Covalent grafting of Diglycolamide functionalities over Merrifield resin for the uptake of trivalent f-block metal ions from acidic aqueous feed

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Abstract

In the present work, N, N- Dibutyl diglycolamide functionalities were covalently grafted over Merrifield resin by following novel green chemistry principles during the entire process of synthesis. Minimal use of hazardous chemicals, improved yields and moderate reaction conditions were the bedrocks throughout the process. This grafted resin was used as an adsorbent for the uptake of trivalent f-block elements from aqueous nitric acid feed (3M HNO₃). The synthesized resin MRBB (N, N- Dibutyl diglycolamide grafted over n-butyl aminated Merrifield resin) was characterized with grafting percentage of >66%. Am^{3+} an actinide was used as a radiotracer for preliminary studies to check the efficacy of synthesized polymeric adsorbent. After optimization of synthesis parameters, Eu^{3+} salt, a surrogate lanthanide ion was used in an aqueous feed to optimize the operating parameters of adsorption. The distribution coefficients K_D for different conditions were in the range of thousands but for a similar kind of work with malonamides the range was just in hundreds as reported in the available literature. The adsorption kinetics predominantly follows pseudo-second order reaction with $k_2 = 6.3 \times 10^{-5}$ g/(mg-min). The work is an important contribution in sustainable organic, polymer and nuclear chemistry.

Keywords: Covalent grafting; Diglycolamide; Adsorption; f-block metal ions.

1. Introduction

With the increasing demand for sustainable and greener sources of energy due to the rise in population and pollution levels of the world, nuclear energy is gaining its importance as it is relatively less polluting, having a lesser carbon footprint, high throughput, and available throughout the year. The major hindrance to the expansion of the nuclear industry is its high initial investment and post-operation costs for waste management. Developing countries are focusing on nuclear fuel reprocessing technologies and how to make these technologies financially feasible without compromising efficiencies of processes. Technologies like PUREX (Plutonium-Uranium reduction extraction), TRUEX (Trans-Uranium Extraction), DIAMEX (Diamide Extraction), UREX (Uranium Extraction), etc are solvent extraction-based techniques and require huge volumes of respective extractants/ligands and organic solvents. This not only adds up to the cost of separation operation but also generates a huge amount of secondary waste which has to be dealt with the utmost care by following the vitrification process and then burying the waste in abandoned coal mines[1-9].

Solvent extraction of metal ions from an aqueous waste stream is the most common technique used in the nuclear industry. In solvent extraction**,** ligands are designed in such a way that they selectively extract particular metal ions over others. The moieties present in these ligands determine the type of ligand viz Phosphorus based[10-13], Nitrogen-based[14-24] , Sulphur based[25-26], etc. Each class of ligand has its pros and cons. Considering post-operation waste management of these used ligands, Nitrogen (N)- based ligands are being preferred over others. Nitrogen-based ligands mainly malonamides and diglycolamides have not only better selectivity and partitioning abilities due to their basic character but are also lesser corrosive and leave no solid residue on incineration as it follows CHON principle of green chemistry. A lot of research is being done on N-based ligands wherein researchers have highlighted the advantages of these ligands over its other competitors[14], [16], [24], [27-29]. Out of all N-based ligands, TODGA (N,N,N',N'-Tetraoctyl Diglycolamide) is a promising extractant for nuclear fuel reprocessing. The alkyl chain lengths of DGA moieties can be altered as per need but even such a versatile ligand has its limitations like adduct and micelle formation in high acidity. Researchers have tried to counter this disadvantage by using ligand facilitated adsorption[30-34], grafted polymeric resins or sorbents[35-38], using dendritic polymers[39-40], blending of extractants[41-42] or altering the structure of DGA (Diglycolamide) functionalties[4], [24], [29], [43-46].

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Even though inert adsorbents with loaded extractants have shown better K_D values than solvent extraction as proved by many researchers[47-49] they face the problem of leaching and can't be used multiple times. It is always better to covalently graft the functional groups to maintain consistency and reusability[50-53]. One of the basic difference between solvent extraction and adsorption is that in solvent extraction solute from aqueous phase first enters the organic phase and then interacts with the ligand. On the other hand, in adsorption, there is no intermediate step and solute from aqueous phase directly interacts with active site. Thus in solvent extraction, it is better to have a hydrophobic environment around the ligand but vice versa in case of adsorption. Thus, shorter chain length around DGA group will help in better uptake than longer chain lengths as used for solvent extraction[49], this is explained in later sections.

