Surface modification of pine bark with quaternary ammonium groups and its use for vanadium removal

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HIGHLIGHTS
- Quaternary ammonium groups were successfully grafted onto pine bark.
- Initial NaOH concentration played an important role in the modification process.
- The maximum capacity for vanadium was found to be 35 mg/g.
- Modified pine bark can be used as a cost-effective adsorbent for vanadium removal.

GRAPHICAL ABSTRACT

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ABSTRACT
Chemically modified pine bark was synthesized by using glycidyl trimethyl ammonium chloride (GTMAC) in the presence of sodium hydroxide. Optimization of the modification parameters was performed in order to maximize vanadium removal. Parameters included the initial NaOH concentration (0.01–2% w/v), GTMAC dosage (0.0067–0.0805 mol/g), modification time (1–6 h), modification temperature (40–80 °C) and volume (25–100 mL). The optimal modification conditions were found to be 0.1% NaOH (w/v), 0.0134 mol/g GTMAC, 3 h and 60 °C. The initial NaOH concentration played the most important role in successful modification while the GTMAC/NaOH ratio and volume had no significant effect under the studied conditions. Leaching of organic substances from the modified product was minor in comparison with raw pine bark. XPS analysis confirmed that quaternary nitrogen was successfully grafted onto the pine bark and that the BET surface area increased in the modification. The maximum vanadium adsorption capacity of the optimized product was found to be 32.3–35.0 mg/g at different temperatures (20 °C, 15 °C and 5 °C) at pH 4 with a contact time of 24 h, and the adsorption data was in very good agreement with the Freundlich and Redlich-Peterson models. The adsorption kinetics can be described well by the Elovich equation. Fitting the kinetic data with intra-particle diffusion and Boyd models showed that the adsorption process was controlled by both film and intra-particle diffusion, while intra-particle diffusion was the rate-limiting step. Regeneration studies demonstrated that, as a recyclable product, modified pine bark can be used effectively in real industrial processes for vanadium removal.

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1. Introduction

Vanadium occurs widely in natural resources such as crude petroleum, uranium ores, phosphate deposits and magnetites but concentrated vanadium deposits are quite rare [1]. As an important element, vanadium has been employed in various fields, for instance, oil refining, metallurgy, mining, pigments or catalyst industry, etc. Due to the extensive use of vanadium and its suspected toxicity, the removal of vanadium from wastewaters has become an important issue in terms of environmental protection. Vanadium exists in different oxidation states in aqueous solution, with vanadium (V^5+) as the major stable species in oxidation states [2]. The speciation of vanadium is highly influenced by the solution pH and vanadium concentration. When the pH < 3, vanadium exists mainly in cationic form and when the pH is higher than 3, anionic species are dominant [3]. Therefore, vanadium (V^5+) can be successfully removed as an anionic pollutant from water. Owing to the obvious advantages of adsorption such as simplicity and low cost, it is commonly used and reported for vanadium removal from aqueous solution [4–6].

Many research studies have investigated the development of low-cost and efficient adsorbents from agricultural by-products and industrial wastes. These materials are normally low-cost, abundant and requiring less processing. Some of the reported materials used for vanadium removal include sawdust [6], iron-modified peat [4], amine-grafted fruit shell [7], kaolin-supported zerovalent iron [5], and waste metal sludge [8]. Recently, adsorption using bark material, a by-product from the forestry industry, has attracted increasing interest. For the purpose of environment protection and resource optimization, direct use of pine bark has been reported in several studies for metal removal [9,10]. Bark materials mainly contain lignin and phenolics, polysaccharide, water and extractives, and a small amount of ash [11], and thus leaching of some components from wood-based material may result in high chemical oxygen demand (COD) in treated water [12]. Therefore, modification of raw bark is needed before its use. For example, the removal of metal cations [12], pesticide [13], reactive dye [14], polycyclic aromatic hydrocarbons [15] and biphenol A [16] with modified pine bark have been reported. However, it is worth noting that many important water pollutants are in anionic form in aqueous solutions. Although some research has studied removal by modified bark materials of anionic pollutants such as nitrate [17], phosphate [18], chromium [19], and arsenic [20], the number of studies remains very limited.

