs from base metals.

3.8 Conclusions

A novel electrospun polystyrene diglycolic acid (PS-DGAnf) nanofiber adsorbent for the efficient and selective adsorption of Nd³⁺ and Ce³⁺ ions was prepared by electrospinning of PS nanofibers, which were chemically modified with diglycolic anhydride (DGA) via an electrophilic aromatic substitution of the ligand onto the PS nanofiber. The optimum polystyrene electrospinning conditions for the experiments were obtained under the operating conditions of concentration (15 wt %); voltage (17 kV); solution flow rate (0.8 mL/h) and collector distance of 15 cm. The advantages of the stable and selective ligand on the nanofiber and high DGA loading of 0.827 g g⁻¹ with fast kinetics make PS-DGAnf nanofiber structure an efficient and selective adsorbant of rare earth metals such as Ce³⁺ and Nd³⁺ ions. The electrospinning and modification of PS-DGAnf was confirmed by ATR-FTIR, HR-SEM, BET and TGA techniques. The kinetic study of PS-DGAnf showed that maximum equilibrium could be attained within 15 mins of the adsorption process. The adsorption at pH 6.0 of Ce³⁺ and Nd³⁺ ions with the maximum equilibrium uptake capacity of 152.5 mg g⁻¹ (1.09 mmol/g) of Ce³⁺ and 146.2 mg g⁻¹ (1.01 mmol/g) of Nd³⁺ respectively was well fitted to the Langmuir isotherm equation. Furthermore, the PS-DGAnf showed higher affinity toward trivalent Ce³⁺ than to other common divalent metal ions such as Co²⁺, Ni²⁺ and Sr²⁺. This PS-DGAnf could be regenerated successfully and retained high uptake capacity in aqueous solution of 0.1M HNO₃ with no significant loss of capacity after four successive cycles. The developed

electrospun polystyrene diglycolic acid nanofiber adsorbents can be utilised for the rapid and selective recovery and separation of rare earth metals ions from base metals in aqueous solution.

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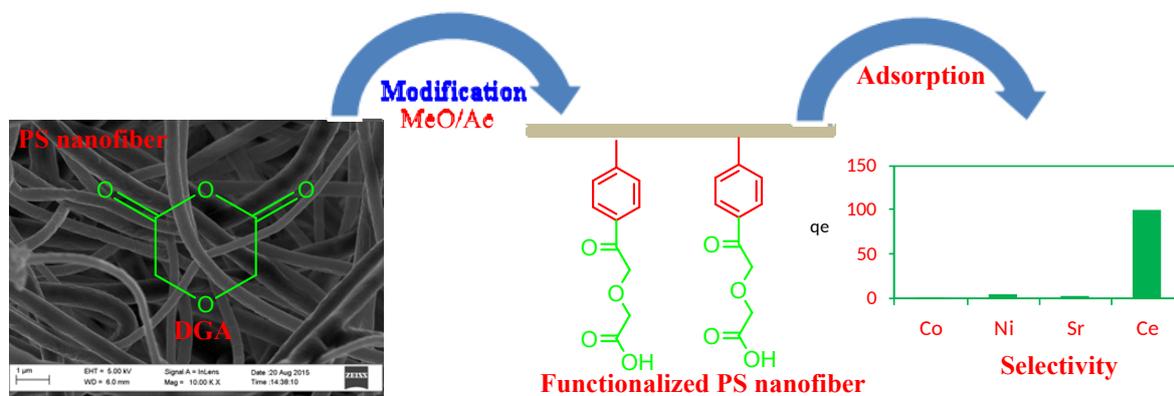
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Highlights

- Describes the synthesis of electrospun polystyrene diglycolic acid nanofiber adsorbent
- The adsorption capacity of PS-DGAnf for Ce^{3+} and Nd^{3+} was as high as 152.5 and 146.2 mg g^{-1} respectively
- Kinetic studies revealed a rapid adsorption within 15 mins
- PS-DGAnf showed excellent regeneration in 4 cycles using 1 M nitric acid

Graphical abstract



Adsorption of Ce³⁺ and Nd³⁺ by Diglycolic acid functionalised electrospun polystyrene nanofiber from aqueous solution

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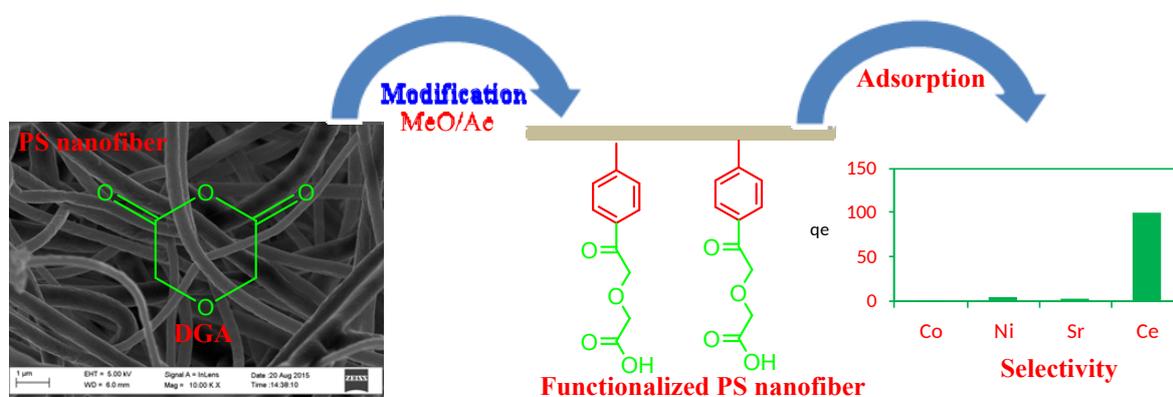
ABSTRACT

Highly selective and stable ligands with fast kinetics for rare earth element extraction are not well developed. Durable attachment of ligands to the support would make regeneration possible. Polystyrene nanofiber supports (PS-nF) were prepared using the electrospinning method. Thereafter, PS-nf were chemically modified with diglycolic anhydride (DGA) to produce novel electrospun polystyrene diglycolic acid nanofiber (PS-DGAnf) adsorbents. The immobilisation reaction proceeded via an electrophilic aromatic substitution of the ligand onto the PS nanofiber. The maximum gravimetric loading of DGA on PS nanofiber was 0.827 g g⁻¹. The unmodified and

modified nanofibers were characterised by ATR-FTIR, HR-SEM, BET and TGA. After optimising pH, time and concentration, the equilibrium adsorption and binding kinetics of cerium (Ce^{3+}) and neodymium (Nd^{3+}) ions on the nanofibers surface were examined at pH 6. The adsorption capacity of PS-DGAnf for Ce^{3+} and Nd^{3+} at pH 6.0 was 152.5 mg g^{-1} (1.09 mmol/g) and 146.2 mg g^{-1} (1.01 mmol/g) respectively. Selectivity of Ce^{3+} over Ni^{2+} , Co^{2+} and Sr^{3+} was also studied at pH 6. The amount of Ce^{3+} adsorbed even in the presence of interfering ions was 100.3 mg g^{-1} , which was only a little lower than 119.4 mg g^{-1} obtained in a single ion solution. The rapid adsorption kinetics of Ce^{3+} and Nd^{3+} ions were achieved within 15 mins. The desorption and regeneration was carried out with 1 M nitric acid and the developed PS-DGAnf adsorbent could be reused for 4 cycles without any substantial loss to its adsorption abilities.

Keywords: Polystyrene, rare-earth elements; diglycolic acid; adsorption; nanofiber, selectivity

Graphical abstract



1 INTRODUCTION

Rare earth elements (REEs) have received increased consideration in recent decades, due to their distinctive properties and diverse applications in modern technologies, particularly in the nuclear fuel control, metallurgy, and ceramic industry [1,2]. Significant amounts of cerium and cerium oxide concentrates are used in glass-polishing applications and many cerium compounds have found important uses in biomedical applications [3] while neodymium, being the first triad of the lanthanide group, is illustrative for most of the valued REEs which are used in steel modifiers,

optical filters, electronics components, superalloys, hydrogen storage and artistic glasses. Several hydrometallurgical techniques exist for the recovery and separation of REEs from aqueous solutions and these include adsorption, precipitation, ion exchange and solvent extraction [2,4,5], but disadvantages, such as the huge volume of chemical reagents needed, sludge generation, poor selectivity, and ineffective recovery from low metal concentrations [6], make obtaining the requisite rare earth metal purity very difficult.

The use of adsorbents and resins for removing or extracting rare earth metals from aqueous solutions was reported [7,8], and ligands comprising of the glycolamic acid group have been developed for REE removal. Results have indicated selectivity for the removal and recovery of REEs [9]. Diglycolic amic acid is comparable to diglycolic acid and well suited as task specific ligands capable of the removal of lanthanides [10], due to an etheric oxygen atom and two carbonyl groups as functional groups. Rare earth elements recovery using this ligand is now being reported [11,12]. In all these studies, ligands comprising of glycol amic acid exhibited very selective and effective extraction of REEs from mixtures of other diverse metals. Adsorbents comprising of glycol amic acid were utilised for scandium (Sc) separation and reported to preferentially extract Sc from a mixture [6]. Modification of *Escherichia Coli* (E. coli) through the succinylation of E. coli amine groups with the diglycolic amic acid ligand indicated high affinity to REEs [13]. Elastic diglycolic amic acid modified chitosan sponges were applied as adsorbents for the removal of REEs and reported to have fast adsorption kinetics [14]. The need for suitable supports in designing a practical adsorbent for the recovery of REE are being investigated and some research on the adsorption of REEs using diglycol amic acid immobilised using different support was published with varied results [15,16].

Nanofibers have high interfiber porosity with excellent interconnectivity, high surface area to volume ratios, layer thinness, low basis weight, controllable thickness of the electrospun scaffold, good structural stability as well as being cost effective, which make them promising materials [17]. Nanofibers can be functionalised with suitable ligands in a viable and cost effective manner [18] and these functionalised nanofibers can provide an effective, high surface area support which could be useful for waste water treatment and purification [19]. Electrospinning is a feasible technique that can be used to fabricate nanofibers of diameters in the range of 40–500 nm with the use of

electrostatic forces [20,21]. Electrospun nanofibers are produced from numerous natural or synthetic polymers, or some blends or hybrids of both types of polymers [22]. Polystyrene (PS) is a versatile synthetic polymer support, due to the large number of ligands that can be covalently bound to it [23]. Because of its outstanding physical and reactive properties, chemical resistance, ease of electrospinning, good mechanical properties and low cost, PS is well studied, but it cannot efficiently adsorb individual metal ions [24].

In this study, the surface of PS nanofibers were modified chemically using diglycolic acid chelating ligands and its effectiveness in aqueous solutions for the recovery of Ce^{3+} or Nd^{3+} was assessed by performing batch adsorption studies. The dependence of factors including contact time, pH and equilibrium concentration on Ce^{3+} and Nd^{3+} adsorption efficiency as well as selectivity was studied. The desorption of REEs from the loaded PS-DGAnf and the regeneration of the functional fibres using nitric acid was determined.

2 EXPERIMENTAL

2.1 Materials

Polystyrene (Mw ~192,000), diglycolic anhydride (90%), neodymium(III) nitrate hexahydrate (99.9%), cerium(III) nitrate hexahydrate (99.99%), N,N-dimethylformamide (DMF) ($\geq 99.8\%$), methanol ($\geq 99.9\%$), acetic acid (100%), tetrahydrofuran (THF) ($\geq 99.0\%$), HNO_3 (69%), NaOH (99.9%), strontium nitrate ($>99.0\%$) were all purchased from Sigma-Aldrich (South Africa), $NiSO_4 \cdot 6H_2O$ (98%), and $CoSO_4 \cdot 7H_2O$ (97.5%) were purchased from Merck Chemicals. Deionised water was used throughout this work. All the reagent grade chemicals were used without any further purification.