In the present work, we first fixated the suitable carbon chain length associated with DGA moiety. Butyl, Hexyl and Octyl derivatives of amine were tried as they are stable compounds compared to ammonia and other smaller amines and diamines. We grafted DGA groups with suitable associated chain lengths onto Merrifield resin, characterized it, and then used it as an adsorbent for adsorption of Eu(III) from aqueous acidic feed and studied various parameters affecting the distribution coefficient.

2. Experimental Work

2.1. Materials and Methods

For synthesizing dialkyl diglycolamide grafted Merrifield resin, Merrifield resin (5.5 mmol Cl/g of resin, Loba Chemicals), diglycolic acid (99% pure, Sigma Aldrich), acetic anhydride (99% pure, Thomas Baker), sulphuric acid (98% conc., Loba Chemicals), n-butylamine (99% pure, Thomas Baker), n-hexylamine (99% pure, Thomas Baker), n-octylamine (99% pure, Thomas Baker), dibutylamine (99% pure, Thomas Baker), dihexylamine (99% pure, Thomas Baker), dioctylamine (99% pure, Sigma Aldrich), pyridine (98% pure, Thomas Baker), *para*-nitrophenol (99% pure, SDFCL), dicyclohexylcarbodiimide (98% pure, SDFCL), 4-dimethylaminopyridine (99% pure, Sigma Aldrich), and triethylamine (99% pure, SDFCL) were used. The various solvents used were, dichloromethane (99% pure, Thomas Baker), methanol (98% pure, Thomas Baker), toluene (98% pure, Thomas Baker) and 1,4-dioxane (98% pure, Thomas Baker).

For intermediate process ivolving acidic and alkaline treatment, Hydrochloric acid (35.4% (v/v), Loba Chemicals) and Sodium Carbonate (solid powder, SDFCL) were used. For removing traces of water, magnesium sulphate (solid powder, Loba Chemicals) was used. For uptake study of trivalent lanthanide, Europium (III) nitrate pentahydrate (Sigma Aldrich) and nitric acid (70% conc., Thomas Baker) were used, Finally, for characterization by NMR, d-CDCl$_3$ (99.9% pure, Sigma Aldrich) and DMSO-d$_6$ (99.9% pure, Sigma Aldrich) were used as solvents.

For analytical analysis, FTIR was carried out with SHIMADZU IRAffinity-1; Solid NMR was carried out with Bruker AV III 500 MHz (SAIF IIT Madras); Initial and final gamma radiation counts were measured on well type NaI(TI) scintillation counter interphased with multichannel analyzer (Radiochemistry division BARC), XPS analysis was carried out using Kratos Analytical Supra (ESCA lab, Dept. of Physics, IIT Bombay) and ICP-AES was carried out with SPECTRO Analytical Instruments GmbH: ARCOS Simultaneous ICP Spectrometer (SAIF IIT Bombay).

2.2. Grafting of Merrifield resin

DGA groups are grafted over Merrifield resin by following 5 step reaction schemes. as shown in Fig.1.

1) 5.5 mmol of Cl per gram of Merrifield resin, 5% DVB, porous, 16-50 mesh size was used. It was reacted with an excess amount of n-butylamine in dioxane at a very mild temperature. The Cl groups get replaced with butylamine and HCl generated forms salt with excess amine thus makes the reaction move in a forward direction[54]. The final product was vacuum filtered and washed with water, methanol and 10% triethylamine in Dichloromethane and then kept for drying to remove unreacted amine and its respective chloride salt.

2) Diglycolic acid, along with acetic anhydride and a few drops of sulphuric acid, was used to produce diglycolic anhydride (DGAn). The reaction temperature was kept at around 140 ºC. At the end of the reaction, the acetic acid was separated by vacuum distillation to get a solid product[28]. The yield was around 93%.

