



Adsorptive performance of an amine-functionalized poly(hydroxyethylmethacrylate)-grafted tamarind fruit shell for vanadium(V) removal from aqueous solutions

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ABSTRACT

A novel adsorbent (PGTFS-NH₃⁺Cl⁻) bearing -NH₃⁺Cl⁻ functional moiety was prepared from tamarind fruit shell (TFS) through graft copolymerization of hydroxyethylmethacrylate onto TFS in the presence of N,N'-methylenebisacrylamide as a cross linking agent using K₂S₂O₈/Na₂S₂O₃ initiator system, followed by transamidation and hydrochloric acid treatment. The applicability of PGTFS-NH₃⁺Cl⁻ for the effective removal of vanadium(V) ions from aqueous solutions was investigated. The maximum adsorption was observed in the pH range 3.0–6.0. The adsorption was found to be concentration dependent and exothermic, and the equilibrium was established within 4 h. The adsorption follows reversible second-order kinetics and the low *E_a* (−4.06 kJ/mol) indicated a diffusion controlled process. Equilibrium studies demonstrated that the adsorption process obeys Langmuir isotherm model and the maximum adsorption capacity of PGTFS-NH₃⁺Cl⁻ towards V(V) was 45.86 mg/g at 30 °C. The values of change in entropy (ΔS^0) and heat of adsorption (ΔH^0) for V(V) adsorption on PGTFS-NH₃⁺Cl⁻ were estimated as −47.20 J/mol K and −15.64 kJ/mol, respectively. The values of isosteric heat of adsorption (ΔH_i) were also calculated at different surface coverages. The results indicate that PGTFS-NH₃⁺Cl⁻ used possessed nearly homogeneous surface sites. The PGTFS-NH₃⁺Cl⁻ was evaluated for its efficiency in V(V) recovery from simulated groundwater. The spent PGTFS-NH₃⁺Cl⁻ was regenerated using 0.2 M NaOH, with up to 96% recovery and the adsorbent was reused in four adsorption–desorption cycles without any substantial loss in adsorption capacity.

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1. Introduction

Vanadium is a well-known toxic metal and exists in environment both as tetravalent [V(IV)] and pentavalent [V(V)] forms of which pentavalent form is more toxic than the tetravalent one [1]. V(V) is the major stable species of this element in oxidative conditions; however, in anoxic medium V(IV) occurs in significant amounts [2]. Vanadium(V) is widely used in industries such as glass, textile, ceramic, photography, metallurgy, rubber and plants producing industrial inorganic chemicals and pigments [3]. In terms of environmental aspects, vanadium is greatly important, because vanadium has been emitted into the environment mainly from industrial sources, especially oil refineries and power plants using vanadium-rich fuel oil and coal. Also, phosphoric acid production using phosphorous ores results in the extraction of large amounts of vanadate ions from the ores, which make the acid unsuitable

for use in food processing because of its toxicity [4]. Such sources can mobilize appreciable amounts of vanadium and increase the natural background level [5]. Excess amount of vanadium in humans can cause anemia, cough, emaciation, irritation of mucous membrane, gastrointestinal disturbances, and bronchopneumonia [6]. Although vanadium acts as a growth-promoting factor in plants, a high concentration of vanadium reduces the productivity of the plants. The Bureau of Indian Standards [7] has put the discharge limit of V(V) in industrial effluents into surface water to be 0.2 mg/L. Therefore, the removal of V(V) from wastewaters is one of the most essential issues in view of environmental protection and conservation.

A wide variety of adsorbents have been cited in the literature for the removal of V(V) ions from aqueous solutions [3,8–13]. Recently, work published by our research group indicates that chemically modified lignocellulosic residues were effective for the treatment of wastewater containing Cr(VI), V(V) and As(V) ions [14–16]. Tamarind fruit shell (TFS) is an underutilized or waste material and is a by-product of the tamarind pulp industry. In tropical countries like India, it is mainly used as solid fuel, which generates a

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large amount of CO₂ and causes environmental pollution. The conversion of this waste material into value added products must be appreciable.

As an extension of our previous studies, the present work explores the synthesis of a novel adsorbent, poly(hydroxyethylmethacrylate)-grafted TFS (PGTFS-NH₃⁺Cl⁻) bearing -NH₃⁺Cl⁻ moiety and was used for the removal of V(V) ions from aqueous solutions. The various operational parameters affecting V(V) ion adsorption were investigated and the system parameters were optimized. The kinetic and isotherm models were applied to the adsorption data to analyze the mechanism involved in V(V) adsorption. Thermodynamic investigations and surface heterogeneity assessments were discussed in detail.

2. Materials and methods

2.1. Chemicals

All chemicals used in the present work were of analytical purity. The stock solution of V(V) was prepared from sodium metavanadate by dissolving it in distilled water. All the working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. Hydroxyethylmethacrylate (HEMA) was obtained from Fluka (Switzerland). N,N'-methylenebisacrylamide (MBA), was procured from Aldrich (WI, USA). Potassium persulphate (K₂S₂O₈), sodium thiosulphate (Na₂S₂O₃), ethylenediamine (en), 1,4-dioxane (99.9% purity), HCl, NaCl, NaNO₃ and NaOH were obtained from E. Merck, India Ltd. The pH of the working solutions was adjusted to the desired value by the addition of 0.1 M HCl or 0.1 M NaOH solutions.