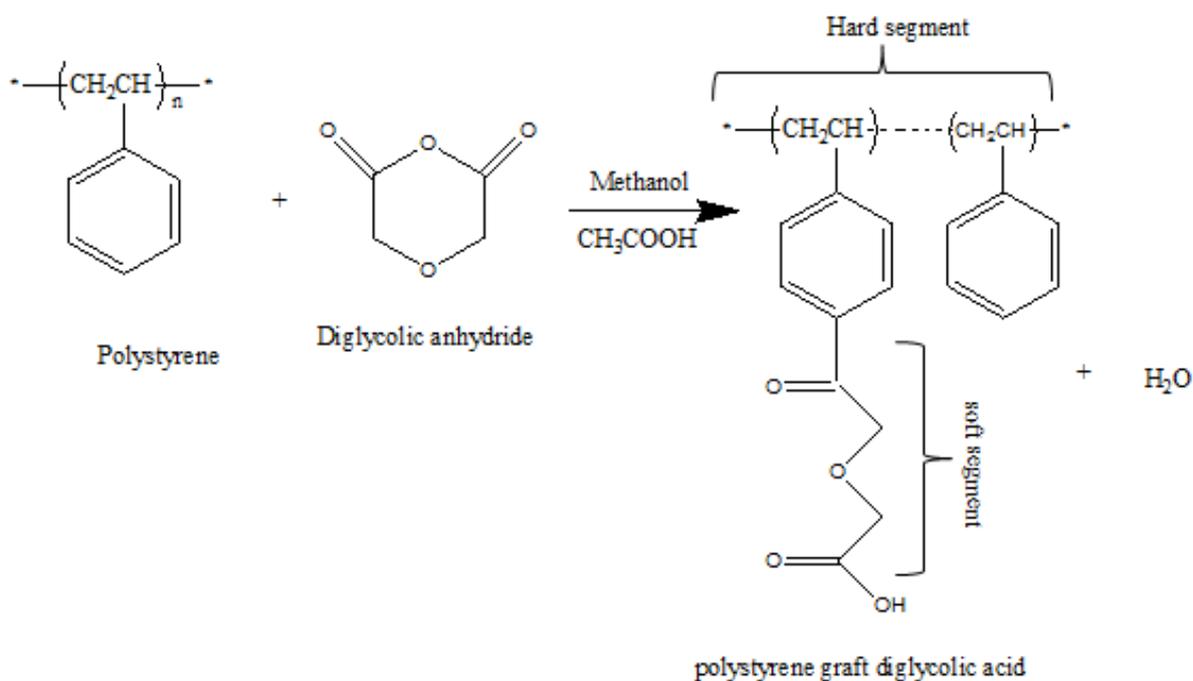
2.2 Electrospinning

Electrospinning was performed using an infusion pump (Harvard Apparatus 33 Twin Syringe Pump) and applied voltages were driven by a high voltage power supply. The PS was dissolved in a 10 mL dimethylformamide and tetrahydrofuran (DMF:THF) (4:1 v/v) solvent system. The mixture was agitated by a magnetic stirrer for 12 h to achieve a consistent and homogenous solution. The attained viscous PS solution was thereafter loaded into a 10 mL glass syringe, and mounted on the programmable infusion pump. The electrospinning procedure was carried out

under ambient conditions, and nanofibers were collected on aluminium foil as a non-woven nanofiber mat. The fibre diameter was evaluated using Image J® software. For this study, PS concentration was investigated, at varied concentration of 10, 15, 20, 25 or 30 wt % PS polymer in DMF:THF (4:1 v/v) with flow rate (1 mL/h), collector distance (17 cm) and applied voltage (20 kV) as fixed parameters. The applied flow rate was also changed from 0.2, 0.4, 0.8 to 1.0 mL/h using a fixed voltage of 20 kV, 15 wt. % PS polymer in DMF:THF (4:1 v/v) solution concentrations and a fixed tip to collector distance of 17 cm.

2.3 Surface modification of PS nanofibers

The experiments were undertaken according to previously reported chemical grafting procedures [25–27]. The reaction is an acid-catalysed process using acetic acid. First, a suitable amount of diglycolic anhydride was added to 10 mL of 5 % (v/v) aqueous acetic acid solution in 40 mL methanol (99.9%) and the reaction mixture was mechanically stirred for 30 min. To functionalise the synthesised electrospun PS with DGA, fibre mats were inserted into the stirred solution and the temperature was slowly raised to 43 °C under reflux with further constant stirring for 4 h (Scheme 1).



Scheme 1 - Modification of PS nanofiber with DGA chelating ligand

Typically, PS electrospun nanofibers were cut into 5cm by 5cm square shapes weighing 0.109 g and immersed in a mixture of different ligand concentration range of 1 to 4 g diglycolic anhydride in 10 mL of 5 % (v/v) aqueous solution of acetic acid in 40 mL methanol (99.9%) and shaken for 4 hours at 43 °C in a beaker. PS nanofibers were tested at different reaction times between 1 to 4 h in 3 g of diglycolic anhydride containing solution under the same conditions and after the reactions, the PS-DGAnf samples were washed in deionised water to remove the residual salts and any unreacted ligand and the fibres were air-dried overnight. Stability experiments were performed to determine if the optimised material (PS-DGAnf) obtained can withstand short term contact with 1M HNO₃ as regenerant for 1 h to mimic the conditions that would be used for batch desorption experiments. The fibre samples were then washed with deionised water and air dried. The modification reaction was carried out using triplicate samples for each considered parameter.

2.4 Analytical methods

Thermo Scientific-Nicolet iS10 Fourier Transform Infrared Spectrophotometer (FT-IR) equipped with diamond Attenuated Total Reflectance (ATR) was used to record spectra in the range of 4000 – 650 cm⁻¹ to assess and identify the specific functional groups on the nanofiber surfaces before and after modification. The morphology of the nanofibers was investigated using the Zeiss Gemini Auriga high resolution scanning electron microscope (HRSEM) fitted with a CDU-lead detector using 25 kV with tungsten filament. Nanofiber diameters were evaluated using Image J[®] analysis software. The nitrogen adsorption/desorption (Brunauer-Emmett-Teller (BET)) isotherms was assessed by using a Micromeritics Tristar porosity and surface area analyser fitted with a Micromeritics flowprep 060 sample degas system and was measured at -196 °C. Thermal behaviour of the fibres and stability of the immobilised ligands were investigated by thermogravimetric analyser (TGA) using STA 6000 (Perkin-Elmer Instrument Model, USA) under nitrogen. The metal ion concentration in solution before and after the adsorption experiments was acidified with 2% HNO₃ and determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The instrument used for determining the metal ion concentrations was a Varian Radial ICP-OES coupled with a High Matrix Introduction (HMI) accessory.

2.5 Batch Adsorption

The surface-modified adsorbents PS-DGANf were applied in batch studies to investigate their performance in the removal of two rare earth metals (Ce^{3+} and Nd^{3+}) from solution. For each REE, 0.0075 g of PS-DGANf was immersed in a vial of the single metal ion solution containing 10 mL of Ce^{3+} or Nd^{3+} (100 mg/L) respectively. The pH was adjusted in the range 1 to 6 by using NaOH or HNO_3 . It was then shaken for a period of 2 h using an agitation speed of 200 rpm until equilibration was reached and the solution was then filtered with 20-25 μm filters (Whatman® qualitative filter paper, Grade 4) before analysis. The ICP OES was used for the determination of the REEs concentration in the aqueous stock, and in extracted solutions. The changes between the initial and final concentration of the solutions were considered to be the concentration of metal ion adsorbed. Initial concentration was changed from 60 to 180 mg/L at pH 6.0 for studying the adsorption isotherms of Ce^{3+} or Nd^{3+} on the surface of functionalised PS-DGANf. Contact times were changed from 1 to 60 min at pH 6.0 to evaluate the efficiency of the adsorption kinetics. The initial and final readings were then calculated using Eq. (1).

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

For aqueous phase adsorption, it is a practice to calculate distribution coefficient (K_d) [28] defined using Eq. (2),

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

where: q_e is the metal ions adsorbed by the nanofiber adsorbent ($mg\ g^{-1}$). M and V are adsorbent weight and solution volume while C_o and C_e are the initial and final equilibrium solution concentrations of metal ions. To confirm the actual concentration of working solutions, negative controls (with no adsorbent) were concurrently carried out to determine the metal ion loss during the adsorption due to the glassware. The experiments were generally carried out at $22 \pm 1^\circ C$ and the entire batch experiments were performed in duplicate.

2.6 Desorption and reusability studies

To examine the feasibility of regenerating PS-DGANf, desorption studies were performed using 1 M HNO_3 for 1h. The regenerated PS-DGANf were then washed about 3 times in 10 mL portions of ultrapure water and dried on a filter using vacuum suction before reuse. The regenerated nanofiber

mats were dried at 40 °C overnight. This regeneration was repeated three times under the same adsorption and desorption conditions to determine how many regeneration cycles were possible. The desorption efficiency was calculated using Eq. (3).

$$D_E = \frac{c \times v}{q \times m} \times 100 \% \quad (3)$$

where C (mg/L) is the concentration of adsorbates in the desorption solution, q (mg g⁻¹) is the amount of adsorbate adsorbed on the nanofiber before the desorption experiment, V is the volume of the desorption solution, and m (mg) the amount of the adsorbent used in the desorption experiments.

2.7 Selective adsorption of Ce(III) and Nd(III) onto PS-DGAnf.

The metal selectivity of PS-DGAnf was examined in 15 mL plastic vials containing 10 mL of aqueous solution of various metal ions (Ce³⁺, Co²⁺, Ni²⁺ and Sr²⁺) using equal concentrations of 100 mg/L each and the nanofiber adsorbent (0.0075 g) was immersed into the solution. The fibre samples in the vials were equilibrated in a shaker operated at 200 rpm for 1 h in pH 6.0. The concentration of the various metal ions initially in solution and after adsorption was determined. The amount of metal ions adsorbed on the nanofiber sample at adsorption equilibrium (q_e, mg g⁻¹) was calculated according to Eq. (1), and the selective coefficient of K_{REE/M} was calculated using Eq. (4)

$$K^{REE_M} = \frac{q_{REE} * C_M}{q_M * C_{REE}} \quad (4)$$

where q_{eREE} and q_{eM} was the amount of REE ion and metal ions adsorbed onto PS-DGAnf at equilibrium.

3 RESULTS AND DISCUSSION

3.1 Electrospinning

The electrospinning effects on the solution polymer concentration and flow rate on the morphology and fibre diameter of polystyrene nanofibers were studied. The fibres produced at the low polymer weight percentage of 10 wt% showed that the bead-on-string morphology turned into blobs of polymer but by increasing the concentration of PS in solution, a morphological

transformation of the beaded fibres to more cylindrical fibres with average fibre diameters ranging from 350 nm to 900 nm at a higher concentrations were obtained as presented in Fig 1 and the fiber diameter further used for this study was in the range of 392 nm. The fibre diameter increased due to a raise in polymer concentration and to insufficient stretching or elongation of the ejected jets with higher viscosity of the electrospinning solution. The beads on strings and bead formation in the electrospinning process was ascribed to lower viscosity, higher surface tension, and the low polymer concentration of the polymer solution [18,29].

Different flow rates were also investigated at 0.2, 0.4, 0.8 and 1.0 mL/h using fixed polymer concentration of 15 wt %; applied electrostatic potential of 20 kV and collection distance of 20 cm. The effect of flow rate on fibre diameter for polystyrene (PS) showed a decrease of fibre diameter (500 to 350 nm) from 0.2 mL/h up to an optimum of 0.8 mL/h flow rate, but there was an increase in fibre diameter when the flow rate was increased to 1.0 mL/h as depicted in Figure 1(b). The fibres produced at the high flow rate of 1.0 mL/h showed the bead-on-string morphology and an increased fibre diameter while too low flow rate (0.2 mL/h) of the spinning solution caused obstructions to the needle nozzles when hanging droplets appeared on the tip of the needle and dried up, thus sealing the nozzle with the solidified polymer residue. The optimal solution flow rate used for fabricating PS nanofibers was determined to be 0.8 mL/h and 15 wt % PS concentrations in DMF:THF (4:1 v/v) were suitable for fabricating a nanofiber with well-defined structure.