3) The Diglycolic anhydride obtained was reacted with a stoichiometric amount of dibutylamine in 1,4-dioxane; pyridine was added as a basic medium for the reaction. The reaction takes place at 130 ºC for four hours. After distilling out dioxane, the product was washed with 20% HCl (v/v) to remove the traces of pyridine. The yield of DBDGA obtained was around 90%.

4) The DBDGA was activated with *para*-nitrophenol, as it is a better leaving group. DBDGA was dissolved in dichloromethane along with DCC (N,N'-dicyclohexyl carbodiimide) and *para*-nitrophenol in the presence of 4-dimethylaminopyridine (DMAP)[55].The yield was more than 99%.

5) Aminated Merrifield resin was reacted with p-nitrophenol activated DBDGA in refluxing toluene with traces of triethylamine. The impeller of the reactor breaks the swelled polymer, so one has to keep the proper flow pattern to maintain the size of the resin. The solid product was vacuum filtered and kept in the oven for drying after washing it with toluene, water and methanol thoroughly to remove p-nitrophenol[56]. The maximum percentage grafting obtained was 66.13%.
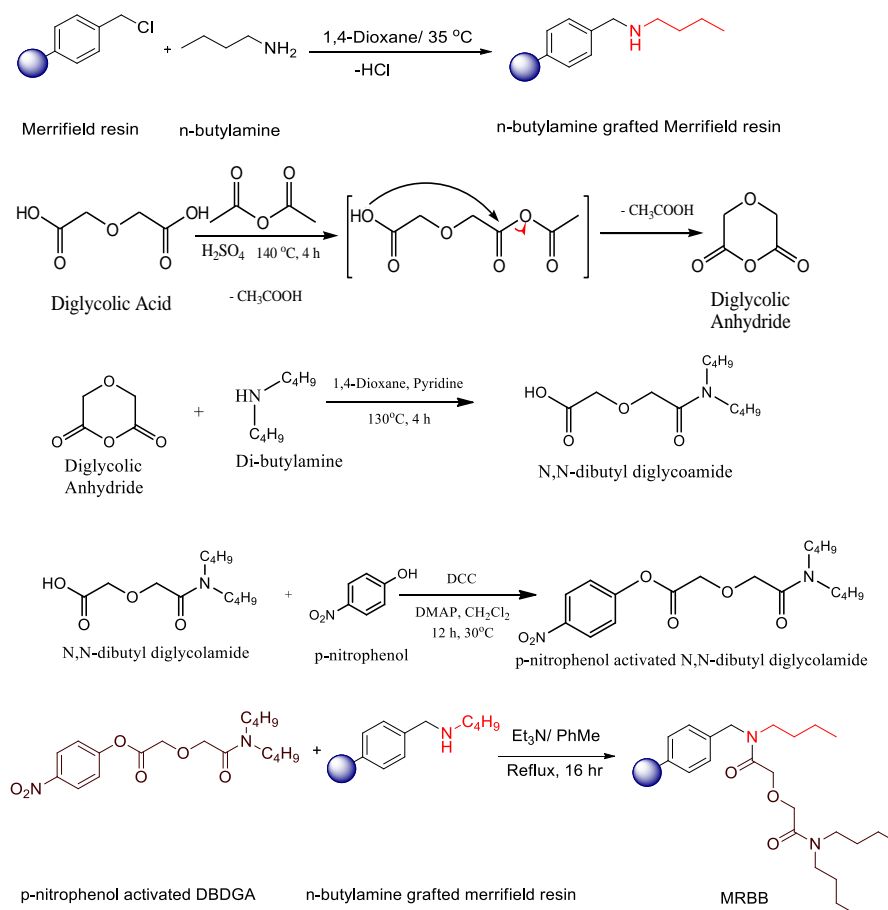

Fig.1. Reaction scheme to form MRBB

2.3. Uptake study with MRBB

The synthesized MRBB was contacted with an acidic aqueous solution of $Eu(NO_3)_3.5H_2O$ salt for 3 hours at 1000 rpm. The volume of feed solution was kept 1 litre for each data point to avoid errors caused due to loss during sampling. Each sample was prepared by following the standard protocol of sample preparation for ICP-AES. Each sample was diluted 50 times with De-ionized water and then analyzed for Eu concentration using ICP-AES. Each experiment was carried out in triplets to minimize experimental errors. For preliminary studies, MRBB was spiked with 3 M HNO_3 aliquot of [241]Am radiotracer for 3 hours at 25 °C in thermostated water bath. After contact, each sample was centrifuged and then tested for gamma counts per minute on well type NaI(TI) scintillation counter interphased with multichannel analyzer.