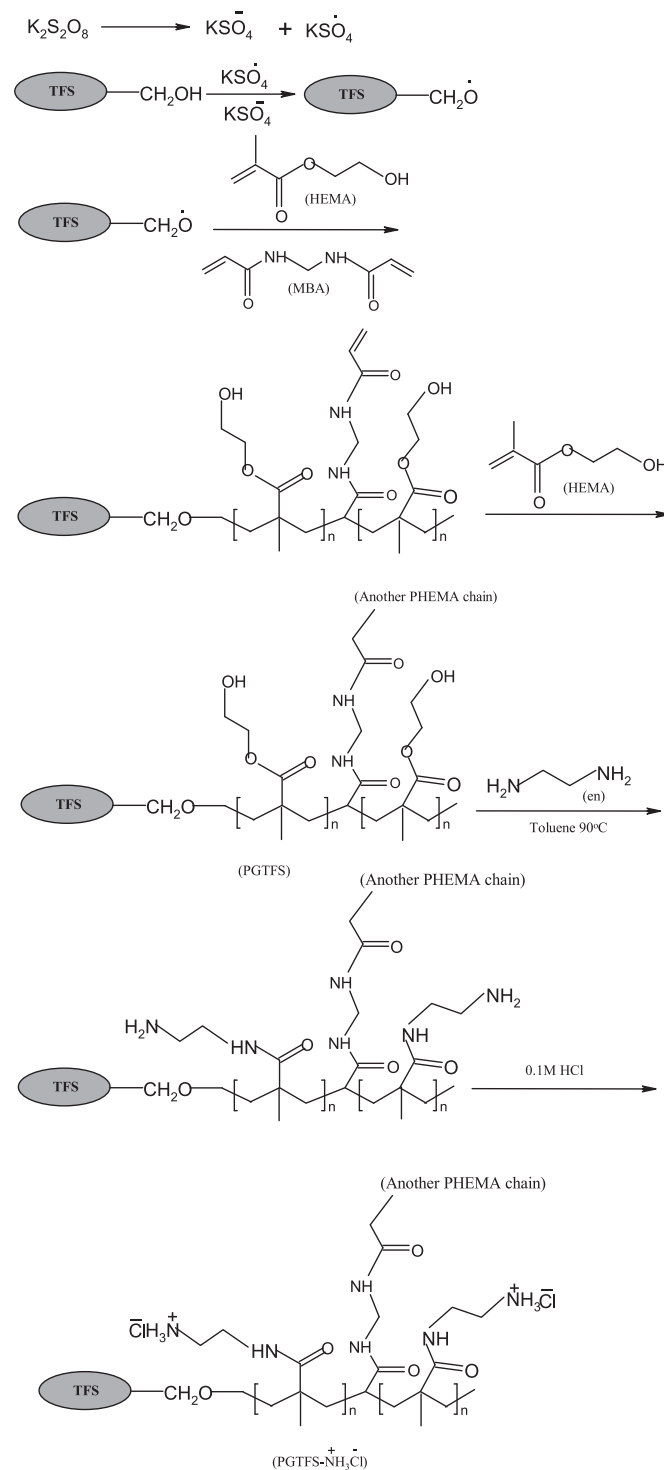
2.2. Adsorbent preparation

TFS used for the preparation of the adsorbent was collected from a local market, washed with distilled water to remove the surface impurities, and dried at 80 °C in an oven. The dried TFS was powdered and particles of 80–230 mesh size were used for chemical modification. The general method adopted for the preparation of PGTFS-NH₃⁺Cl⁻ is presented in Scheme 1. TFS powder (50.0 g) was suspended in 150.0 mL distilled water in a glass reactor containing 0.346 M MBA, 0.134 M potassium persulphate (K₂S₂O₈) and 0.05 M sodium thiosulphate (Na₂S₂O₃). After proper soaking, HEMA (3.21 M) was added into the reaction mixture and stirred vigorously at 70 °C for 2 h. The product was filtered, washed with hot water and dried under vacuum at 40 °C. The grafted polymer (PGTFS) was ground and then refluxed with ethylenediamine (en) at 90 °C for 6 h (transamidation). The product was filtered and washed with 1,4-dioxane and dried at 80 °C. To convert into anion exchanger (PGTFS-NH₃⁺Cl⁻), the ethylenediamine treated PGTFS was shaken with 0.1 M HCl for 4 h. It was washed with distilled water to remove excess chloride ions and dried at 80 °C and powdered. The powdered PGTFS-NH₃⁺Cl⁻ was sieved to get particles of 80–230 mesh using standard sieves and were used for adsorption studies. The percentage graft yield and efficiency of grafting were calculated as under

$$\% \text{ graft yield (\%G)} = \frac{W_1 - W_0}{W_1} \times 100 \quad (1)$$

$$\% \text{ grafting efficiency (\%GE)} = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

where W₁, W₀ and W₂ denote, respectively, the weight of the grafted TFS, the weight TFS and weight of the monomer used. The values of (%G) and (%GE) were found to be 52.2% and 79.1% respectively.



Scheme 1. Preparation of PGTFS-NH₃⁺Cl⁻.

2.3. Analytical methods

Characterization of the TFS and PGTFS-NH₃⁺Cl⁻ was carried out by surface area analysis, bulk density, potentiometric titration, and FTIR studies. The surface areas of the adsorbents were determined using a Quantasorb surface area analyzer (QS/7). C, H, and N contents of the sorbents were analyzed by Perkin Elmer Elemental Analyzer Model 240. Scanning electron micrographs (SEM) were taken on a Philips XL 30 CP scanning electron microscope. The density of the adsorbents was determined by specific gravity bottle.

The point of zero charge (pH_{pzc}) of TFS and PGTF $\text{S-NH}_3^+\text{Cl}^-$ was determined by potentiometric titration method [17]. FTIR (Perkin Elmer IR-180) spectrometer was employed to determine the type of functional groups in TFS and PGTF $\text{S-NH}_3^+\text{Cl}^-$ responsible for metal adsorption. The anion-exchange capacity (AEC) was determined by the column process using 1.0M NaNO_3 as the eluent at a flow rate of 0.2 mL/min. The amount of Cl^- ions released from the exchanger was estimated by precipitation titration with standard AgNO_3 solution. Atomic absorption spectrophotometer, AAS (GBC Avanta A 5450, Australia) was used for the determination of V(V) concentration. The pH of the solution was measured with a Systronic microprocessor pH meter (model 362; India), calibrated with standard buffer solutions.

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted by agitating 100.0 mg of adsorbent with 50.0 mL of V(V) solution of desired concentration in 100 mL stoppered conical flask using a temperature controlled water bath flask shaker (Labline, India) at a shaking speed of 200 rpm for 4 h except for the contact time experiments. The effect of solution pH on the equilibrium adsorption of V(V) was investigated under similar experimental conditions between pH 2.0 and 8.0. In the kinetic experiments, 5.0, 10.0, 25.0, and 50.0 mg/L solutions were used at pH 6.0. The temperature influence on adsorption kinetics was studied with an initial concentration of 25.0 mg/L, between 10 and 40 °C. The sorption time was varied between 0 and 240 min. Isotherm experiments were conducted with V(V) solutions at various concentrations (10.0–300.0 mg/L) at 10, 20, 30 and 40 °C. Once the pre-set contact time (4 h) reached, the samples were withdrawn and centrifuged and the supernatant solutions were analyzed for the residual metal ion concentration by using AAS. The flame type, optimum lamp current, wavelength, and sensitivity of the AAS measurements were nitrous oxide-acetylene, 18.0 mA, 318.3 nm, and 0.5 $\mu\text{g/L}$, respectively.

The amount of adsorption (q_e) was calculated by the following equation:

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (3)$$

where C_0 and C_e are the initial and equilibrium metal ion concentrations (mg/L) respectively, m is the mass of the PGTF $\text{S-NH}_3^+\text{Cl}^-$ (g) and V is the volume of the solution (mL). All the adsorption experiments were conducted in duplicate, and the mean values were reported.