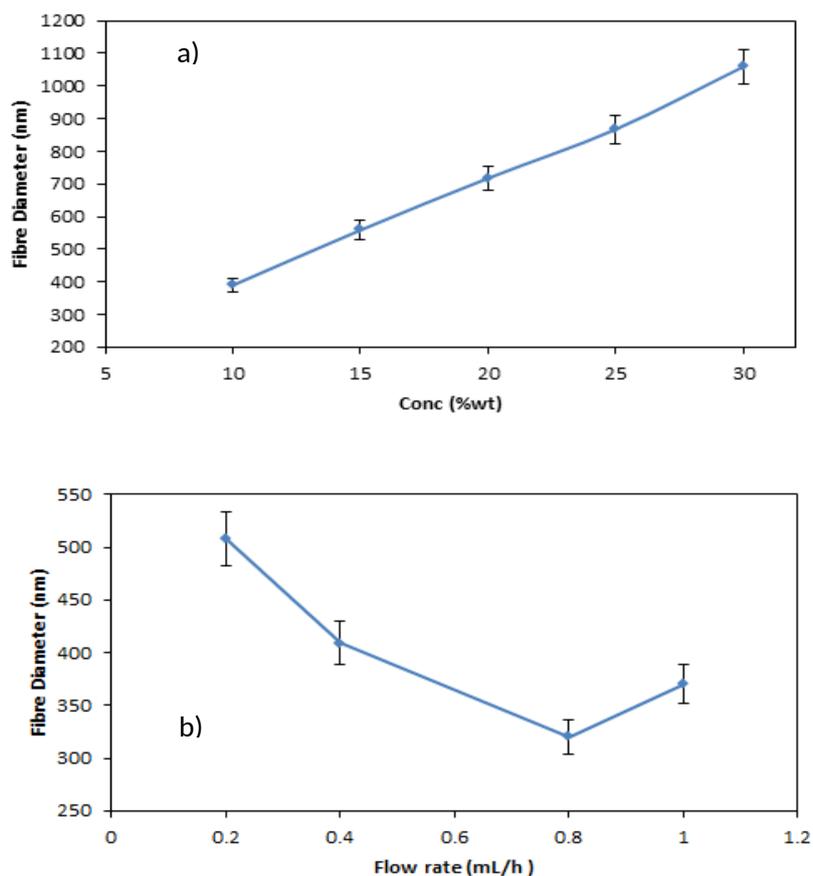


Fig 1. Trend of the effect of (a) solution concentration (b) flow rate on the fibre diameter

3.2 Surface modification and morphology of PS-DGAnf

To examine and confirm the effective synthesis of PS-DGAnf, various characterisation techniques were used. The as-made and modified PS-DGAnf obtained after DGA functionalising at different reaction times of 2, 3, and 4 h was studied by HRSEM and shown in Fig. 2. The PS nanofiber mats obtained are very similar with uniform surface morphology to that of the as-made PS fibres. However, there is a slight increase in fibre diameter from 392 nm to 462 nm, 475 nm and 485 nm respectively with increased DGA reaction time during fibre modification. The smooth fibre structures were not altered due to DGA attachment, and 3 h was selected because this afforded sufficient time for the modification without denaturing the nanofiber.

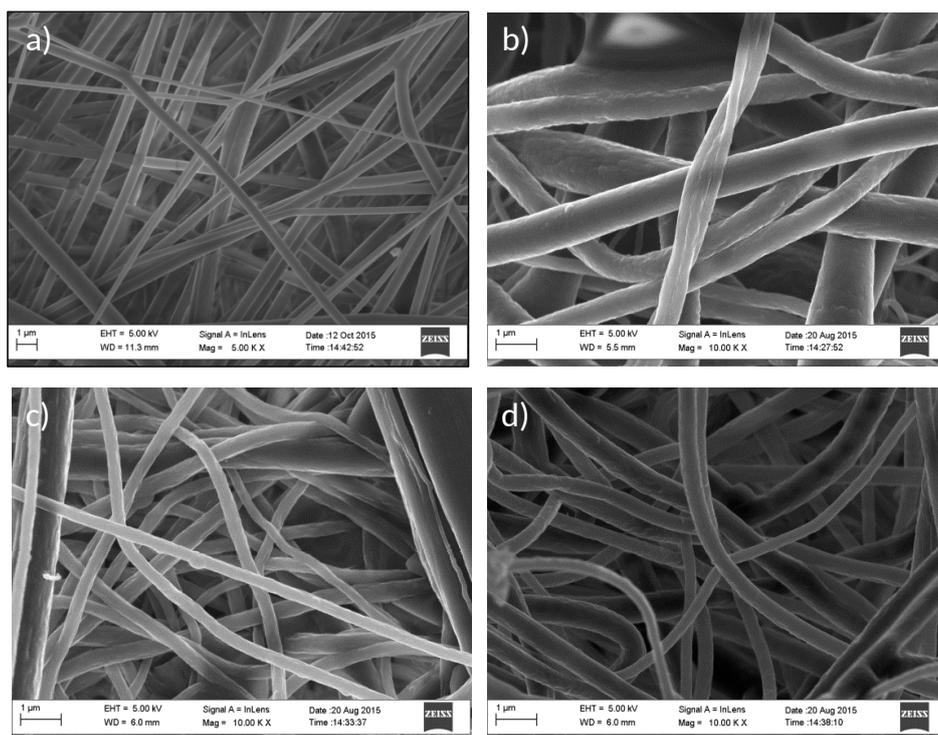


Fig 2. SEM micrograph a) pristine PS b) PS-DGAnf at 2 h c) PS-DGAnf at 3 h d) PS-DGAnf at 4 h (DGA conc - 3 g; initial fibre weight - 0.109 g)

The effect of the ligand concentration on the modification of PS-DGAnf was investigated and showed smooth fibres with no beads or beads-on-strings prior to modification and afterwards but an increase in fibre diameter from 392 nm to 456 and 481 nm respectively for 2 and 3 g ligand concentration. 3 g was selected as the characteristic FTIR bands and peaks for DGA were already present as shown in Fig 3 (b). Increasing DGA concentration may result in a waste of ligands and anchoring of the ligand showed no morphological changes or damage to the PS nanofibers after the functionalisation steps. The known poor mechanical characteristics of PS adsorbents may make them susceptible to impairment [30] but as revealed from the HRSEM, the fibres remained smooth and still retained their fibre structure up to 4 h of functionalisation time. Physical examination showed no mechanical damage to the fibre.

3.3 Characterisation of PS-DGAnf

The effective functionalisation of PS nanofiber with the diglycolic acid moiety was confirmed by FT-IR spectroscopy. As depicted in Fig. 3, the FTIR spectrum in Fig 3a identified aromatic C-H bond stretching vibrations at 1601; 1493; 1453 cm^{-1} , deformation of the aromatic ring CH_2 and $\text{C}=\text{C}$

at 1026 cm^{-1} ; 756 cm^{-1} which confirmed the presence of the main characteristic peaks of PS. Fig 3b depicts the FTIR spectrum of the two C=O groups of DGA band at $1800\text{ -}1700\text{ cm}^{-1}$ that is related to the stretching vibrations. The bands due to the scissoring vibrations of CH_2 groups are observed in the 1425 cm^{-1} range.

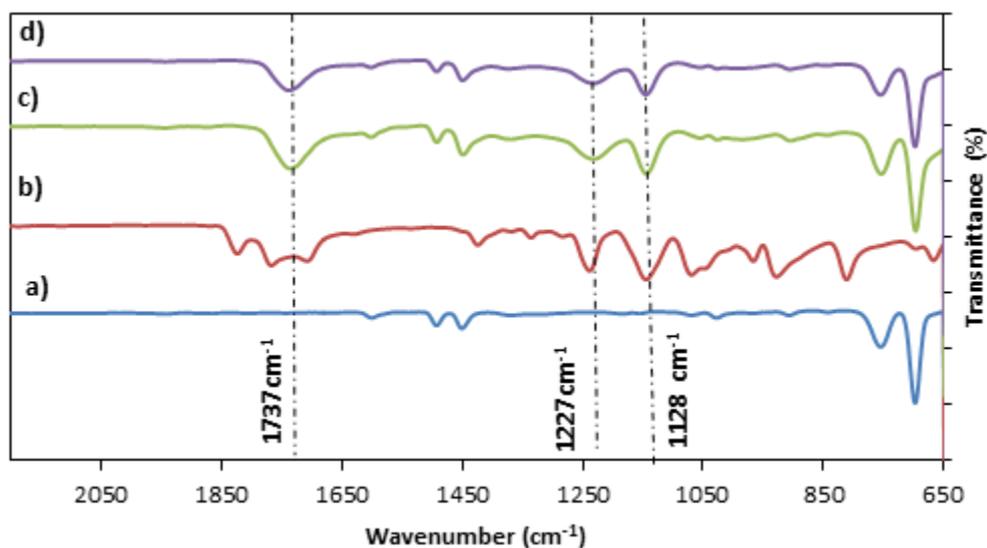


Fig 3. FTIR spectra of a) Pristine PS, b) DGA and c) PS-DGAnf (time - 240 mins; PS fibre weight - 0.109 g; temp - $43\text{ }^{\circ}\text{C}$; 5 mL acetic acid; 40 mL 99% methanol) d) regenerated-PS-DGAnf (Vol - 10 mL; time - 1 h; rpm - 240; Conc - 1.0M of HNO_3)

Fig 3c depicts the spectra of the functionalised nanofibers and the presence of C=O groups on the PS polymer matrix. The carbonyl ($-\text{C}=\text{O}$) group stretching vibration peak at 1737 cm^{-1} , 1128 cm^{-1} and 1227 cm^{-1} confirmed the successful functionalisation of PS nanofiber with DGA while the $-\text{CH}_2$ bending peak at 1454 cm^{-1} of the polymer support confirmed the presence of PS backbone structure. The PS-DGAnf spectra exhibited a very strong peak at 1737 cm^{-1} that is representative of the C-O stretch. The adsorption band at 1227 cm^{-1} could possibly be allotted to the asymmetric stretching of the C-O and C-C bonds attached to the carbonyl carbon while the band at 1128 cm^{-1} may be due to vibrations relating to the two carbons and oxygen attached to the chain. PS-DGAnf was shaken in 1.0 M of HNO_3 for 1 h to mimic the conditions utilised for batch desorption testing. As shown in Fig 3d, the peak positions and shapes were consistent with Fig 3c (PS-DGAnf) after the nitric acid regeneration test. These results indicate that the chemical modification and structure of

the PS-DGAnf were not adversely affected by any chemical destruction or degradation up to 1.0 M nitric acid after 1 h exposure.

The TGA thermograms weight loss curve of electrospun PS nanofiber showed that PS nanofibers (Fig. 4) only started losing their thermal stability at temperatures around 215 °C and were completely pyrolysed at 487 °C in two steps. However, the PS-DGAnf TGA thermograms showed loss of a small amount of mass at 80-100 °C due to the solvent used because oxygen-containing functional groups of DGA resulted in water adsorption and thus, some mass loss below 100 °C was expected. The second weight loss between 215 and 350 °C, corresponded to CO₂, CO, and steam released from the labile oxygen containing functional groups. The additional mass loss between 405 and 498 °C was ascribed to the degradation of more stable oxygen functionalities which was an indication of the independent decomposition of components (PS nanofiber; DGA functionalities) in the modified nanofiber adsorbent.