3. Results and Discussions

The present work is broadly divided into two major sub-parts viz Synthesis and Characterization of MRBB; Uptake study with synthesized MRBB.

3.1. Characterization of MRBB

The use of the adsorbent is based upon the presence of diglycolamidic functional group on its surface, which entrap the metal ions. To verify the presence of these functional groups conclusively, *FTIR (Fourier Transform Infrared Spectroscopy)* analysis was carried out to study various functional groups present in the synthesized adsorbent. Major

peaks are 2927 cm^{-1} (C-H stretching), 1738 cm^{-1} (Ester, C=O stretching), 1645.79 cm^{-1} (associated tertiary amide, >CO-N<), 1454.7 cm^{-1} (alkane, C-H bending), 1217.2 cm^{-1} (ester, C-O stretching), 1110 cm^{-1} (ether, C-O-C stretching), 817 cm^{-1} (1,4-disubstituted benzene, C-H bending). Absence of 670 cm^{-1} corresponds to –CH$_2$-Cl confirming that significant grafting has been done (refer Fig. 2.). *Solid NMR* shows that DBDGA is covalently grafted on Merrifield and is not just a physical mixture of Merrifield and DBDGA. Important peaks observed were 168.82 ppm (tertiary amide), 157.69 to 104.99 ppm (aromatic), 88.69 to 65.82 ppm (C-O bond), 47.62 to 40.37 ppm (C-N), 31.62 to 14.71 ppm (alkyl groups) (refer Fig. 3.). Inspite of the high percentage grafting the distribution coefficient of Am^{3+} radiotracer on MRBB was varying with the size of resin and was found to be higher for resins of large surface area (K$_D$ =5500 ml/g for 200-400 mesh size; K$_D$ =1150 ml/g for 16-50 mesh size under same conditions). Thus, it was inferred that DGA groups within the hydrophobic Merrifield matrix were unutilized and only groups on the surface were contributing for uptake of metal ions. The percentage of N atoms or DGA groups on the surface was determined using *XPS (X-ray Photoluminescence)* analysis. The value of nitrogen content on surface was inversely proportional to size of resin. Fig. 3. exhibits XPS plot of MRBB which gives atomic and mass concentrations of N (1s) as 9.9 and 10.63% respectively, which is in coherence with results we got from quantitative CHNS analysis.
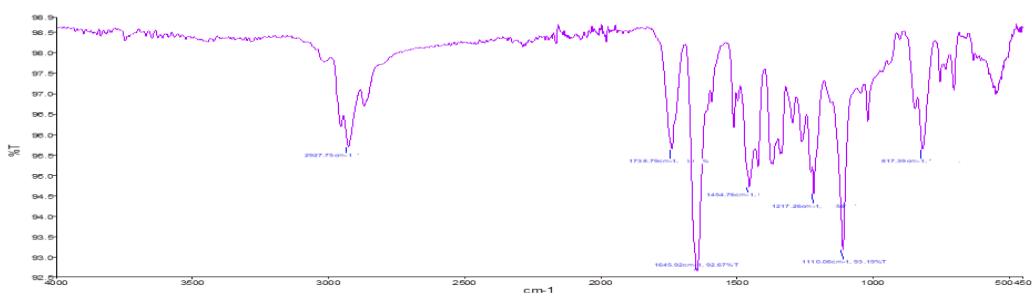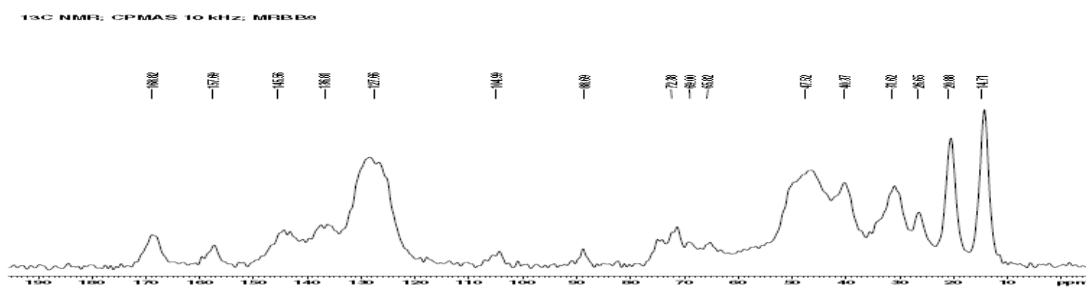