In recent years, various surface modification methods have been suggested for anionic pollutant removal. The most commonly used methods involve acid or alkaline treatment [21,22], metal impregnation [23], esterification [24] and/or cationization [25–27]. The principles of surface modification are based on biomass carbonization or the introduction of some functional groups or positively charged sites onto the adsorbent [28]. Of these methods, surface modification using cationic polymers has been proved to be efficient. Amines and quaternary ammonium reagents, such as cetyl trimethyl ammonium bromide (CTAB), 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHMAC), glycylid trimethylammonium chloride (GTMAC), polyethyleneimine (PEI) and hexadecyltrimethylammonium (HDTMA) etc., can provide positively charged sites on the adsorbent. However, in many studies, highly toxic cross-linking reagents have been used and the modification process is sometimes quite complicated.

In this study, a new, simple and less hazardous modification route has been developed to prepare quaternized pine bark using GTMAC and has been tested for vanadium removal. A systematic and in-depth study was conducted to optimize the modification by studying the following factors: the initial NaOH concentration, GTMAC dosage, modification time, temperature and volume. Moreover, this study also compared the effect of modification volume, GTMAC/NaOH molar ratio and initial NaOH concentration on the success of the modification and identified the determining factor in the GTMAC modification of pine bark.

2. Materials and methods

2.1. Raw materials and chemicals

Pine bark (PB), obtained from the Roihupuu Company (Oulu, Finland), was dried at 80 °C for 24 h. Then the dried pine bark was ground and sieved to obtain a fraction of 90–250 µm. Glycidyl trimethyl ammonium chloride (GTMAC) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. A stock solution of vanadium was prepared by dissolving NaVO3 (Sigma-Aldrich) in Milli-Q water (Merck Millipore). HCl (37%, Merck) and NaOH were used for pH adjustment. All the chemicals used in the study were of analytical grade.

2.2. Preparation of modified pine bark and vanadium adsorption test

The effect of NaOH concentration was studied by weighing one gram of pine bark and mixing it with 50 mL of NaOH solution (0.01–2% w/v) and 2 mL of GTMAC (0.0134 mol/g) in a 250 mL round-bottom glass flask. The mixed solution was then submerged in a water bath and continuously stirred for 3 h at 60 °C. Upon completion, the obtained product was washed thoroughly several times with deionized water until the pH reached neutral and the supernatant became clear. The washed product was dried in an oven at 60 °C for 24 h to form GTMAC-modified pine bark (referred to hereinafter as GPB).

Regarding the GTMAC dosage studies, the initial NaOH concentration was fixed as 0.1% NaOH (w/v) and different amounts of GTMAC (0.0067–0.0805 mol/g) were added. Other parameters were kept the same as in the NaOH studies.

The effects of the modification time (1–6 h) and temperature (40–80 °C) were studied with the optimal initial NaOH concentration and GTMAC dosage. The effect of the modification time was investigated at a constant temperature (60 °C) and the effect of the modification temperature was studied with a fixed modification time (3 h).

The effect of the modification volume was studied in two parts. The optimal GTMAC dosage (0.0134 mol/g), modification time (3 h) and temperature (60 °C) were used. Firstly, the GTMAC/NaOH molar ratio was kept constant (10.7) and three different NaOH solution volumes were studied: 25 mL (0.2% NaOH w/v), 50 mL (0.1% NaOH w/v) and 100 mL (0.05% NaOH w/v). In the second part, the initial NaOH concentration was kept at the same value of 0.1% (w/v) for the different NaOH volumes (25 mL, 50 mL and 100 mL) and resulted in different GTMAC/NaOH molar ratios.

Vanadium removal efficiency was used as the indicator to evaluate the performance of modified pine bark. In the optimization studies, batch testing was carried out as follows: 0.1 g of modified adsorbent was weighed and then 50 mL of synthetic vanadium solution with an initial concentration of 20 mg/L of vanadium was added. Based on the preliminary studies, the pH of the vanadium solution was pre-adjusted to 4. The mixed solutions were placed in a rotary shaker (20 rpm) for 24 h, followed by 10 min of centrifugation (2500 rpm). Then the supernatant was taken for residual vanadium analysis. The experiments were carried out in duplicate and conducted at room temperature (20 °C).