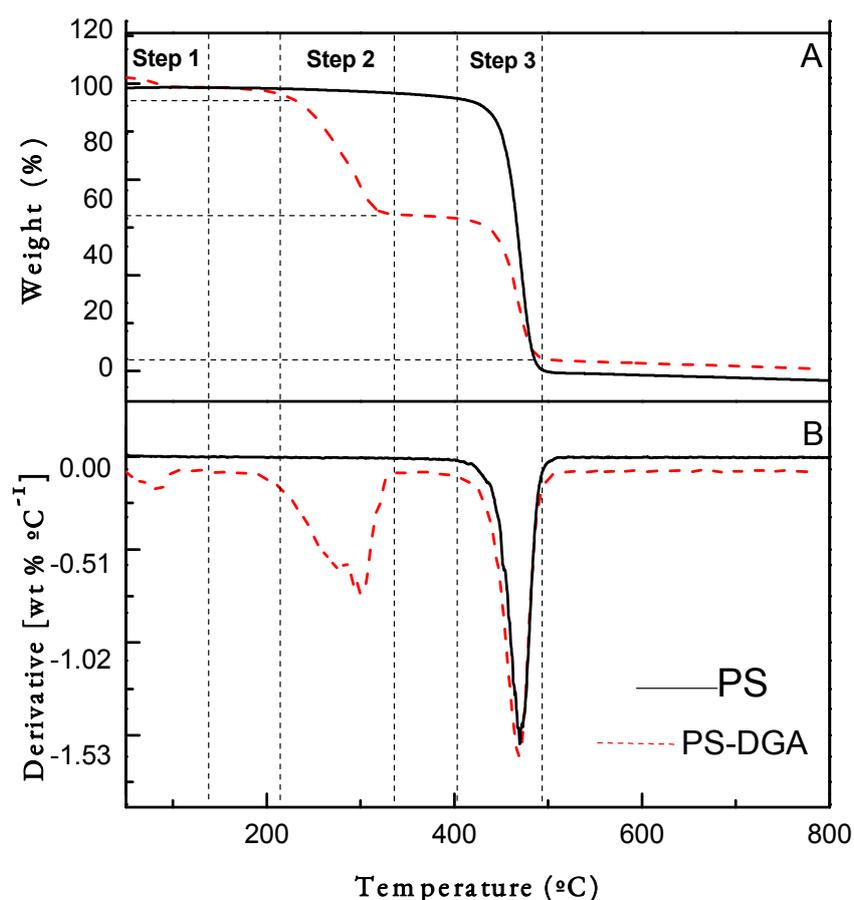


Fig 4. (a) TGA profile (b) TGA derivatives of pristine PS and PS-DGAnf

The TGA results showed good attachment of DGA onto PS. Thus, the TGA result confirmed that the surface of PS-DGAnf was successfully functionalised with DGA. PS and PS-DGAnf reached a char value of about 40.5 wt. % at 500 °C. The amount of DGA adsorbed onto the PS nanofiber was gravimetrically determined by TGA and was estimated to be 0.827 g g⁻¹. This deduction was made from the TGA profile as shown in Figure 4 using the mass of ligand immobilised per gram of PS-DGAnf. The N₂ BET adsorption–desorption characterisation in Fig 5a depicts the N₂ adsorption–desorption isotherm for PS, showing a substantial uptake of nitrogen because of the capillary condensation in the range of 0.6 to 0.99 at relative pressure (P/P₀) which is indicative of multiform distribution of the interfiber pores. The BET surface area of PS-DGAnf (67.3 m²/g) was higher than that of the pristine PS (41.3 m²/g).

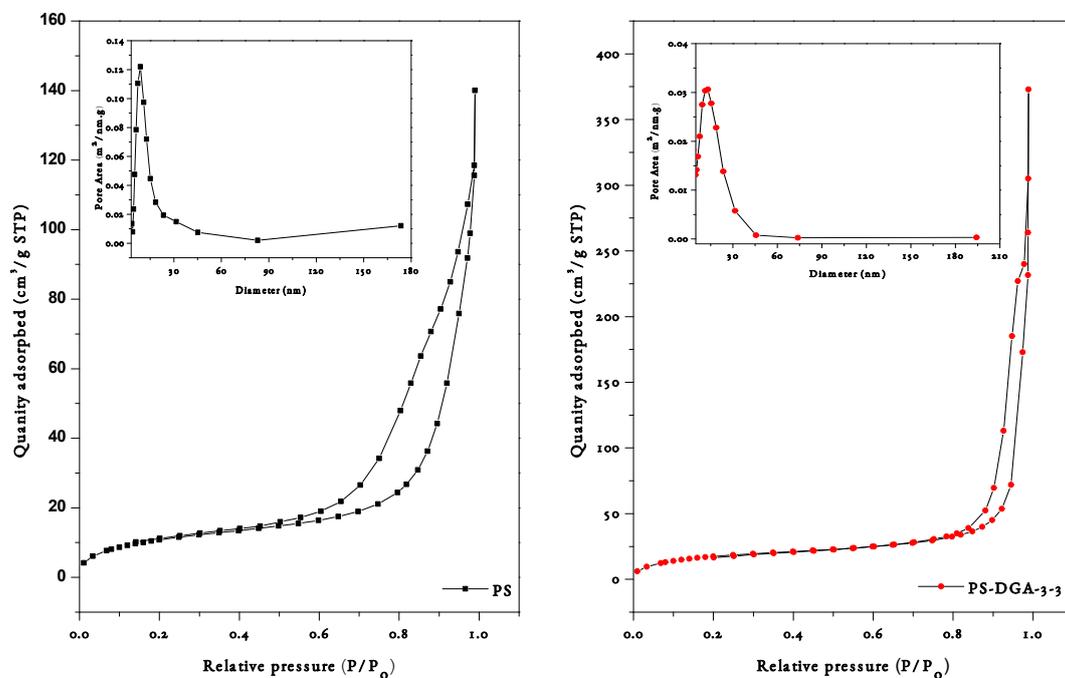


Fig 5. N₂ adsorption–desorption isotherm for (a) PS and (b) PS-DGAnf. (Inset) Pore size distribution of PS and PS-DGAnf

Figure 5b shows that PS-DGAnf has a hysteresis loop at relative pressure which is >0.8. This hysteresis loop Type H₁ which is associated with porous materials that consist of compacts or agglomerates in fairly regular array and of approximately uniform spheres [31]. The average pore diameter between the as-made nanofibers was measured to be 8.86 nm in the range of 1 to 18 nm. The measured PS-DGAnf average pore diameter was 13.2 nm in the range of 6 to 23 nm. The

average pore size between fibres of surface modified PS-DGAnf was higher than that of untreated nanofiber and could be associated with crosslinking between ligand and the nanofiber matrix and the creation of mesopores between adjacent nanofibers. The nitrogen adsorption–desorption isotherm for the PS-DGAnf may be assigned to a type V isotherm [32] and the porous structure and large specific surface area showed that the PS-DGAnf will have prospective applicability in adsorption or separation.

3.4 Batch adsorption studies

The feasibility of PS-DGAnf as adsorbent was demonstrated for the removal of rare earth metals, (Ce^{3+} and Nd^{3+}) from solution. The removal and extraction effectiveness can be studied by using several factors as described below. The pH experiment was manually adjusted to a pH ranging between 1 to 6 with 0.1 M HNO_3 or NaOH solution. In previous studies, precipitation was noticeable at a higher pH than 6 [33] due to the speciation of REEs. Therefore, this study was limited to a maximum pH of 6.

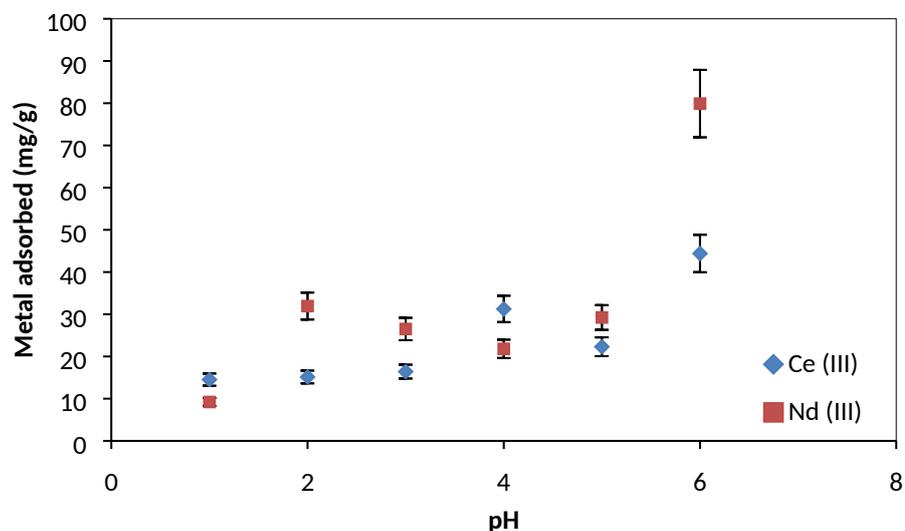


Fig 6. Dependence of Nd^{3+} and Ce^{3+} adsorption on pH of solution using PS-DGAnf (contact time - 120 min; Ce^{3+} or Nd^{3+} concentration - 100 mg/L; adsorbent dosage - 0.0075 g/10 mL)

Fig 6 displays an initial low adsorption capacity of Ce^{3+} at very low pH values, since the active sites on PS-DGAnf are mostly protonated. But as the pH increases, the H^+ ions concentration decreased leading to less protonation and increased vacant sites available for metal ion adsorption. Nd^{3+}

adsorption improved after pH 4 and increased rapidly up to pH 6 while Ce^{3+} adsorption started from pH 3 and increased gradually up to pH 6. The adsorption reached the maximum amount of 44.42 or 79.86 mg g^{-1} for Ce^{3+} or Nd^{3+} at pH 6, respectively. The pH of 6 was used to monitor the adsorption for Ce^{3+} or Nd^{3+} from synthetic aqueous solutions for subsequent adsorption studies in order to avoid metal hydroxide formation. The dependence of Ce^{3+} and Nd^{3+} adsorption on the increasing pH of the solution suggested that the carboxylic groups progressively formed carboxylate functions that can bind metal cations by chelation [34].

The PS-DGAnf adsorbent functionality with the large number of active sites was investigated for the interaction with Ce^{3+} or Nd^{3+} ions by testing the solution concentration to understand the adsorption capacity. The different initial concentrations of the metal ions investigated ranged from 60 to 180 mg/L while other factors, such as equilibration time, pH and adsorbent quantity, were kept constant. At a concentration of metal ion of 100 mg/L , there were sufficient sites for all the available metal ions, and on increasing the concentration, there was an increased adsorption up to 140 mg/L indicating enhanced capacity. The attained results indicated that binding efficiency increased together with increased metal ion concentrations up to 140 mg/L until the equilibrium was reached. As shown in Fig. 7, the equilibrium was reached at metal ion concentrations of between 140 and 180.0 mg/L because of the saturation of the available ligand binding sites present on the PS-DGAnf. This increase in uptake with a rise in concentration may be associated with the large surface area and the numerous vacant binding sites upon inter fibrous pores of the nanofibers. The high uptake capacities observed was mainly due to the specific interaction between the metal ion and the functional groups on the nanofiber surface since only a negligible amount of the target metal ions was adsorbed by pristine PS nanofibers (not shown). The maximum adsorption capacities of Ce^{3+} or Nd^{3+} ions on the PS-DGAnf were 152.0 or 144.0 mg g^{-1} respectively indicating that the available sites were fully occupied.