2.5. Desorption and regeneration studies

The metal releasing capacity of V(V)-loaded PGTF $\text{S-NH}_3^+\text{Cl}^-$ was estimated by carrying out desorption experiments. For desorption studies, 100 mg of PGTF $\text{S-NH}_3^+\text{Cl}^-$ was loaded with V(V) ions using 50 mL (10.0 mg/L) metal ion solution at 30 °C, pH 6.0 and contact time of 4 h. The agitation rate was fixed as 200 rpm. Metal ion-loaded PGTF $\text{S-NH}_3^+\text{Cl}^-$ was collected, and gently washed with distilled water to remove any unadsorbed metal ions. The spent adsorbent was then shaken with 50 mL of 0.2 M NaOH. The final concentration of metal ions in the aqueous phase was determined by means of an atomic absorption spectrophotometer. The desorption ratio of metal ions from PGTF $\text{S-NH}_3^+\text{Cl}^-$ was calculated from the amount of metal ions adsorbed on PGTF $\text{S-NH}_3^+\text{Cl}^-$ and the final concentration of metal ions in the desorption medium, by using the following equation

$$\text{desorption (\%)} = \frac{\text{amount of V(V) desorbed to the desorption medium}}{\text{Amount of V(V) adsorbed on the adsorbent}} \times 100 \quad (4)$$

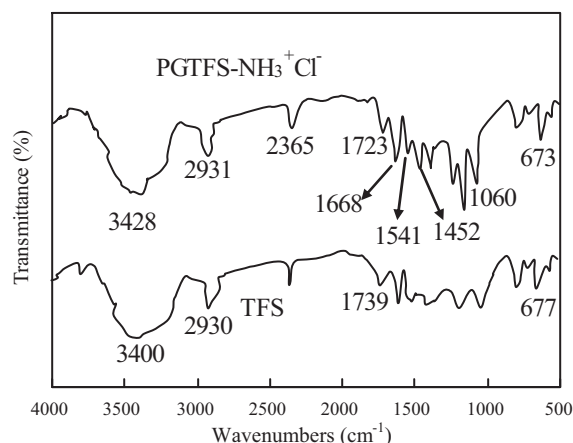


Fig. 1. FTIR spectra of TFS and PGTF $\text{S-NH}_3^+\text{Cl}^-$.

To test the reusability of the PGTF $\text{S-NH}_3^+\text{Cl}^-$, this adsorption–desorption cycle was repeated several times by using the same adsorbent.

3. Results and discussion

3.1. Characterization of adsorbent

Fig. 1 represents the FTIR spectra of TFS and PGTF $\text{S-NH}_3^+\text{Cl}^-$. The spectrum of TFS shows an absorption band at 3400 cm^{-1} which is attributable to the hydrogen-bonded O–H stretching vibration from the cellulose structure of the TFS. The peak at 2930 cm^{-1} is indicative of the C–H stretching vibration of cellulose. The bands at 1739 and 677 cm^{-1} arise due to C=O stretching of hemicellulose and β -glycosidic linkage respectively.

The FTIR spectra of PGTF $\text{S-NH}_3^+\text{Cl}^-$ shows strong absorption band at 3428 cm^{-1} due to the overlap of C–H, N–H and C=O stretching vibrations. The peak at 1723 cm^{-1} gives the C=O stretching of hemicellulose. The symmetric and asymmetric stretching of -NH_3^+ are observed at 2365 and 2931 cm^{-1} , respectively [18]. The bands at 1541 and 1452 cm^{-1} are characteristic of -NH_3^+ groups. The band at 1668 cm^{-1} indicate the C=O stretching of aliphatic amide group of PGTF $\text{S-NH}_3^+\text{Cl}^-$. Additional peaks at 1452 and 1060 cm^{-1} in PGTF $\text{S-NH}_3^+\text{Cl}^-$ (which is absent in TFS) indicate the presence of aliphatic C–N vibration and $\text{-CH}_2\text{NH}_3^+$ type nitrogen arise due to the ethylenediamine bonded to the hydroxyethylmethacrylate grafted TFS through transamidation reaction [19]. The band at 673 cm^{-1} may be assigned to β -glycosidic linkage. These observations clearly indicate the formation of polymeric chain and the presence of $\text{-NH}_3^+\text{Cl}^-$ functional group.

The SEM micrographs of TFS and PGTF $\text{S-NH}_3^+\text{Cl}^-$, taken at magnification 1500 \times are presented in Fig. 2. The TFS displayed extensive three-dimensional network. The SEM image of TFS shows that the pores within TFS particles are highly heterogeneous. After modification, a significant change is observed in the structure of the adsorbent. The size of the voids in the original TFS is reduced after graft polymerization and some distortion of shape can be seen in the SEM of PGTF $\text{S-NH}_3^+\text{Cl}^-$. It has a rough surface caused by the rigid and hydrophobic nature of the N,N'-methylenebisacrylamide cross-links. The porous nature of PGTF $\text{S-NH}_3^+\text{Cl}^-$ provides new adsorption sites from the interior cavities to participate in the binding of metal ions.

The amount of C, H, and N in PGTF $\text{S-NH}_3^+\text{Cl}^-$ were found to be 53.6, 6.1, and 2.3% where as TFS contained 49.8, 5.4, and 0.72%, respectively. The increase in the percentage of N confirmed the proper modification of the TFS through polymer grafting and

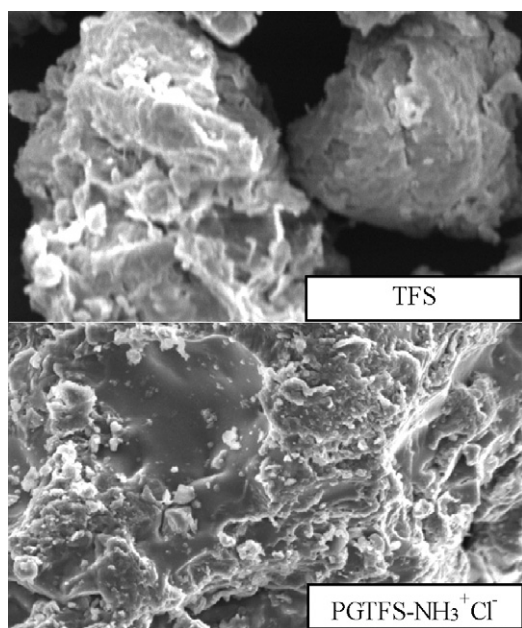


Fig. 2. SEM photographs of TFS and PGTFs-NH₃⁺Cl⁻.

transamidation reactions. The degree of substitution of amine functionality of TFS was calculated to be 0.368. pH_{pzc} values for TFS and PGTFs-NH₃⁺Cl⁻ were found to be 7.4 and 8.2, respectively. The increase in pH_{pzc} of PGTFs-NH₃⁺Cl⁻ shows that the surface becomes more positive after chemical modification and will help the adsorption of negatively charged species more easily. The surface area, density, and anion-exchange capacity of TFS and PGTFs-NH₃⁺Cl⁻ were found to be 13.3 and 21.4 m²/g, 1.02 and 1.42 g/mL, and 0.89 and 1.32 meq/g, respectively. These physico-chemical analyses clearly shows that PGTFs-NH₃⁺Cl⁻, due to its improved physico-chemical, properties can be used as a better adsorbent for remediation of metal ions from aqueous solutions.