2.3. Water analysis

Vanadium concentration was analysed by the phosphorus-tungsten-vanadium spectrophotometry method (UV-1800, Shimadzu) [29] except for the samples from the pH studies (pH 2, 3 and 4), which were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo Scientific).

The chemical oxygen demand (COD) for raw and modified pine bark under the optimal modification conditions (referred to as GPB-opt) was analysed once after batch adsorption (two repeats were made for each sample) using a Hach Lange cuvette (LC3 314 for 15–150 mg/L and
LCR 514 for 100–2000 mg/L and a Hange Lange DR2800 spectrophotometer.

2.4. Adsorbent characterization

Raw pine bark (PB), GTMAC-modified pine bark (GPB) under different modification conditions including the optimized product (GPB-opt) and the vanadium-treated optimized product (V-GPB-opt) were characterized by X-ray photoelectron spectroscopy (XPS). V-GPB-opt was prepared by collecting and drying GPB-opt after batch adsorption (dosage 2 g/L; solution pH 4; initial vanadium concentration 20 mg/L; contact time 24 h). XPS experiments were conducted on a Thermo Fisher Scientific ESCALAB 250XI with a monochromatic Al Kα source (1486.6 eV). The survey and high-resolution spectra were recorded with a pass energy of 150 eV and 20 eV, respectively. The charge calibration was made by setting the binding energy of adventitious carbon to 284.8 eV.

The surface area and pore size distributions of PB, GPB-opt and V-GBP-opt were measured using the nitrogen adsorption technique at −195.86 °C, with an ASAP 2020 surface area and porosity analyser (Micromeritics). Before analysis, the samples were outgassed in an oven for 24 h (150 °C) and in a vacuum for 22 h at a temperature of 70 °C. The surface area was measured by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated by analysing the desorption branches of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

The elemental composition (C, H and N), was determined for PB and GPB-opt. The analysis was conducted using a 2400 Series II CHNS/O analyser (PerkinElmer) and three repeats were done for each sample.

2.5. Vanadium removal with optimized GTMAC-modified pine bark (GPB-opt)

2.5.1. Effect of pH of aqueous media

The pH of the vanadium solution was adjusted in the range of 2.0–9.0 using different concentrations of NaOH and HCl. A dosage of 2 g/L, an initial vanadium concentration of 20 mg/L and a contact time of 24 h were kept constant. All the tests were done in duplicate, and the batch test procedure was similar to that described in Section 2.2 (vanadium adsorption test).

2.5.2. Effect of contact time

Different contact times (10 min, 30 min, 1 h, 6 h, 24 h, 48 h, 72 h) were selected to study the effect of time on vanadium adsorption. The pH of the prepared vanadium solution (20 mg/L) was adjusted to 4, and the adsorbent dosage was kept as 2 g/L. Otherwise, the batch test procedure described in Section 2.2 was followed. All the experiments were done in duplicate. The pseudo-first-order (PFO) equation [30], pseudo-second-order (PSO) equation [31], Elovich equation [32], intra-particle diffusion model [33] and Boyd model [34] were studied to describe the adsorption kinetics.

Pseudo-first-order (PFO):

\[ q_t = q_e \left(1 - e^{-kt}\right) \]  

\[ q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_t} \]  

Elovich equation:

\[ q_t = \frac{1}{\beta} \ln(1 + \alpha q_t) \]  

Intra-particle diffusion equation:

\[ q_t = k_p t^{0.5} + C \]  

Boyd equation:

\[ B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \]  

In the equations above, \( q_t \) (mg/g) and \( q_e \) (mg/g) are the adsorption capacity at time \( t \) (min) and in equilibrium, respectively; \( k_1 \) (1/min) is the PFO adsorption rate constant; \( k_2 \) (g/mg × min) is the PSO rate constant; \( \alpha \) (mg/g × min) is the initial rate constant and \( \beta \) (mg/g) is the desorption constant; \( k_p \) (g/mg × min\(^{1/2}\)) is the rate constant of the intra-particle diffusion model; \( C \) (mg/g) is a constant related to the thickness of the boundary layer, where a higher value of \( C \) corresponds to a greater effect on the limiting boundary layer [35]; \( B_t \) is a mathematical function of \( q_t/q_e \) and can be calculated from Eq. (5).