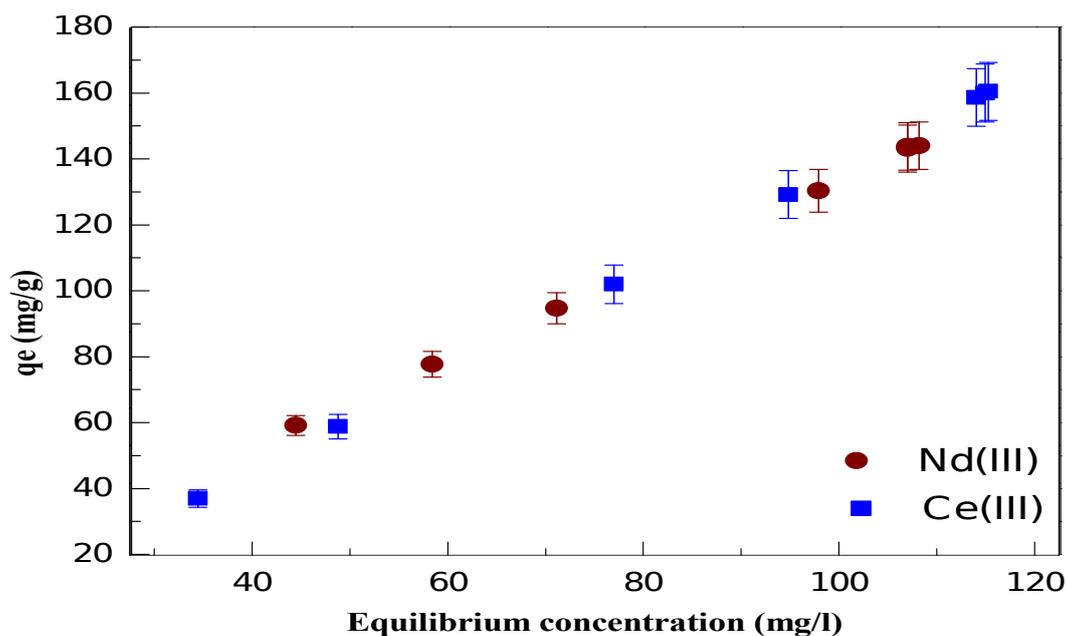


Fig 7. Adsorption isotherm models fitted to experimental adsorption of (a) Ce^{3+} (b) Nd^{3+} onto PS-DGANf (contact time - 90 min; initial concentrations - 60 to 180 mg/L; pH - 6; adsorbent dosage - 0.0075 g /10 mL)

The adsorption isotherms were analysed by using Langmuir and Freundlich models [35,36] to interpret and elucidate the experimental data and matching parameters associated with the models are illustrated in Table 1. The maximum Langmuir adsorption capacities (q_e) for Ce^{3+} or Nd^{3+} were 152.5 mg g^{-1} (1.09 mmol/g) or 146.2 mg g^{-1} (1.01 mmol/g) respectively. This number is very close to the measured values of 152.1 mg g^{-1} (1.09 mmol/g) for Ce^{3+} ; and 144.0 mg g^{-1} (0.998 mmol/g) for Nd^{3+} at the C_e of 140 mg/L, indicating the dependability of q_e value.

Table 1. Parameters obtained from the plot of Langmuir and Freundlich isotherms for Ce^{3+} or Nd^{3+} adsorption using PS-DGANf.

	Langmuir isotherm				Freundlich isotherm		
	q_e (exp) mg g^{-1}	R^2	b_1 (L/mg)	q_m (mg g^{-1})	R^2	n	k_f [(mg g^{-1}) (mg/L) $^{1/n}$]
Nd^{3+}	144.0	0.992	0.00356	146.2	0.816	2.15	14.6
Ce^{3+}	152.1	0.999	0.00013	152.5	0.988	1.12	2.10

The correlation coefficient R^2 values for the Langmuir equation were 0.999 or 0.992 for Ce^{3+} or Nd^{3+} respectively which indicated that the Langmuir isotherm was better fitted to the experimental data than the Freundlich model and could better explain the Ce^{3+} or Nd^{3+} adsorption process. The Langmuir advocates 3 major situations such that (i) there is no inter-action between the monolayer of molecules (ii) the intermolecular attractive forces among the adsorbate molecules in the solution and the monolayer decreases significantly with distance, and (iii) the sorption of adsorbate molecules in neighbouring sites do not influence or impact the adsorption of other molecules in other adsorbing site [37], therefore, the Langmuir isotherm model suggest homogeneous binding sites on the surface of PS-DGAnf.

The evidence provided by FTIR data showed that strong adsorption is likely involved in the interactions of Ce^{3+} or Nd^{3+} with multiple carbonyl groups on the nanofiber. Hence, the Ce^{3+} and Nd^{3+} adsorption tended to be homogeneous and showed monolayer coverage, because of the strong interactions between the surface functional groups of PS-DGAnf and Ce^{3+} and Nd^{3+} which is also consistent with the much higher K_d value (Fig. 8). The sorption properties of the nanofiber adsorbents for Ce^{3+} or Nd^{3+} were matched to the sorption capacities of alternative or commercial sorbents also fitted by the Langmuir model which are typically adopted in the studies of absorbents for the extraction of REEs. Due to the different bulk and surface properties, it was difficult to perform a fair comparison. However, the data in Table 2 still provided useful information especially on the order of magnitude of removal of the metal ions.

Table 2. Sorption capacities of different sorbents in comparison to PS-DGAnf

Sorbent	Metal	pH	time (h)	Adsorption capacity ($mg\ g^{-1}$)	Reference
Arthrospira cyanobacteria	Ce^{3+}	5.5	1	38.2	[38]
Hybrid nano-material	Ce^{3+}	5	3.5	130	[39]
Amino Phosphate Nano TiO_2	Ce^{3+}	6	1.5	21.39	[40]
Aminomethylphosphonic acid modified chitosan	Nd^{3+}	5	7	30.32	[41]

Calcium alginate–poly glutamic acid	Nd ³⁺	3.5	24	237.99	[42]
Phosphoric acid on silica matrix	Nd ³⁺	6	24	160	[43]
Aspartic acid grafted Cellulose	Nd ³⁺	5	3	81.2	[34]
Extractant impregnated alginate microcapsules	Nd ³⁺	4	20	149.3	[44]
chitosan/ polyvinyl/Alcohol/3-mercapto Beads	Ce ³⁺	5	6	251.41	[45]
EDTA and DTPA-functionalised chitosan	Nd ³⁺	4	3	74 77	[46]
Phosphorous functionalized nanoporous carbon	Nd ³⁺	-	1	335.5	[47]
4-dodecyl-6-((4-(hexyloxy)phenyl)diazanyl) benzene-1,3-diol mesoporous silica nano-composite	Ce ³⁺	2.5	2	150.37	[48]
PS-DGAnf	Nd ³⁺	6	0.4	146.2	This work
PS-DGAnf	Ce ³⁺	6	0.4	152.5	This work

The adsorption capacity (q_e) value of PS-DGAnf is competitive with and out performs other adsorbents when compared with the previously reported adsorbents. Even though some materials such as phosphoric acid functionalised adsorbents [43], calcium alginate–poly glutamic acid [42], Chitosan/Polyvinyl Alcohol/3-mercaptopropyltrimethoxysilane beads [45] or impregnated alginate microcapsules [44] showed considerably higher sorption levels than those achieved with PS-DGAnf, their modification and synthesis was more complex. These new nanofiber adsorbents have improved sorption capacities and rapid kinetics (Section 3.5) when compared to other similar conventional adsorbents, and were made using a simple, one-step grafting procedure to obtain the functionalised adsorbents. Ogata et al [16] clarified the adsorption mechanism of immobilized

diglycolic amic acid ligands by showing that adsorbents with diglycolic amic acid ligands adsorb REE ions via three oxygen atoms and that the tridentate chelation conferred high selectivity for REE ions.

The REE cations are strong Lewis acids and easily coordinate nucleophiles to form stable complexes and they show a clear tendency towards oxygen donors which is advantageous for their efficient extraction. The derivatives of DGA are used for the selective extraction of REEs from aqueous solutions, because they are recognised as effective and size selective binders of trivalent f-elements [49]. The structural analysis of complexes bearing the DGA ligands shows that REEs bind traditionally in a tridentate fashion, where each metal ion is coordinated by the three oxygen atoms of DGA-type ligands. The lanthanide ions (e.g., La, Nd, Ce) are sterically saturated in their nine-coordinate geometry with three DGA ligands [50]. Therefore, by the right tailoring of chemically similar chelating ligands and their grafting on solid supports, it is possible for functional materials to exhibit selective affinities for smaller or larger ions [51,52].

The distribution coefficient values as a function of initial concentration is shown in Fig. 8 and the values are between ca. 10251 to 3000 mL/g and 10400 to 3300 mL/g for Ce^{3+} or Nd^{3+} , respectively. The high values of K_d represents more effective adsorbent for the separation of REEs [53]. For the PS-DGAnf studied, the K_d value is attributed to the chelation mechanism of diglycolic amic acid and the distribution coefficient values for Ce^{3+} or Nd^{3+} are higher or showed similar values to several studies reported in literature [10,54–56]. Demir et al, [28] reported a high K_d value ca. 30,000 mL/g for Nd at higher pH using carboxylic acid functionalized porous aromatic frameworks though the value dropped to below 20 at a lower pH. Roosen and Binnemans [46] also reported high K_d values for Nd(III) and Dy(III) at about 10000 mL/g with DTPA chitosan-based sorbents which dropped below 1000 mL/g at pH 2.

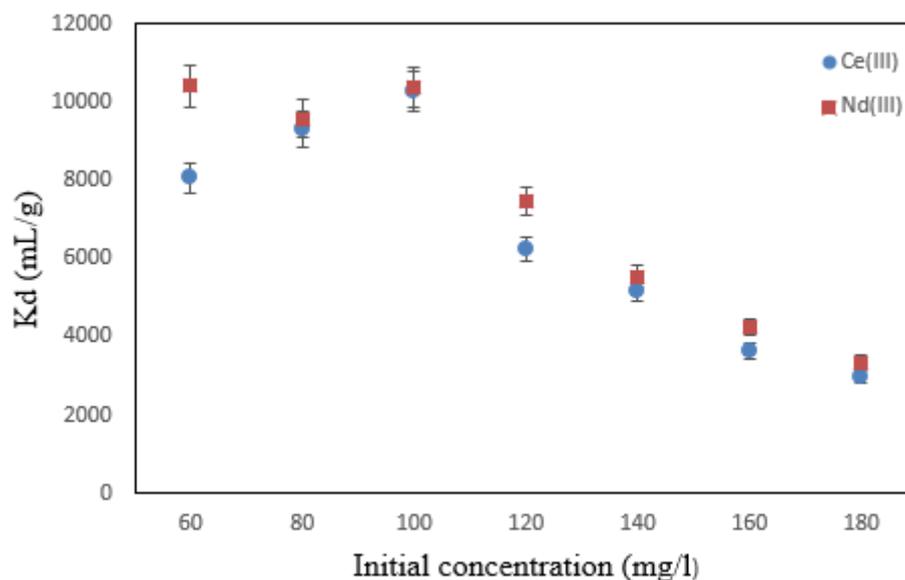


Fig. 8. Dependence of distribution coefficient (K_d) on initial concentration of Ce^{3+} or Nd^{3+} in the equilibrium adsorption study.

3.5 Effect of contact time

Another important parameter investigated was contact time which could be used for evaluating the adsorption kinetics. The result showed that the adsorption rate increased sharply within the first minute before the rate of adsorption slowed down gradually to attain the maximum equilibrium within 10 mins for Ce^{3+} and 20 min for Nd^{3+} ions as represented in Fig. 9. The fast adsorption rate during the first 10 min was associated with the high number of vacant surface sites of the nanofiber adsorbent available during the adsorption of the metal ions. Within the first 20 min, the amount adsorbed reached $119.4 \text{ mg g}^{-1} Ce^{3+}$ and $108.4 \text{ mg g}^{-1} Nd^{3+}$ of the available concentration of metal ions present in the solution. Hence, a contact time of 20 min was adequate to reach equilibrium for PS-DGAnf.

The high adsorption rate was attributed to low diffusional constraints as well as the high surface area and numerous binding sites of PS-DGAnf. After 20 mins, no further adsorption occurred on the adsorbent due to limited supply of metal ions in solution as more than 90 % of the adsorbate was removed from solution. The short time required to attain equilibrium shows that the PS-DGAnf has a great potential and very high adsorption efficiency for Ce^{3+} or Nd^{3+} uptake when

compared to other adsorbent surface modification using diglycolic-based selective ligands which reported fast metal binding kinetics toward REEs [10,15,57].