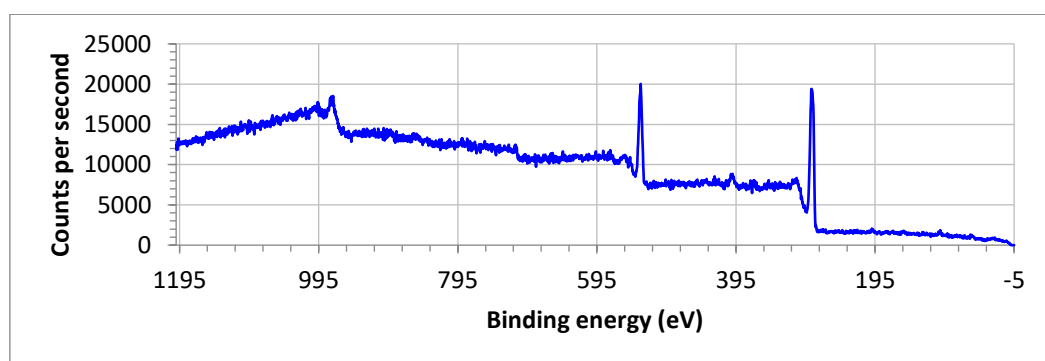Fig. 2. FTIR plot of MRBB

Fig. 3. ^{13}C NMR plot of MRBB

Fig. 4. XPS plot of MRBB

3.2. Uptake studies with Eu^{3+}

For each parameter, the distribution coefficient, K$_D$ values were determined by measuring initial and final concentrations of feed sample and putting those values in equation given below (refer Fig. 5. and Table 1.):-

$$K_D = \frac{c_i - c_f}{c_f} * \left(\frac{V}{W}\right) \qquad\qquad (1)$$

Where, K_D= Distribution Coefficient

C_i = Initial Concentration of Eu^{3+} in aqueous feed, in ppm

C_f = Final Concentration of Eu^{3+} in aqueous feed, in ppm

V = Volume of feed, in ml

W = Weight of resin, in g

3.2.1. Concentration Vs Time

A 250 ppm of Eu^{3+} in 3 M HNO_3 feed solution with 100 mg of MRBB was used for finding equilibrium time at 25 ºC. Samples were taken in between 0 to 120 minutes. The steady state was achieved in first 30 minutes as shown in Fig. 5(a).

3.2.2. K_D Vs [HNO_3]

Feed solution of 250 ppm Eu^{3+} in varying concentrations of HNO_3 was contacted for 3 hours with 100mg of MRBB at 25 ºC for each separate data point. Concentrations of HNO_3 for feed solution used were 1 M, 3 M, 5 M, 7 M and 9 M. K_D values were calculated using the equation 1 and plotted against [HNO_3] as shown in Fig. 5(b). The trend shows that at high concentrations of feed solution desorption takes place. The reason is that the basic DGA groups start getting preoccupied with a high concentration of protons in feed at higher acidity thus inhibits the adsorption of metal ions on its surface[14]. This disadvantage can be used for reactivation of used MRBB thus makes MRBB reusable for multiple times. The plot is exhibited in Fig. 5(b).

3.2.3. K_D Vs [MRBB]

Feed solution of 250 ppm Eu^{3+} in 3 M HNO_3 was contacted for 3 hours with varying amounts of MRBB at 25 ºC for each separate data point. The amount of MRBB used was 100, 200, 300, 400 and 500 mg per litre of feed. K_D values were plotted against [MRBB] as shown in Fig. 5(c). No significant change was observed in K_D values (as amount of adsorbed species is increasing but so is the amount of adsorbent, so both negates each other) thus signifying that there were no significant hydrodynamic interactions during uptake process. The plot is exhibited in Fig. 5(c).