3.2. Effect of chemical modification

The effect of chemical modification on V(V) adsorption was studied by conducting batch experiments using an initial concentration of 25.0 mg/L with adsorbent doses of TFS and PGTFs-NH₃⁺Cl⁻ ranging from 0.5 to 5.0 g/L. Fig. 3 shows that the percentage of adsorption increased with increase in adsorbent doses and for the quantitative removal of 25.0 mg/L V(V) ions from aqueous solutions, a minimum adsorbent dosage of 3.5 g/L of PGTFs-NH₃⁺Cl⁻ and 5.0 g/L of TFS were required, respectively.

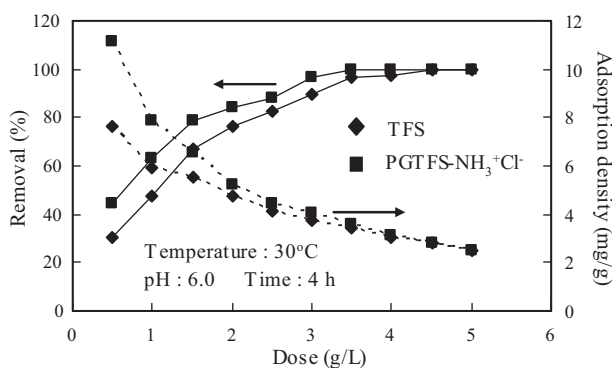


Fig. 3. Effect of adsorbent dose on the adsorption of V(V) ions from aqueous solutions by TFS and PGTFs-NH₃⁺Cl⁻.

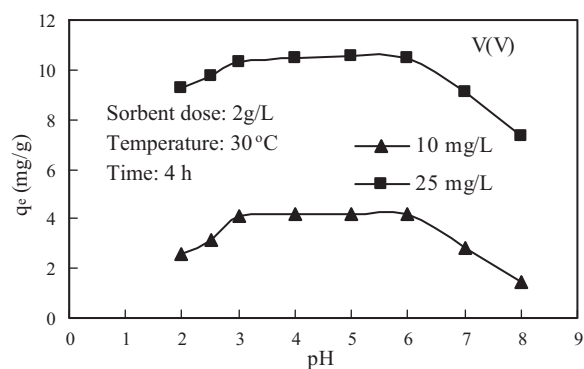


Fig. 4. Effect of pH on the adsorption of V(V) ions onto PGTFs-NH₃⁺Cl⁻.

However, the adsorption density showed an opposite trend. As the adsorbent dosage was increased from 0.5 to 5.0 g/L, the adsorption density reduced from 11.17 to 2.50 mg/g, for PGTFs-NH₃⁺Cl⁻ and 7.67 to 2.50 mg/g, for TFS respectively. This is a clear indication that an increase in adsorbent dosage results in higher number of unoccupied binding sites in PGTFs-NH₃⁺Cl⁻. The data clearly shows that PGTFs-NH₃⁺Cl⁻ is 1.42 times more effective than TFS for the removal of V(V) ions from aqueous solutions. Accessibility of more adsorption sites at high doses ensured the enhanced uptake of V(V) ions. The high percentage removal obtained for PGTFs-NH₃⁺Cl⁻ may be due to the introduction of -NH₃⁺Cl⁻ group on the PGTFs-NH₃⁺Cl⁻ surface through graft copolymerization and transamidation reactions. Also the high pH_{pzc} of PGTFs-NH₃⁺Cl⁻ (8.2) compared to TFS (7.4) indicates that PGTFs-NH₃⁺Cl⁻ surface became more positive due to chemical treatment and this increases the extent of V(V) adsorption onto PGTFs-NH₃⁺Cl⁻. Since PGTFs-NH₃⁺Cl⁻ is more effective than TFS for the removal of V(V) ions from aqueous solutions, further adsorption experiments were carried out using PGTFs-NH₃⁺Cl⁻.

3.3. The effect of pH on the adsorption of V(V) ions

The pH of aqueous solution is an important factor that influences the adsorption of metal ions at solid-liquid interfaces. The effect of pH on the adsorption of V(V) is shown in Fig. 4. For an initial concentration of 10 and 25 mg/L, the adsorption capacity of V(V) increased with pH at the beginning, and then attained a plateau in the pH range from 3.0 to 6.0 and afterwards, the adsorption capacity dramatically decreased. At pH 6.0, for an initial concentration of 10 and 25 mg/L, the amount adsorbed was found to be 4.19 and 10.50 mg/g respectively.

The pH allied adsorption behavior of V(V) is greatly related to the speciation of V(V) in aqueous solution as well as the surface characteristics of the PGTFs-NH₃⁺Cl⁻. According to Baes and Mesmer [20], the speciation diagram for vanadium indicated the existence of 12 vanadium species in aqueous solution. These can be categorized as cationic VO₂⁺, neutral VO(OH)₃ and anionic species V₁₀O₂₆(OH)₂⁴⁻, V₁₀O₂₇(OH)⁵⁻, V₁₀O₂₈⁶⁻ and other mono or poly-vanadate species VO₂(OH)²⁻, VO₃(OH)²⁻, VO₄³⁻, V₂O₆(OH)³⁻, V₂O₇⁴⁻, V₃O₉³⁻ and V₄O₁₂⁴⁻. Speciation diagrams for vanadium [20,21] imply that below pH 3.0, vanadium exists in cationic forms and anionic form dominates in the pH range of 4–11. In the pH range 4.0–10.0, V(V) exists mainly as VO₃⁻ [22]. The decrease of adsorption below pH 3.0 might be due to the existence of VO₂⁺ ion, which experiences electrostatic repulsion from the protonated amino groups of the adsorbent. Maximum adsorption at pH 3.0–6.0 indicates that the predominant VO₃⁻ species of V(V), adsorbed preferentially on the positively charged adsorbent surface. Above the pH_{pzc} (8.2), the adsorbent surface is negatively charged. The decrease in adsorption

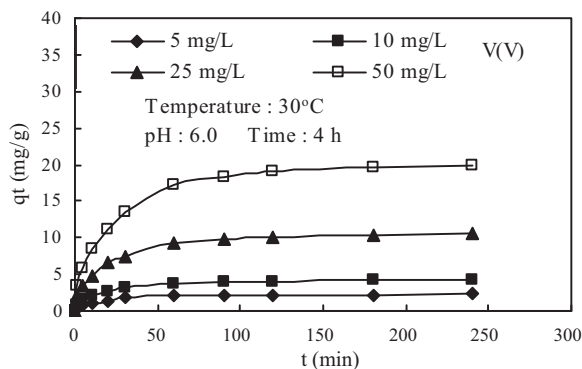


Fig. 5. Effect of contact time and initial concentration on the adsorption of V(V) ions onto PGTFS-NH₃⁺Cl⁻.

capacity at higher pH values may be due to the electrostatic repulsion between the anionic V(V) species and the negatively charged surface of the adsorbent. The decrease in V(V) adsorption at high pH may also be due to competition between OH⁻ and aqueous vanadium anions for available surface sites. The adsorption of V(V) ions can be schematically represented as:



This result agrees with previous studies that the optimum pH range for sorption of V(V) ions is between 3.0 and 7.0 [8].