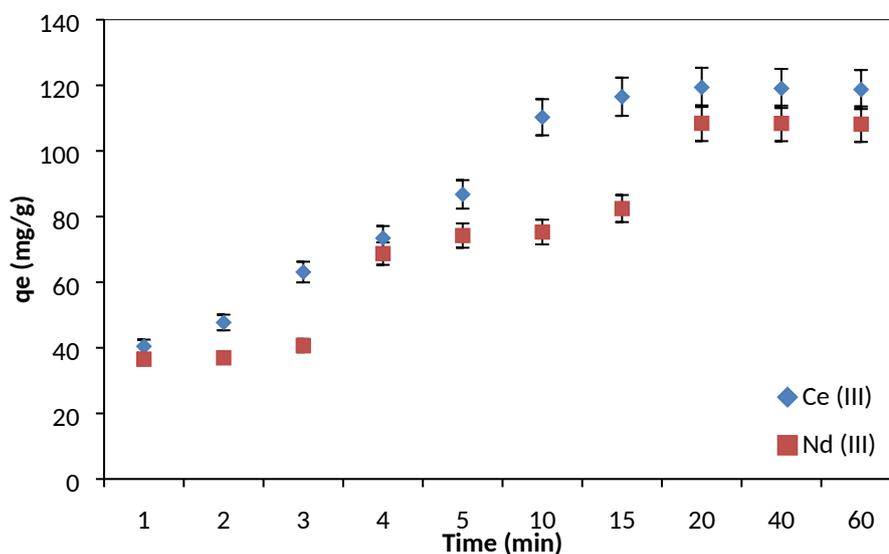


Fig 9. The effect of contact in the time removal efficiency of (a) Ce^{3+} (b) Nd^{3+} from aqueous solution by PS-DGANf (Ce^{3+} or Nd^{3+} concentration - 100 mg/L; pH - 6; adsorbent dosage - 0.0075 g /10 mL)

3.6 Desorption and reusability studies

The regeneration and desorption cycle of an adsorbent is crucial and essential for its possible practical application. The reusability of PS-DGANf for Ce^{3+} or Nd^{3+} was studied by evaluating four consecutive cycles using 1 M HNO_3 solution as regenerant and the results are depicted in Fig 10. The nanofibers retained high uptake capacity after the third and the fourth cycles of adsorption-desorption. PS-DGANf maintained up to 92 % capacity for the removal of Nd^{3+} after 4 cycles and was able to maintain capacity for Ce^{3+} uptake up to 96.7 % of the initial concentration after four adsorption-desorption cycles. The key objective of the regeneration and desorption procedure was to reinstate the adsorption capacity of the used adsorbent and to recover valued metal ions existing in the adsorbed phase. These results compare favourably to the study by Galhoum et al. (2017) [34] which used nitric acid (0.5 M solution) as regenerant to desorb Nd^{3+} from loaded sorbents. Regeneration was carried out with 1 M HNO_3 to desorb the metal ions taken up on the adsorbent for reuse without disrupting the ligand attached. It was considered that the desorption by HNO_3 is

caused by ion exchange reaction between protons and adsorbed ions and this stripping agent was earlier tested for ligand stability to confirm whether the functional fibers can withstand its short term contact.

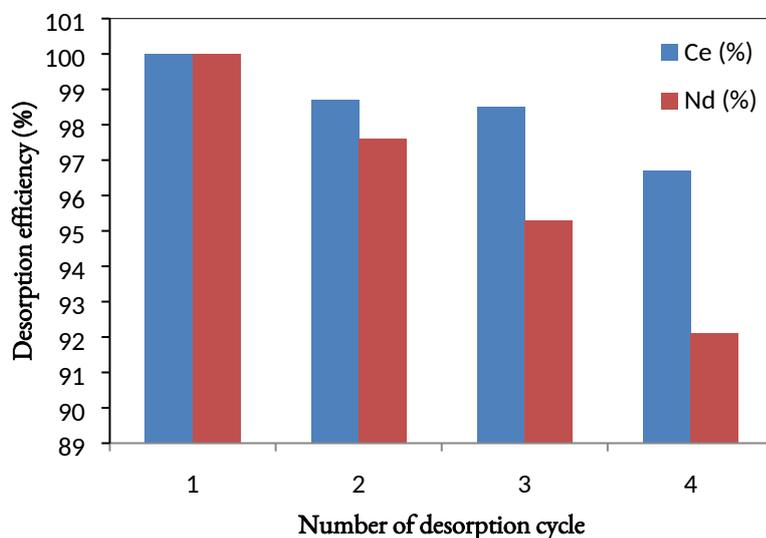


Fig 10. Desorption efficiency for Ce³⁺ or Nd³⁺ from PS-DGANf for three cycles of adsorption–desorption (initial concentration - 100 mg/L; adsorbent dosage - 0.0075 g/10 mL; stripping agent - 1 M HNO₃; desorption time - 60 min).

3.7 Selective adsorption

To investigate the selectivity of the PS-DGANf toward Ce³⁺, the selective adsorption study was carried out in an aqueous solution containing mixed ions of Ce³⁺, Co²⁺, Ni²⁺ and Sr²⁺. Similarly, the adsorption of the different metal ions in solutions of single ions using PS-DGANf was also evaluated. The amount of every single metal ion sorbed onto the PS-DGANf was calculated and the results are summarised in Table 3. The amount of Ce³⁺ adsorbed despite the existence of competing ions was 100.3 mg g⁻¹, which was only slightly lower (119.4 mg g⁻¹) than what was obtained in the single ion solution. The selectivity was attributed to the low amount of competing adsorption of other different metal ions such as Co²⁺, Ni²⁺ and Sr²⁺ present in solution which is suggested to have led to a small alteration in the Ce³⁺ adsorption equilibrium. The high selective adsorption coefficient revealed that the PS-DGANf showed much higher selectivity toward Ce³⁺ in the modelled solution than to the other metals investigated. The PS-DGANf depicted better adsorption selectivity toward Ce³⁺ over other metal ions which may be related to the chelating bonding orbital and the ion radius of the different metal ions. The N₂ BET adsorption–desorption

characterisation indicated a porous structure for the adsorbent and the surface area was large enough to result in a high adsorption rate compared to the pristine nanofiber adsorption (not shown). The high selectivity for the rare earth elements was therefore attributed to chelation by the tridentate diglycolic acid framework. PS-DGANf containing diglycolic acid exhibit higher extraction of trivalent lanthanides such as Ce^{3+} compared to divalent metal ions and this finding solves the first major challenge for the REE industry, which is the separation of REEs from base metals [61]. The co-existence in solution of selected metal ions did not significantly interfere with the adsorption of REEs binding to PS-DGANf as can be deduced from the high selectivity coefficient.

Table 3. Selectivity coefficients (S) and adsorption capacities of diverse metal ions in solution using PS-DGANf (Contact time - 200 rpm for 1 h; concentration - 100 mg/L; pH - 6; solution pH 6; adsorbent dosage - 0.0075 g /10 mL)

Adsorption capacity, (mg g ⁻¹)	Co ²⁺	Ni ²⁺	Sr ²⁺	Ce ³⁺
Single solution	2.76	5.50	18.6	119.4
Mixed solution	2.01	4.99	3.30	100.3
Selectivity coefficient (S) (Ce/Co, Ni or Sr)	49.9	20.1	30.4	1

Ce^{3+} was selected for the experiments because both dynamic and equilibrium experiments indicated that the nanofiber adsorbents had very comparable sorption properties and capacities for the two REEs (Ce^{3+} and Nd^{3+}) signifying that a selective separation between different REEs may be challenging at the metal-binding equilibrium due to their close sorption capacities as shown previously in Table 1. Their individual differences were therefore not large enough and would therefore require more enrichment steps to achieve metal separation between these two REEs. The selective separation and extraction of dilute rare earth metal ions from solutions containing higher concentrations of base metal ions is necessary in the recovery process of rare earth elements from low grade ores and scrap. This adsorbent, PS-DGANf can therefore be useful for the recovery and separation of REEs from base metals.

3.8 Conclusions

A novel electrospun polystyrene diglycolic acid (PS-DGANf) nanofiber adsorbent for the efficient and selective adsorption of Nd^{3+} and Ce^{3+} ions was prepared by electrospinning of PS nanofibers, which were chemically modified with diglycolic anhydride (DGA) via an electrophilic aromatic substitution of the ligand onto the PS nanofiber. The optimum polystyrene electrospinning conditions for the experiments were obtained under the operating conditions of concentration (15 wt %); voltage (17 kV); solution flow rate (0.8 mL/h) and collector distance of 15 cm. The advantages of the stable and selective ligand on the nanofiber and high DGA loading of 0.827 g g^{-1} with fast kinetics make PS-DGANf nanofiber structure an efficient and selective adsorbant of rare earth metals such as Ce^{3+} and Nd^{3+} ions. The electrospinning and modification of PS-DGANf was confirmed by ATR-FTIR, HR-SEM, BET and TGA techniques. The kinetic study of PS-DGANf showed that maximum equilibrium could be attained within 15 mins of the adsorption process. The adsorption at pH 6.0 of Ce^{3+} and Nd^{3+} ions with the maximum equilibrium uptake capacity of 152.5 mg g^{-1} (1.09 mmol/g) of Ce^{3+} and 146.2 mg g^{-1} (1.01 mmol/g) of Nd^{3+} respectively was well fitted to the Langmuir isotherm equation. Furthermore, the PS-DGANf showed higher affinity toward trivalent Ce^{3+} than to other common divalent metal ions such as Co^{2+} , Ni^{2+} and Sr^{2+} . This PS-DGANf could be regenerated successfully and retained high uptake capacity in aqueous solution of 0.1 M HNO_3 with no significant loss of capacity after four successive cycles. The developed electrospun polystyrene diglycolic acid nanofiber adsorbents can be utilised for the rapid and selective recovery and separation of rare earth metals ions from base metals in aqueous solution.

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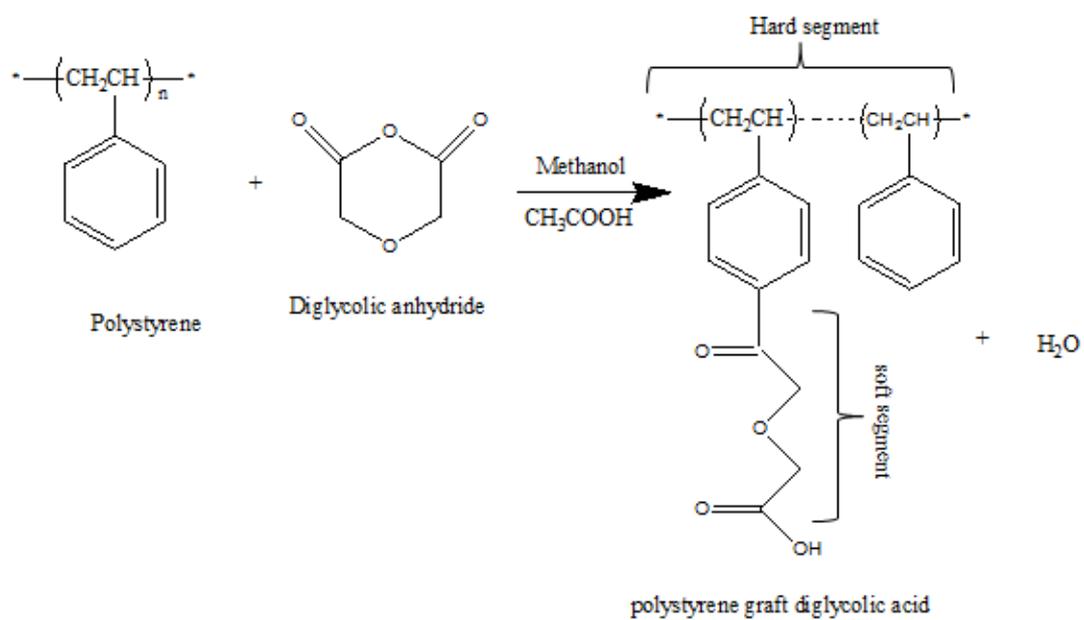
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Scheme 1 - Modification of PS nanofiber with DGA chelating ligand