2.5.3. Vanadium adsorption capacity

Vanadium solutions of different initial concentrations (10–591 mg/L) were prepared and the pH of the solution was adjusted to 4 before use. Adsorption experiments were conducted at different temperatures: 20 °C, 15 °C and 5 °C. All the tests were done in triplicate with a 24-hour contact time and an adsorbent dosage of 2 g/L. Otherwise, the batch test procedure described in Section 2.2 was followed. The vanadium adsorption capacity \( q \) was calculated as shown in Eq. (6).

\[ q = \frac{(C_i - C_f)V}{m} \]  

where \( C_i \) is the initial vanadium concentration in solution (mg/L), \( C_f \) is the residual vanadium concentration in solution (mg/L), \( V \) is the solution volume (L) and \( m \) is the mass of the adsorbent (g).

The experimental data was fitted to the non-linear form of Langmuir [36], Freundlich [37], Redlich-Peterson [38], and Dubinin-Radushkevich [39] isotherms, see Eqs. (7)–(12).

Langmuir isotherm:

\[ q = \frac{Q_0 k_L C_f}{1 + K_L C_f} \]  

Freundlich isotherm:

\[ q = K_F C_f^n \]  

Redlich-Peterson isotherm:

\[ q = \frac{K_R C_f}{1 + a_{RP} C_f^2} \]  

Dubinin-Radushkevich isotherm:

\[ q = q_{0b} e^{-K_R e^{\varepsilon^2}} \]  

\[ \varepsilon = R T \ln \left(1 + \frac{1}{C_f}\right) \]  

\[ E = \frac{1}{\sqrt{2K_{des}}} \]  

In the equations above, \( q_e \) (mg/g) is the vanadium adsorption capacity and \( C_f \) (mg/L) is the vanadium concentration in solution in equilibrium; \( Q_0 \) (mg/g) is the maximum adsorption capacity of the adsorbent obtained from the Langmuir model; \( K_L \) (L/mg) is a constant related to the energy of adsorption; \( K_F \) (mg/g)/(mg/L)\(^n\) is the Freundlich constant, and \( n \) (dimensionless) is the Freundlich intensity parameter; \( K_R \) (L/g) and \( a_{RP} \) (L/mg) are the Redlich-Peterson constants; \( g \) is an exponent whose value must lie between 0 and 1 [35]; \( q_{0b} \) (mg/g) is the adsorption capacity obtained from the Dubinin-Radushkevich model; \( K_R \) (mol\(^2\)/kJ\(^2\)) is the Dubinin-Radushkevich constant related to adsorption energy; \( \varepsilon \) is the Polanyi potential; \( R \) is the gas constant; \( T \) (Kelvin) is the temperature and \( E \) (kJ/mol) is the mean adsorption energy.
2.5.4. Regeneration experiments
Regeneration studies of the optimal product were conducted first in batch mode using 0.1 g of GPB-opt for three adsorption–desorption cycles. In each adsorption cycle, 50 mL of synthetic vanadium solution (20 mg/L, pH 4) was mixed with a weighed amount of GPB-opt and shaken for 24 h. After the adsorption cycle, the spent material was washed with Milli-Q water three times to remove residual vanadium solution. The wet material was then regenerated with 20 mL of 4 M NaCl for a period of 30 min and the supernatant was removed and pipetted for vanadium analysis. After that, the regenerated GPB-opt was again washed with Milli-Q water three times and the wet material was directly used in the next adsorption–desorption cycle.