3.4. Effect of contact time and initial concentration

Fig. 5 shows the effect of contact time and initial V(V) concentration on the adsorption capacity of PGTFS-NH₃⁺Cl⁻. It can be noticed that the contact time significantly affects the V(V) uptake; more than 90% of adsorption takes place in the first 60 min and tapers off there after, and equilibrium was approached within 4 h. With the change in concentration of the solution from 5.0 to 50.0 mg/L, the amount adsorbed increased from 2.25 to 19.80 mg/g. The equilibrium time was independent of initial metal ion concentration. The initial relatively rapid V(V) uptake indicates that the adsorption occurs mainly on the surface of the adsorbent. According to Sag and Kutsal [23], the uptake of heavy metal ions by biosorbents occurs in two stages: the first rapid and quantitatively predominant and the second slower and quantitatively insignificant. The initial rapid stage of adsorption is probably due to the abundant availability of active sites on the adsorbent, and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage [24]. In the present study, the initial rapid V(V) uptake by the PGTFS-NH₃⁺Cl⁻ may be attributed to its porous structure, which provides ready access and large surface area for the sorption of V(V) ions on the binding sites. The relatively rapid kinetics has a significant practical importance, as it will facilitate smaller reactor volumes ensuring efficiency and economy.

3.5. Effect of temperature

The effect of temperature on V(V) adsorption was carried out in temperature ranging from 10 to 40 °C (Fig. 6). An increase in temperature leads to decrease in V(V) adsorption. The amount of V(V) adsorbed was 11.43, 10.88, 10.29, and 9.66 mg/g at 10, 20, 30, and 40 °C, respectively for an initial concentration of 25.0 mg/L. This indicates that low temperature favors the adsorption process. Solution temperature affect to electro-selectivity reaction, ion solvation, formation of ion pairs, and association and formation of complexes between V(V) ions and the adsorbent. It has been suggested that the adsorption of water molecules on PGTFS-NH₃⁺Cl⁻ is higher at lower temperatures due to the competition of V(V)

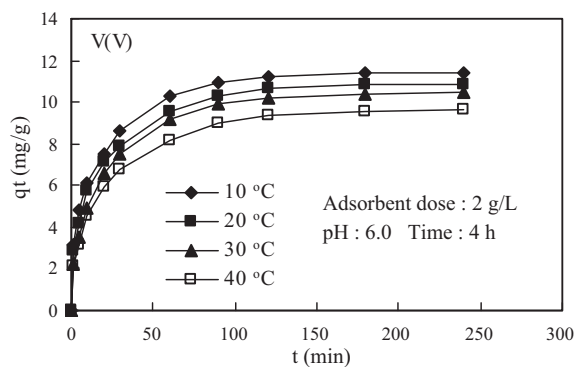


Fig. 6. Effect of temperature on the adsorption of V(V) ions onto PGTFS-NH₃⁺Cl⁻.

ions with water molecules. Hence, at lower temperatures, there are more rigorous electrostatic interactions between the V(V) anions and the active sites on the PGTFS-NH₃⁺Cl⁻, comparing to dipole-dipole interactions between water molecules and the active sites on PGTFS-NH₃⁺Cl⁻. The high charged, associated V(V) anions stabilized at lower temperature may be responsible for the strong interactions with the active sites on PGTFS-NH₃⁺Cl⁻ through ion-pairing mechanism. With the increasing of the adsorption temperature, the monomeric forms become dominant and so the adsorption process occurs through normal ion exchange mechanism.

3.6. Adsorption kinetic studies

The V(V) adsorption from liquid phase onto solid PGTFS-NH₃⁺Cl⁻ can be considered as a reversible process. The kinetic data can be studied by a reversible second-order rate equation as cited by Fox et al. [25], which is represented by

$$k_1 t = \frac{C_0 - C_e}{2C_0 C_e} \ln \left(\frac{C_0 C_e - 2C_t C_e + C_t C_0}{C_0 (C_t - C_e)} \right) \quad (6)$$

where k_1 is the conditional rate constant, C_0 , C_t , and C_e refer to concentrations at time 0, t , and equilibrium, respectively. The straight-line plot of $k_1 t$ versus t (figure in supplementary material) with a correlation coefficient (r^2) of more than 0.988 at different concentrations and temperatures indicates that the adsorption process follows reversible second-order kinetics. The k_1 values calculated from the slopes of the plots are presented in Table 1. The linearized k_1 and C_0 values on a double logarithmic plot (figure not shown) showed a correlation coefficient (r^2) of 0.992, the relationship between k_1 and C_0 being of the type

$$k_1 = 0.164 C_0^{-1.362} \quad (7)$$

Table 1

Kinetic parameters for the adsorption of V(V) ions onto PGTFS-NH₃⁺Cl⁻ at different initial concentrations and temperatures.

	Reversible second-order		Reichenberg	
	k_1 (L/mg min)	r^2	D_i (m ² /s)	r^2
Concentration (mg/L)				
5	20.3×10^{-3}	0.982	6.78×10^{-12}	0.998
10	6.0×10^{-3}	0.992	6.43×10^{-12}	0.999
25	2.2×10^{-3}	0.997	5.91×10^{-12}	0.999
50	0.8×10^{-3}	0.998	5.49×10^{-12}	0.998
Temperature (°C) ^a				
10	4.4×10^{-3}	0.980	6.61×10^{-12}	0.998
20	2.8×10^{-3}	0.993	6.26×10^{-12}	0.995
30	2.2×10^{-3}	0.996	5.91×10^{-12}	0.999
40	1.5×10^{-3}	0.998	5.61×10^{-12}	0.999

^a Concentration: 25 mg/L.

Table 2
Langmuir, Freundlich and Redlich–Peterson isotherm constants for the adsorption of V(V) ions onto PGTFs–NH₃⁺Cl[–].