3.2.4. K_D Vs Temperature

Feed solution of 250 ppm Eu^{3+} in 3 M HNO_3 was contacted for 3 hours with 100mg of MRBB at 25 ºC, 30 ºC, 40 ºC and 50 ºC for each separate data point. K_D values were calculated using the equation 1 and plotted against [MRBB] as shown in Fig. 5(d). A typical chemisorptions plot was observed in which K_D value initially increased with temperature as it facilitates to surpass the activation energy barrier but on further increment in temperature it drops drastically as coordination bonds between DGA groups and Eu^{3+} starts breaking at higher temperatures[57-58]. The plot and values are exhibited in Fig. 5(d).

Table 1. K_D values with corresponding parameters

[HNO_3] in M	K_D in ml/g	[MRBB] in mg	K_D in ml/g	Temperature in ºC	K_D in ml/g
1	1520	100	2315	30	2315
3	2315	200	2184	40	3158
5	2755	300	2375	50	1521
7	504	400	2345	60	504
9	81	500	2425	-	-

(a)

♦ KD Vs Amount of Resin
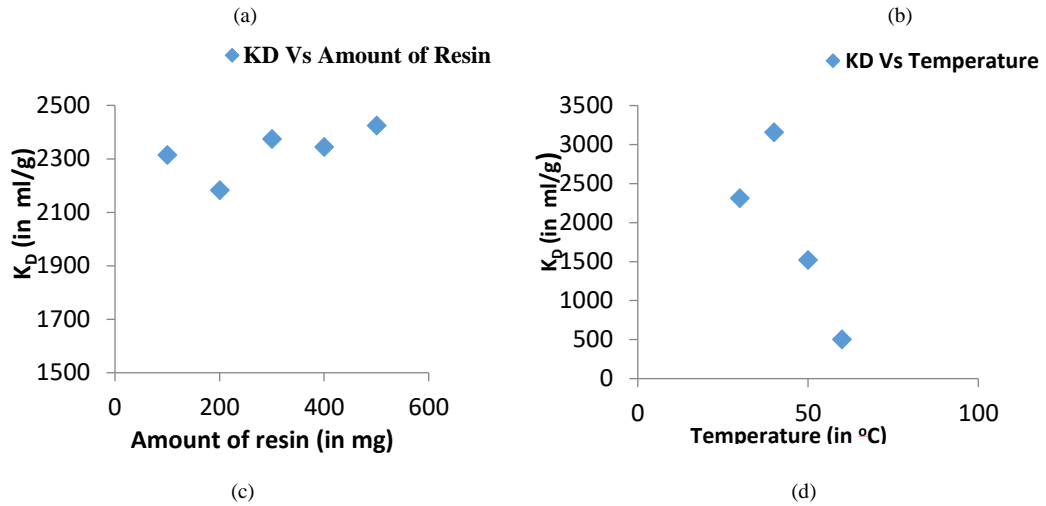
(b)

♦ KD Vs Temperature

(c)

(d)
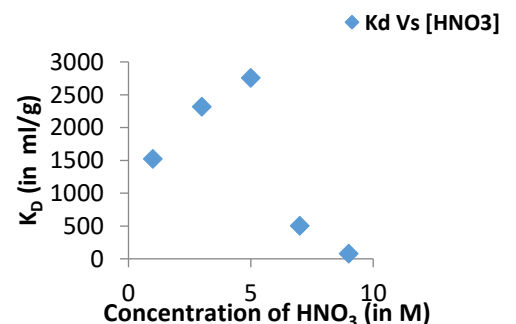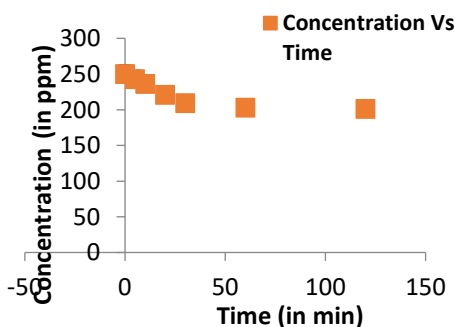
Fig. 5. Varying K_D values with varying conditions

3.3. Adsorption Kinetics

Data from Concentration Vs Time was used to find the order of adsorption (reaction). Data points only in between 5 to 30 minutes were used to determine the kinetics as they exhibit a significant change in concentration of Eu^{3+}. Curve fitting of data for Pseudo first order and Pseudo second-order were tried as shown in Fig. 6. followed by calculations of respective rate constants. By comparing regression coefficients we can conclude that the adsorption kinetics predominantly follows pseudo-second order reaction with $k_2 = 6.3 \times 10^{-5}$ g/(mg-min).