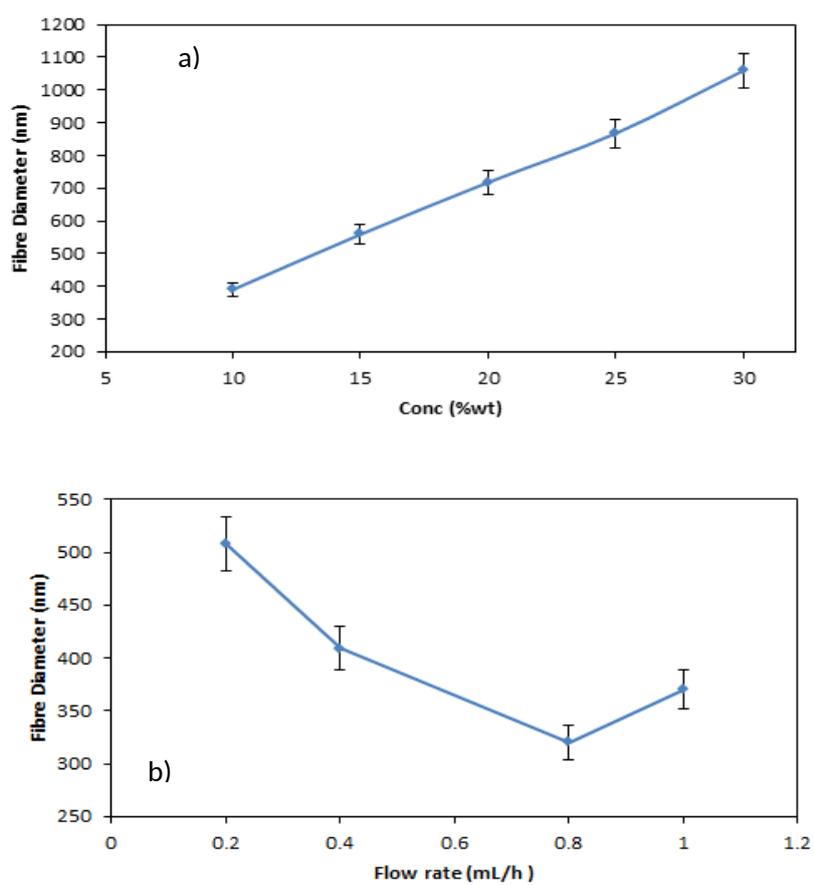


Fig 1. Trend of the effect of (a) solution concentration (b) flow rate on the fibre diameter

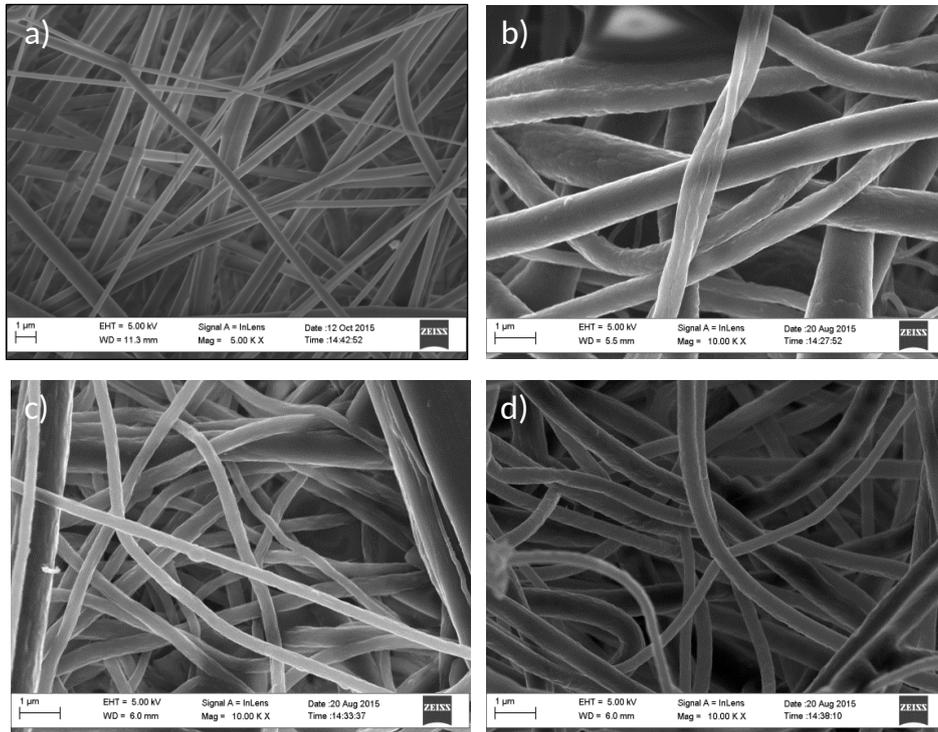


Fig 2. SEM micrograph a) pristine PS b) PS-DGAnf at 2 h c) PS-DGAnf at 3 h d) PS-DGAnf at 4 h (DGA conc - 3 g; initial fibre weight - 0.109 g)

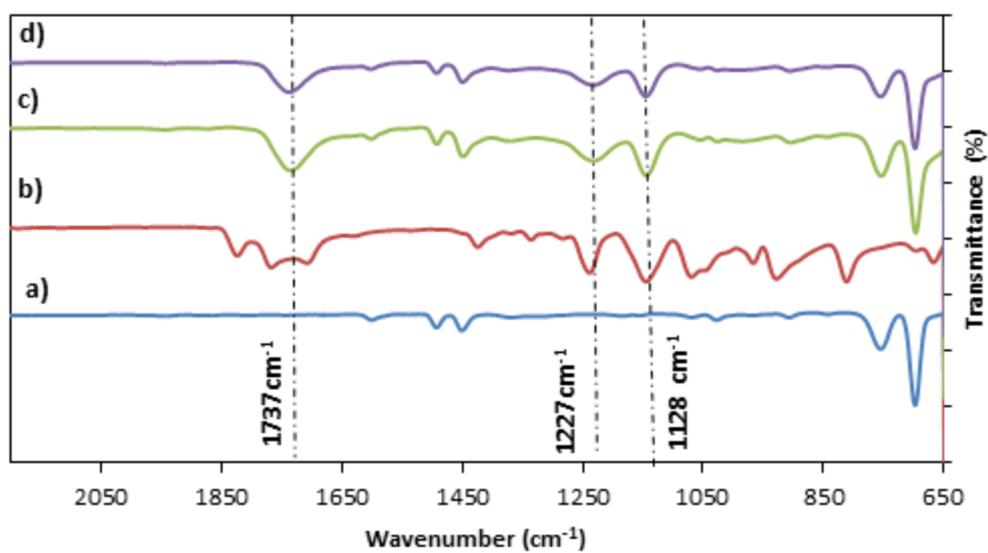


Fig 3. FTIR spectra of a) Pristine PS, b) DGA and c) PS-DGAnf (time - 240 mins; PS fibre weight - 0.109 g; temp - 43 °C; 5 mL acetic acid; 40 mL 99% methanol) d) regenerated-PS-DGAnf (Vol - 10 mL; time - 1 h; rpm - 240; Conc - 1.0M of HNO₃)

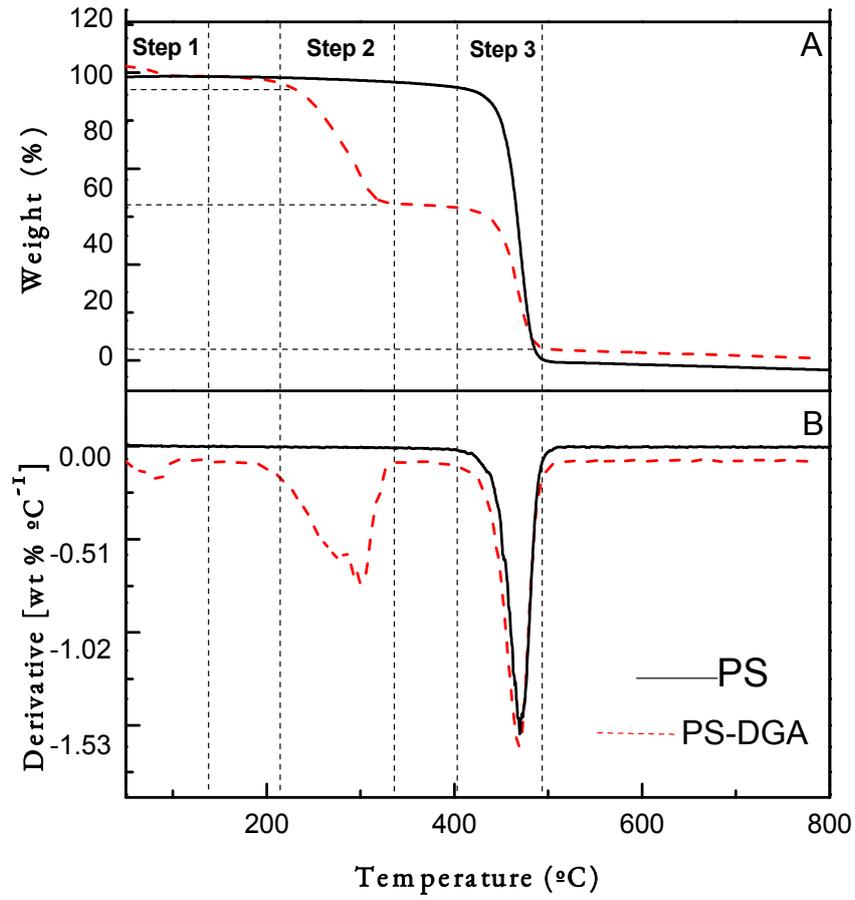


Fig 4. (a) TGA profile (b) TGA derivatives of pristine PS and PS-DGAnf

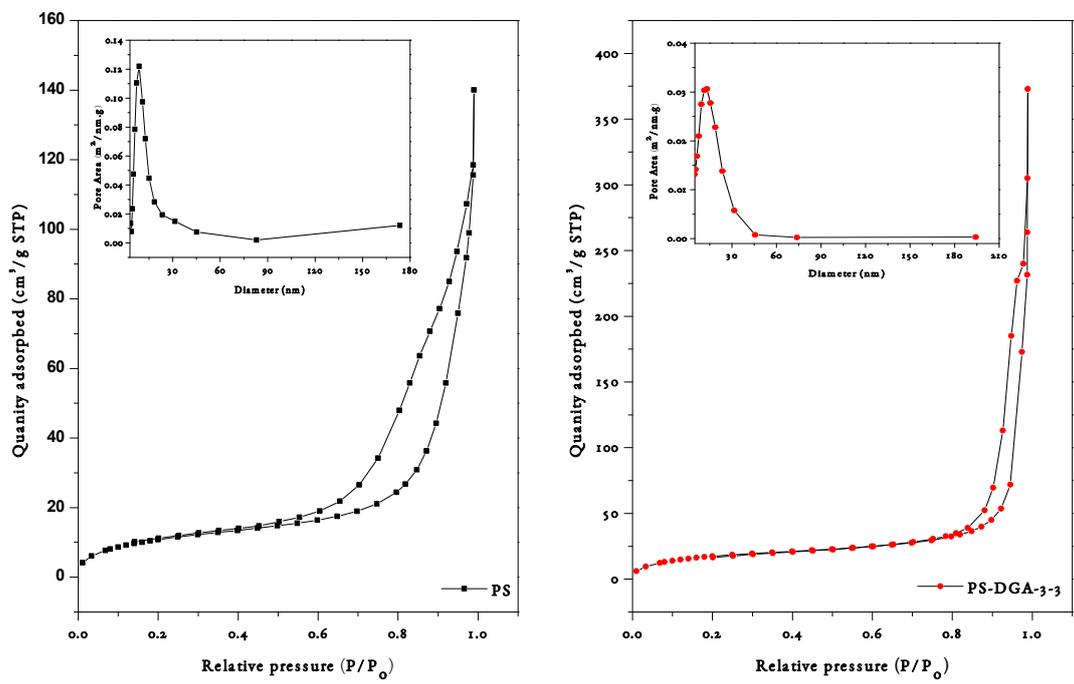


Fig 5. N_2 adsorption–desorption isotherm for (a) PS and (b) PS-DGAnf. (Inset) Pore size distribution of PS and PS-DGAnf