Temperature (°C)	Langmuir			Freundlich			Redlich–Peterson			
	q_{mL}	K_L	Hybrid	K_F	n_F	Hybrid	K_R	a_R	b_R	Hybrid
10	51.98	0.128	1.96	9.98	2.97	165.60	7.20	0.161	0.968	1.12
20	48.56	0.094	2.77	8.34	2.85	133.20	4.82	0.110	0.978	2.85
30	45.86	0.070	1.78	6.52	2.63	131.23	3.22	0.068	1.00	2.06
40	38.56	0.061	0.485	5.46	2.62	85.86	2.42	0.067	0.985	0.456

It is found that the k_1 values decreases both with increase in initial concentration and temperature.

Kinetic data obtained in this work were further analyzed by applying the Reichenberg equation as:

$$Bt = 6.28318 - 3.2899F - 6.28318(1 - 1.047F)^{1/2} \text{ for } F = 0 - 0.85 \quad (8)$$

$$Bt = -2.30258 \log(1 - F)^{-0.4977} \text{ for } F = 0.86 - 1.0 \quad (9)$$

where F is the fractional equilibrium that is reached at time t obtained by the expression

$$F = \frac{q_t}{q_e} \quad (10)$$

where q_t is the amount of adsorbate taken up at time t . q_e is the maximum equilibrium uptake. B is given by

$$B = \frac{\pi^2 D_i}{r_0^2} = \text{constant} \quad (11)$$

where D_i is the effective diffusion coefficient of ions in the adsorbent phase and r_0 is the radius of spherical adsorbent particles.

Bt values (the product of multiplying B by time t) were obtained for each observed value of F from Reichenberg's table [26] at different initial concentrations and temperatures. The linearity test of Bt versus time plots was employed to distinguish between adsorption controlled by film versus particle diffusion. If a Bt versus time plot (slope = B) is linear and passes through the origin, then the adsorption rate is governed by diffusion in the particle. Otherwise, it is governed by film diffusion. The Bt versus time plots at different initial concentrations and temperatures are given in supplementary material. The Bt versus time plots are nearly linear and pass through the origin at different initial concentrations and temperatures indicating the mechanism's rate controlling step is diffusion in the particle.

The values of D_i at different initial concentrations and temperatures were estimated from the slopes of the Bt plots and were shown in Table 1. The values show that the diffusion of the V(V) ions onto PGTFs–NH₃⁺Cl[–] is more favorable at lower initial concentrations and temperatures. The values of energy of activation (E_a), the entropy of activation (ΔS^\ddagger) and the pre-exponential factor (D_0) were also evaluated using the following Arrhenius and Eyring equations

$$D_i = D_0 \exp\left(\frac{E_a}{RT}\right) \quad (12)$$

$$D_0 = 2.72d^2 \left(\frac{k_b T}{h}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (13)$$

where k_b is the Boltzmann's constant, h is the plank's constant, R is the gas constant and d is the distance between two active sites of the adsorbent, which is conveniently taken as 5 Å. The values of E_a , D_0 and ΔS^\ddagger for the diffusion of V(V) in PGTFs–NH₃⁺Cl[–] were found to be -4.06 kJ/mol, 1.78×10^{-12} m²/s and -125.47 J/mol K. Relatively low value of E_a further confirmed that metal adsorption is a diffusion controlled process and the negative value suggests that the

decrease in solution temperature does favor the metal ion adsorption by PGTFs–NH₃⁺Cl[–]. The negative value of ΔS^\ddagger (-47.20 J/mol K) indicates that the adsorption leads to order through the formation of activated complex suggesting that V(V) adsorption on PGTFs–NH₃⁺Cl[–] surface is an associated mechanism [27].

3.7. Equilibrium isotherms

An adsorption isotherm is a good tool for understanding the nature of a surface. However, a correct selection of adsorption equation for different concentration ranges reveals a true picture of the surface. The equilibrium adsorption data from the batch experiments were modeled using Langmuir (Eq. (14)) and Freundlich (Eq. (15)) and Redlich–Peterson (Eq. (16)) adsorption isotherms.

$$q_e = \frac{q_{mL} K_L C_e}{1 + K_L C_e} \quad (14)$$

$$q_e = K_F C_e^{1/n_F} \quad (15)$$

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} \quad (16)$$

where q_e is the adsorbed amount at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), q_{mL} is the Langmuir monolayer sorption capacity (mg/g) and K_L is the Langmuir equilibrium constant (L/mg). K_F is the Freundlich constant related to adsorption capacity (mg/g) and n_F is a constant indicative of intensity of adsorption. K_R , a_R and b_R are Redlich–Peterson constants. The Langmuir model [28] describes the monolayer coverage at high concentrations and is best suited for an adsorbent with homogeneous surface sites. The Freundlich isotherm [29] gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Redlich–Peterson isotherm [30] which contains three parameters incorporating the features of the Langmuir and the Freundlich isotherms.

The Langmuir, Freundlich and Redlich–Peterson isotherm constants were calculated using non-linear optimization method and the results are presented in Table 2. The low values of HYBRID error function show that the adsorption process is best fitted to the Langmuir equation over the entire range of concentrations. The theoretical Langmuir, Freundlich and Redlich–Peterson isotherms are plotted in Fig. 7 together with the experimental data points. The calculated q_e values for different concentrations, using the Langmuir equation agree very well with the experimental data. The Langmuir monolayer adsorption capacity and equilibrium constant decreases with increase in temperature indicating that the adsorption is more favorable at low temperatures. At high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the PGTFs–NH₃⁺Cl[–] surface to the solution phase, which results in a decrease in adsorption as temperature increases [31]. The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between PGTFs–NH₃⁺Cl[–] surface and the V(V) ion, which supports physisorption.

In order to predict whether the adsorption process by PGTFs–NH₃⁺Cl[–] is favorable or not for the Langmuir type adsorp-

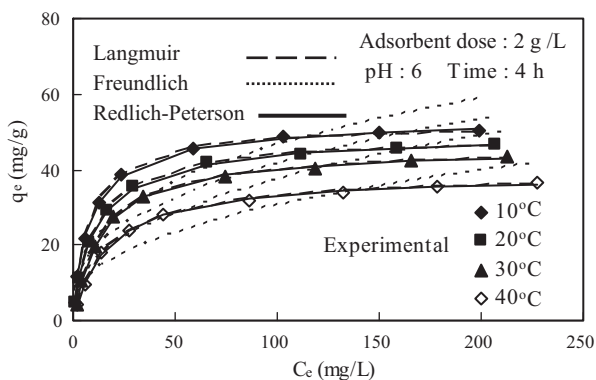


Fig. 7. Comparison of the model fit of Langmuir, Freundlich and Redlich–Peterson isotherms to the experimental data for the adsorption of V(V) ions onto PGTF5–NH₃⁺Cl[−].

tion method, the isotherm shape can be classified by a term R_L , a dimensionless constant separation factor [32], which is defined below

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (17)$$

The parameter R_L indicates the shape of the isotherm accordingly:

$R_L > 1$ unfavorable, $R_L = 1$ linear, $R_L < 1$ favorable, $R_L = 0$ irreversible.