3.3.1. Pseudo First Order Reaction

The plot and values are exhibited in Fig. 6(a). and Table 2. respectively

Calculations

The general equation for Pseudo first order reaction is given below

$$\ln(q_E) = \ln q - k_1.t \qquad (2)$$

Equilibrium Concentration on adsorbent, $q_E = 470$ mg/L

From plot between $\ln(q_E-q)$ Vs t and equation, we get $k_1 = 0.0756$ min^{-1}

3.3.2. Pseudo Second Order Reaction

The plot and values are exhibited in Fig. 6(b). and Table 2. respectively

Calculations

The general equation for pseudo second order equation is given below

$$(1/q) = (1/q_E) + (1/k_2 q_E^2)(1/t) \qquad (3)$$

Equilibrium Concentration on adsorbent, $q_E = 470$ mg/L

From curve between $1/q$ Vs $1/t$ and equation, we get $k_2 = 6.3 \times 10^{-5}$ g/(mg-min)

Table 2. Adsorption Kinetics calculations

Pseudo First order calculations (ln(q_E-q) Vs time)			
Time, t (in min)	**Concentration, C (in ppm)**	**q_E-q (q_E = 470)**	**ln(q_E-q)**
0	250	470	6.152733
5	243	400	5.991465
10	236	330	5.799093
20	221	180	5.192957
30	209	60	4.094345

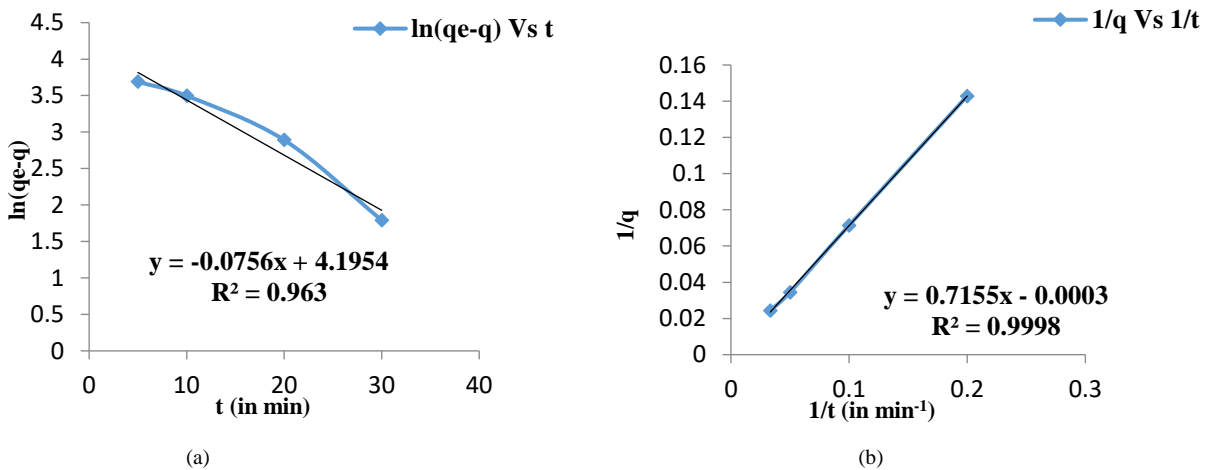| **Pseudo Second order calculations (1/q Vs 1/t)**			
Time, t (in min)	**Concentration, C (in ppm)**	**1/q**	**1/t**
5	243	0.014286	0.20
10	236	0.007143	0.10
20	221	0.003448	0.05
30	209	0.002439	0.03

(a)   (b)