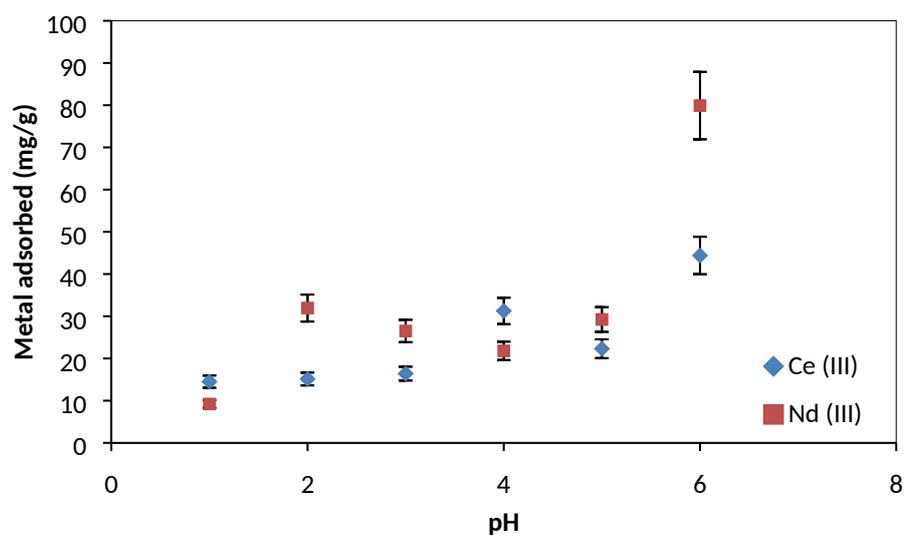


Fig 6. Dependence of Nd^{3+} and Ce^{3+} adsorption on pH of solution using PS-DGAnf (contact time - 120 min; Ce^{3+} or Nd^{3+} concentration - 100 mg/L; adsorbent dosage - 0.0075 g/10 mL)

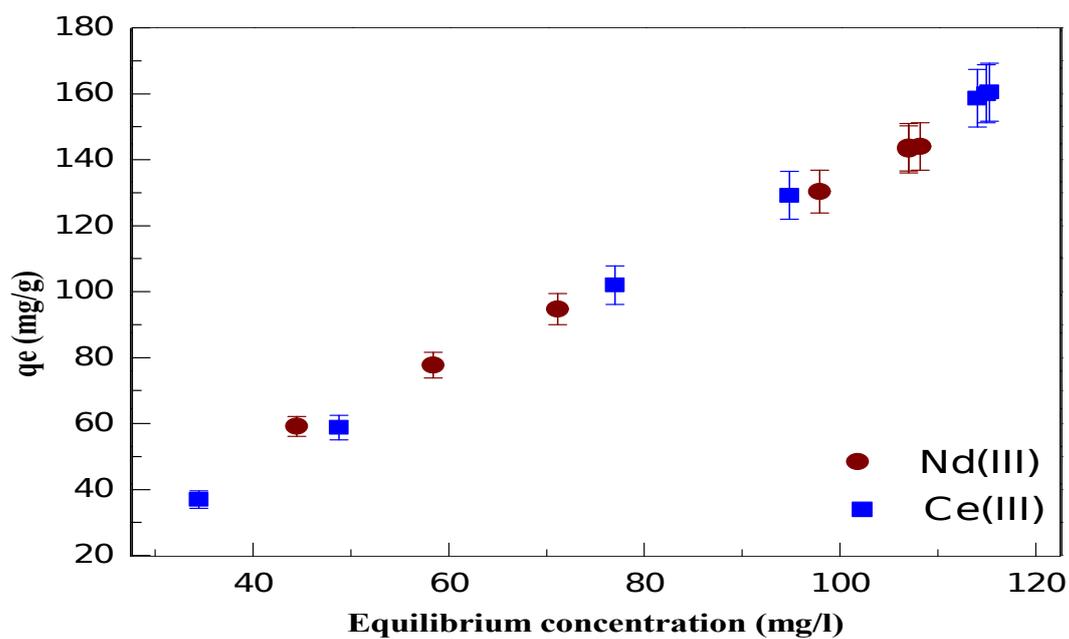


Fig 7. Adsorption isotherm models fitted to experimental adsorption of (a) Ce^{3+} (b) Nd^{3+} onto PS-DGAnf (contact time - 90 min; initial concentrations - 60 to 180 mg/L; pH - 6; adsorbent dosage - 0.0075 g/10 mL)

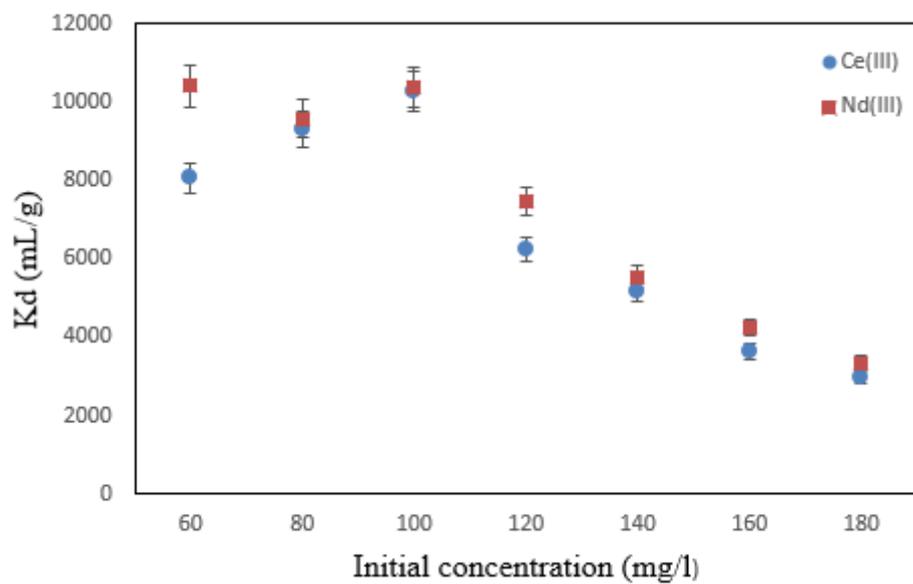


Fig. 8. Dependence of distribution coefficient (K_d) on initial concentration of Ce^{3+} or Nd^{3+} in the equilibrium adsorption study.

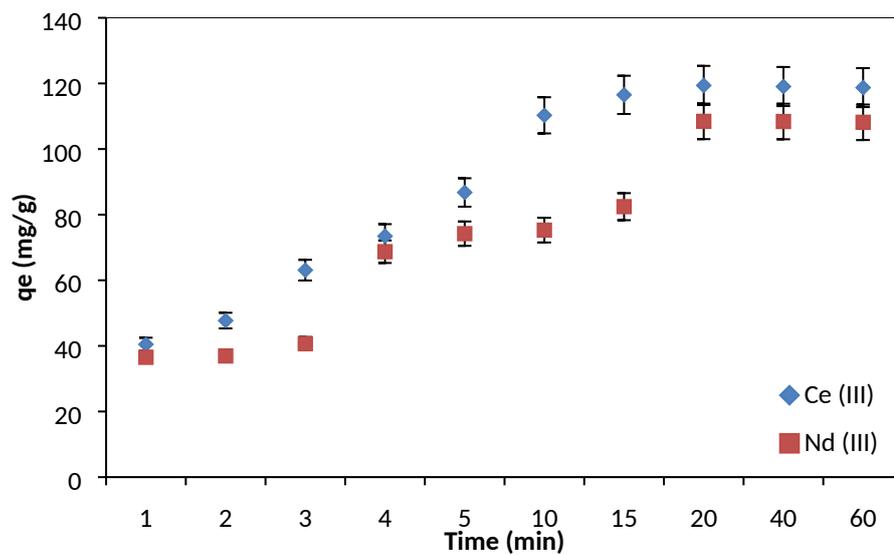


Fig 9. The effect of contact in the time removal efficiency of (a) Ce^{3+} (b) Nd^{3+} from aqueous solution by PS-DGAnf (Ce^{3+} or Nd^{3+} concentration - 100 mg/L; pH - 6; adsorbent dosage - 0.0075 g/10 mL)

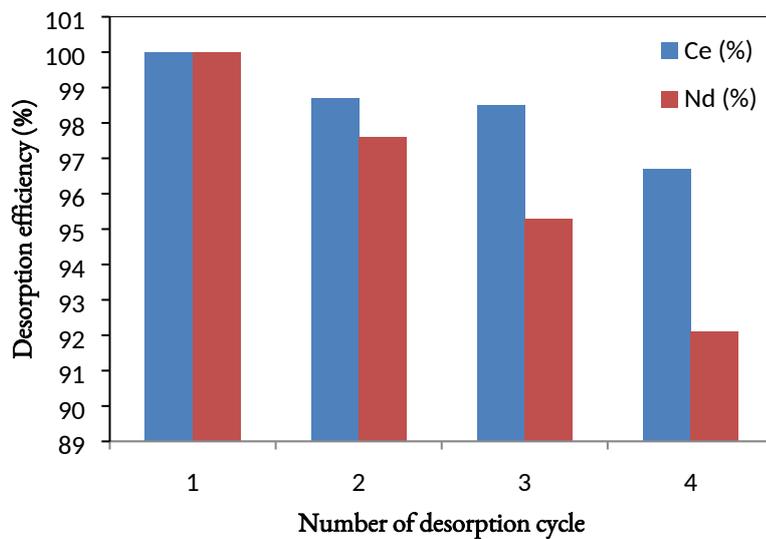


Fig 10. Desorption efficiency for Ce^{3+} or Nd^{3+} from PS-DGAnf for three cycles of adsorption-desorption (initial concentration - 100 mg/L; adsorbent dosage - 0.0075 g/10 mL; stripping agent - 1 M HNO_3 ; desorption time - 60 min).

Table 1. Parameters obtained from the plot of Langmuir and Freundlich isotherms for Ce³⁺ or Nd³⁺ adsorption using PS-DGAnf.

	Langmuir isotherm				Freundlich isotherm		
	q _e (exp) mg g ⁻¹	R ²	b _l (L/mg)	q _m (mg g ⁻¹)	R ²	n	k _f [(mg g ⁻¹) (mg/L) ^{1/n}]
Nd ³⁺	144.0	0.992	0.00356	146.2	0.816	2.15	14.6
Ce ³⁺	152.1	0.999	0.00013	152.5	0.988	1.12	2.10

Table 2. Sorption capacities of different sorbents in comparison to PS-DGAnf

Sorbent	Metal	pH	time (h)	Adsorption capacity (mg g ⁻¹)	Reference
Arthrospira cyanobacteria	Ce ³⁺	5.5	1	38.2	[38]
Hybrid nano-material	Ce ³⁺	5	3.5	130	[39]
Amino Phosphate Nano TiO ₂	Ce ³⁺	6	1.5	21.39	[40]
Aminomethylphosphonic acid modified chitosan	Nd ³⁺	5	7	30.32	[41]
Calcium alginate–poly glutamic acid	Nd ³⁺	3.5	24	237.99	[42]
Phosphoric acid on silica matrix	Nd ³⁺	6	24	160	[43]
Aspartic acid grafted Cellulose	Nd ³⁺	5	3	81.2	[34]
Extractant impregnated alginate microcapsules	Nd ³⁺	4	20	149.3	[44]
chitosan/ polyvinyl/Alcohol/3-mercapto Beads	Ce ³⁺	5	6	251.41	[45]
EDTA and DTPA-functionalised chitosan	Nd ³⁺	4	3	74 77	[46]
Phosphorous functionalized nanoporous carbon	Nd ³⁺	-	1	335.5	[47]
4-dodecyl-6-((4-(hexyloxy)phenyl)diazenyl) benzene-1,3-diol mesoporous silica nano-composite	Ce ³⁺	2.5	2	150.37	[48]
PS-DGAnf	Nd ³⁺	6	0.4	146.2	This work
PS-DGAnf	Ce ³⁺	6	0.4	152.5	This work

Table 3. Selectivity coefficients (S) and adsorption capacities of diverse metal ions in solution using PS-DGAnf (Contact time - 200 rpm for 1 h; concentration - 100 mg/L; pH - 6; solution pH 6; adsorbent dosage - 0.0075 g /10 mL)

Adsorption capacity, (mg g ⁻¹)	Co ²⁺	Ni ²⁺	Sr ²⁺	Ce ³⁺
Single solution	2.76	5.50	18.6	119.4
Mixed solution	2.01	4.99	3.30	100.3
Selectivity coefficient (S) (Ce/Co, Ni or Sr)	49.9	20.1	30.4	1

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Conflict of Interest statement

The authors wish to confirm that there are no known conflicts of interest associated with this publication. Therefore, there are no competing interests to declare.