The R_L values between 0 and 1 at different concentrations and temperatures (table presented in supplementary material) indicate favorable adsorption of V(V) onto PGTF5–NH₃⁺Cl[−].

The Langmuir monolayer sorption capacity can be used to evaluate the relative adsorption performance of PGTF5–NH₃⁺Cl[−]. To validate the utility of PGTF5–NH₃⁺Cl[−] as an anion exchanger for V(V) removal from aqueous solutions, its adsorption capacity should be compared with a commercial synthetic polymer-based anion-exchange resin. For this a commercial chloride form anion exchanger, Dowex was used and adsorption isotherm studies were conducted at an initial pH of 6.0 at 30°C. The experimental data were modeled with Langmuir equation and the fitting plots are presented in supplementary material. The Langmuir monolayer adsorption capacity (q_{mL}) and equilibrium constant (K_L) were 39.69 mg/g and 0.067 L/mg, respectively, which are somewhat lower than those of the newly developed adsorbent material.

3.8. Thermodynamic parameters

The equilibrium constant K_0 for the adsorption process was determined by plotting $\ln(q_e/C_e)$ versus q_e (figure not shown) at different temperatures and extrapolating to zero q_e using a graphical method described by Khan and Singh [33]. Regression straight lines are fitted through the data points by least-square method and their intersections with the vertical axis give the value of K_0 at different temperatures. The K_0 values are found to be decreasing with increase in temperature in all cases. This shows the decreasing trend in adsorption with the increase in temperature. In order to evaluate the feasibility of the adsorption process, thermodynamic parameters such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were determined. To calculate the values of the parameters the following equations were used:

$$\Delta G^0 = -RT \ln K_0 \quad (18)$$

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (19)$$

Table 3

Thermodynamic parameters for the adsorption of V(V) onto PGTF5–NH₃⁺Cl[−].

Temperature (°C)	K_0	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
10	2.60	−2.25	−15.64	−47.20
20	2.19	−1.90		
30	1.66	−1.28		
40	1.40	−0.88		

where R is the gas constant, and T is the temperature (K). The ΔH^0 and ΔS^0 values were determined from the slope and intercept of the plot of $\ln K_0$ versus $1/T$ and the results are shown in Table 3. Negative values of ΔG^0 obtained indicated the feasibility of the adsorption process and the spontaneous nature of the V(V) adsorption onto PGTF5–NH₃⁺Cl[−]. A slight decrease in ΔG^0 value with decrease of temperature indicates that the adsorption is more favorable at lower temperature. It must be taken into account that ΔG^0 values up to -20 kJ/mol indicate electrostatic interaction between sorption sites and the metal ion (physical adsorption), while more negative values up to -40 kJ/mol involve electron sharing (chemical adsorption) [34]. The ΔG^0 values obtained in this study indicate that physical adsorption is the predominant mechanism in the sorption process. The negative values of ΔH^0 (-15.64 kJ/mol) on to the PGTF5–NH₃⁺Cl[−] further confirm the exothermic nature of the adsorption process. The value of ΔH^0 is less than -40.0 kJ/mol, indicating that adsorption process is physical in nature [35]. The negative values of ΔS^0 (-47.20 J/mol K) indicate the higher order of reaction during the adsorption of V(V) ions onto PGTF5–NH₃⁺Cl[−] and also reflects the affinity of the adsorbent materials for V(V) ions.

3.9. Isotheric heat of adsorption

The isotheric heat of adsorption (ΔH_i) is a differential molar quantity, which gives a measurement of the heat energy released during the process of adsorption. ΔH_i at constant surface coverage $q_e = (2, 4, 6, 8, 10, 12, 14, 16)$ mg/g is calculated using Clausius–Clapeyron equation [36]:

$$\frac{d(\ln C_e)}{dT} = -\frac{\Delta H_i}{RT^2} \quad (20)$$

For this purpose, the equilibrium concentration (C_e) at constant amount of adsorbed V(V) is obtained from the adsorption isotherm data at different temperatures. Adsorption isotheres were plotted between $\ln C_e$ versus $1/T$ corresponding to different equilibrium uptake of V(V) by PGTF5–NH₃⁺Cl[−] (figure in supplementary material). ΔH_i , calculated from the slope of adsorption isotheres remains constant (~ 26.0 kJ/mol) and is found to be independent of the surface loading. This trend in ΔH_i clearly confirms that PGTF5–NH₃⁺Cl[−] contains almost homogeneous surface sites and there is no lateral interaction between the adsorbed V(V) ions. The values of ΔH_i for V(V) ions adsorption fall in the range of physical adsorption as stated by Dogan and Alkan [37], indicating that some electrostatic interactions are involved in adsorption process.

The extent of surface homogeneity (heterogeneity) of PGTF5–NH₃⁺Cl[−] as well as the PGTF5–NH₃⁺Cl[−]–V(V) interactions were further substantiated by a new isotherm proposed by Do and Do [38] as:

$$\Delta H_i = \Delta H_0 \left\{ 1 - \frac{\alpha \beta \theta}{1 + (\beta - 1) \theta} \right\} + \mu \theta \quad (21)$$

where ΔH_i corresponds to the isotheric adsorption enthalpy at fractional loading (θ) of V(V), ΔH_0 is the isotheric adsorption enthalpy at zero loading of V(V). The α reflects the extent of the surface heterogeneity of the adsorbent called heterogeneity factor. The

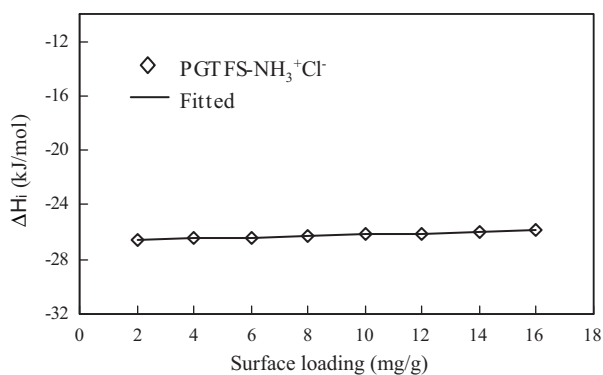


Fig. 8. Variation of ΔH_i with respect to surface loading.

larger the value of α , the greater the extent of surface energy heterogeneity. The parameters β and μ respectively, indicates the surface heterogeneous pattern and the interaction energy of the adsorbed adsorbate. The ΔH_i and θ values were fitted in Eq. (21) and the model parameters were estimated by non-linear regression method. A comparison between the isosteric adsorption enthalpy and the calculated value using Do's model as a function of surface loading was shown in Fig. 8. The values of ΔH_0 , α , β , and μ are found to be -26.60 kJ/mol, 0.375, 0.850, and 0.247 respectively. Relatively low values of surface heterogeneity factor (0.375) and surface heterogeneous pattern parameter (0.850) compared to reported values in literature [39] also confirms the surface homogeneity of PGTFs- NH_3^+Cl^- . The results obtained from ΔH_i modeling studies also support the applicability of Langmuir adsorption isotherm to the present system.