Fig. 6. (a) Plot of Pseudo First Order; (b) Plot of Pseudo Second Order

3.4. Adsorption Isotherm

Data from K_D Vs [MRBB] was used to determine the isotherm followed by the system. Curve fitting of data for Frendulich and Langmuir were tried as shown in Fig. 7, followed by calculations of respective constants in Table 3. Amongst the isotherms, Frendulich fits with n=1.13507 and k=4.09261 and Langmuir constants a = 9.6 x 10^{-4} and b =2.78474. Regression coefficients exhibit that the adsorption process follows characteristics of both physisorption and chemisorption but from K_D Vs Temperature we have already concluded that the adsorption process is following chemisorptions, thus we can say the system follows chemisorption predominantly than physisorption.

Table 3. Adsorption Isotherm calculations

Frendulich Isotherm calculations (log(x/m) Vs log C)

Quantity of resin, m (in g)	Amount of adsorbate, x (in mg/L)	Final Concentration of feed, C (in mg/L)	x/m	log(x/m)	logC
0.1	47	203	470	2.67	2.31
0.2	76	174	380	2.58	2.24
0.3	104	146	346.6	2.54	2.16
0.4	121	129	302.5	2.48	2.11
0.5	137	113	274	2.44	2.05

Langmuir Isotherm calculations (M/Y Vs 1/C)

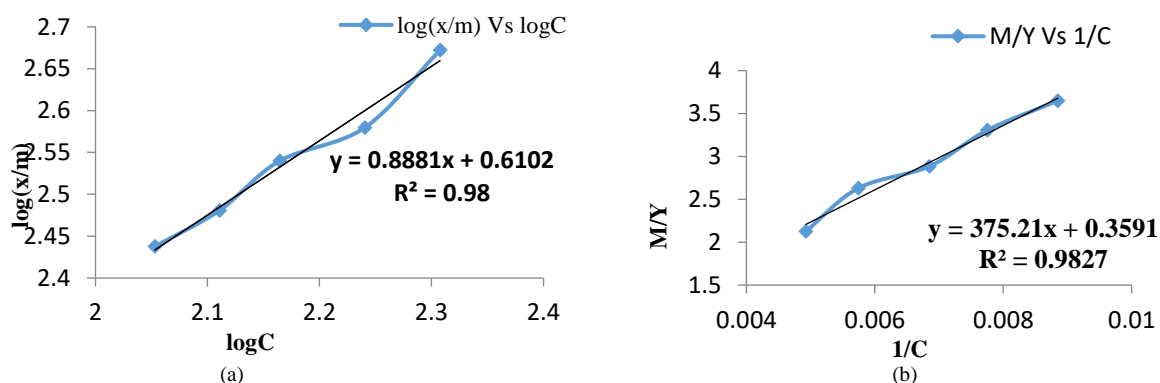| Quantity of resin (in mg)	Amount of adsorbate, Y (in mg/L)	Final Concentration of feed, C (in mg/L)	Adsorbent concentration, M (in mg/L)	M/Y	1/C
100	47	203	100	2.128	0.0049
200	76	174	200	2.632	0.0057
300	104	146	300	2.885	0.0068
400	121	129	400	3.306	0.0078
500	137	113	500	3.650	0.0089

Fig. 7(a). Frendulich Isotherm; 7(b) Langmuir Isotherm

Conclusions

The work deals with grafting of diglycolamide functionality over Merrifield resin and then utilizing the same for adsorption of trivalent f-block elements.

1) The work provides the grafting mechanism which is in tandem with green chemistry principles thus it not only provides a better polymeric adsorbent but also takes care of the waste generated durng synthesis of adsorbent making it a commercially viable option.
2) For better uptake, a shorter chain length associated with diglycolamide moiety should be preferred and the uptake mechanism is surface area dependent as microenvironments within the polymer matrix is too hydrophobic thus reduces the availability of metal ions to active sites.
3) The maximum K_D value viz 3158 ml/g was obtained when 1 litre of aqueous feed Eu^{3+} solution in 3 M HNO_3 was contacted with 100 mg of MRBB at 40 °C. The value is significantly higher when compared with other reported covalently grafted solid polymeric resins.

Conflict of Interest

We have no conflict of interests with anyone

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