3.10. Removal of V(V) by PGTFs- NH_3^+Cl^- from synthetic groundwater sample

Experiments were carried out to find the effectiveness of the PGTFs- NH_3^+Cl^- for removing V(V) ions from synthetic groundwater samples. The composition (mg/L) of the V(V) containing groundwater sample is; V(V): 20; Cl^- : 63.6; SO_4^{2-} : 55.1; NO_3^- : 36.5; PO_4^{3-} : 34.9; Na^+ : 56.9; Ca^{2+} : 36.4; and K^+ : 59.3 [12]. The batch studies were conducted at different adsorbent doses and the results were presented in Fig. 9. The removal efficiency for V(V) was found to be $\sim 99\%$ using 4.5 g/L of adsorbent dose and at this stage, the V(V) concentration in water sample after adsorption decreased below 0.05 mg/L, which is the maximum permissible limit as per EPA norms. The results indicated that the presence of other anions in the medium do not caused an appreciable impact on the adsorption performance of PGTFs- NH_3^+Cl^- . These results were almost

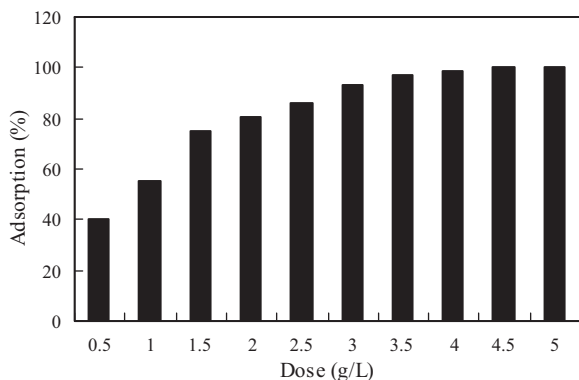


Fig. 9. Effect of adsorbent dose on the adsorption of V(V) ions from wastewater onto PGTFs- NH_3^+Cl^- .

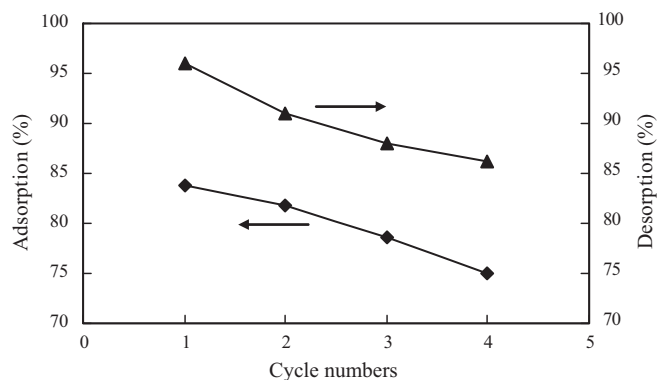


Fig. 10. Four cycles of V(V) adsorption–desorption with 0.2 M NaOH as the desorbing agent.

consistent with that obtained from batch experiments and this confirms that PGTFs- NH_3^+Cl^- is a very good adsorbent for the removal of V(V) ions from synthetic groundwater.

3.11. Desorption and regeneration studies

Desorption studies were conducted to probe further into the mechanistic aspects of V(V) adsorption onto PGTFs- NH_3^+Cl^- . The economic feasibility of using adsorbent to remove contaminants from wastewater relies on its regeneration ability during multiple adsorption/desorption cycles. In addition, the reversibility of the adsorption process has been studied in a qualitative manner through desorption studies. Each adsorption (PGTFs- NH_3^+Cl^- –10 mg/L of V(V)) and desorption cycle (V(V) loaded PGTFs- NH_3^+Cl^- –0.2 M NaOH) was allowed 240 min of contact time at 30 °C and successive adsorption–desorption cycles were repeated four times using the same adsorbent in solutions (Fig. 10). After four cycles, the adsorption capacity decreased from 83.8 to 75.1% while the recovery of V(V) ions decreased in the first cycle from 95.9 to 86.2% in the fourth cycle. There was a slight decrease in both the percentage of V(V) ion adsorbed and the percentage of V(V) ion desorbed from the first to the fourth cycle. This small decrease may be due to the fact that the V(V) ion are bound to the anion-exchange resin through electrostatic interactions and are not recoverable fully in subsequent cycles. The results showed that the spent PGTFs- NH_3^+Cl^- can be effectively regenerated for further use for adsorption process.

4. Conclusions

An amine-functionalized polymer grafted tamarind fruit shell anion exchanger (PGTFs- NH_3^+Cl^-) bearing $-\text{NH}_3^+\text{Cl}^-$ moiety was prepared by graft copolymerization of TFS with hydroxyethyl-methacrylate followed by transamidation, and hydrochloric acid treatment and used as an adsorbent for the removal of V(V) ions from aqueous solutions. Experimental data revealed that maximum adsorption was occurred at the pH range 3.0–6.0. The amount adsorbed increased with increase of initial concentration and equilibrium was established within 4 h. The kinetic data at different initial concentrations and temperatures can well be described by reversible-second-order kinetic model. The Bt versus time plots of Reichenberg model indicates that particle diffusion is the rate controlling step in the process of adsorption. The fact that, V(V) adsorption onto PGTFs- NH_3^+Cl^- can be best described with Langmuir isotherm points out the homogeneous surface sites of PGTFs- NH_3^+Cl^- and also the monolayer formation of V(V) ions over the adsorbent surface. The thermodynamic study showed that the adsorption process was spontaneous and exothermic and the sys-

tem disorder decreased during the adsorption process. The values of ΔG^0 and ΔH^0 suggested that the interaction between V(V) ions and PGTF₅-NH₃⁺Cl⁻ surface was weak enough to be considered as physical sorption. The ΔH_i variation pattern with surface loading also indicated the homogeneous surface sites of PGTF₅-NH₃⁺Cl⁻. The utility of PGTF₅-NH₃⁺Cl⁻ as an adsorbent for removing V(V) ions from synthetic groundwater samples was also evaluated. The regeneration studies performed using 0.2 M NaOH as the desorbing agent provided beneficial results without any loss in adsorption capacity. The practical implication of this study is the development of an effective and economic technology for V(V) removal from aqueous solutions, especially useful when TFS is locally available.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cej.2010.09.005](https://doi.org/10.1016/j.cej.2010.09.005).

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