2.5.5. Column adsorption and regeneration
The adsorption and regeneration tests were then conducted in column mode for three cycles. The column (length 30 cm; inner diameter 19 mm) was firstly packed with quartz (particle size 0.5–1 mm; height 8 cm) at the bottom. Then 1 g of GPB-opt was mixed with 20 g quartz and added to the middle part of the column with a bed height of 7 cm. Above the mixture, a quartz layer was added (height 15 cm). The vanadium solution (20 mg/L, pH 3.5–3.9) was pumped from the bottom of the column at a flow rate of 2.75 mL/min. The effluent solution was collected in 50 mL fractions. The collected fractions were then taken for residual vanadium analysis. In the breakthrough curve, the value of Ct/C0 was plotted as a function of vanadium solution volume. The purpose of the column adsorption and regeneration tests was to maintain a higher concentration of GPB-opt at a constant pH value.

Fig. 1. (a) Effect of NaOH concentration and GTMAC dosage on vanadium removal efficiency. Modification: NaOH solution volume 50 mL; time 3 h; temperature 60 °C. Adsorption: dosage 2 g/L; solution pH 4; contact time 24 h; initial vanadium concentration 20 mg/L; temperature 20 °C; NaOH molar amount in the reaction, resulting in inadequate quaternization and thus low vanadium removal efficiency. However, with an excess dosage of GTMAC, the hydrolysis of GTMAC may occur more easily and thus the quaternization efficiency of pine bark may be decreased. Therefore, the

3. Results and discussion
3.1. Optimization of modification conditions
3.1.1. Effect of initial NaOH concentration and GTMAC dosage
Raw pine bark provided only 39% vanadium removal efficiency (dosage 2 g/L; solution pH 4; initial vanadium concentration 20 mg/L) and increased the COD concentration of the treated water. Thus, the raw material would need to be pretreated or modified before use. Fig. 1 illustrates the effect of the initial NaOH concentration and GTMAC dosage on the efficiency of the modified pine bark. When the initial NaOH concentration was increased from 0.01% to 0.1% (w/v) (GTMAC dosage was kept constant at 0.0134 mol/g), vanadium removal efficiency increased significantly from 56% to 91% (Fig. 1a). The removal efficiency tended to be stable at concentrations of 0.1–0.5% (w/v) but decreased significantly at very high NaOH concentrations of 1% and 2% (w/v). The dosage of GTMAC also had an effect on the performance of the modified pine bark when the initial NaOH concentration was kept at a constant 0.1% (w/v). The optimum GTMAC dosage was in the range of 0.0134–0.0537 mol/g. Either a lower or higher GTMAC dosage resulted in a decrease in vanadium removal efficiency (Fig. 1b). It is remarkable that the GTMAC/NaOH molar ratio could vary so much without affecting the efficiency. It should also be noted that, as the total reaction volume was fixed at 52 mL (NaOH volume + GTMAC volume), the molar amount of NaOH varied slightly (0.001000–0.001275 mol/g) with the increased GTMAC dosage (0.0067–0.0805 mol/g), see Fig. 1b.

NaOH makes biomass more soluble and thus increases the accessibility of reaction sites [27]. As reported in previous studies, NaOH is also considered a catalyst in quaternization, generating a nucleophilic intermediate that is able to attract the reactive epoxy group on GTMAC through a ring opening reaction and enhance the quaternization reaction [41,42]. Thus, a certain amount of NaOH was a necessity for the reaction. A lower concentration would be insufficient to activate the modification reaction, whereas in the presence of excessive NaOH, degradation of the biomass and hydrolysis of quaternary ammonium salt may occur [43]. Therefore, based on the results in this study, an initial NaOH concentration in the range of 0.1%–0.5% (w/v) was considered an efficient concentration to use. As the 0.1% (w/v) NaOH resulted in the highest vanadium removal efficiency, this concentration was also selected for the further studies.

In the modification process, GTMAC was consumed in two competing reactions: quaternization of the biomass, which is desirable, and hydrolysis of GTMAC, which is defined as a side reaction here [27,44]. At a lower GTMAC dosage, limited GTMAC is available to be involved in the reaction, resulting in inadequate quaternization and thus lower vanadium removal efficiency. However, with an excess dosage of GTMAC, the hydrolysis of GTMAC may occur more easily and thus the quaternization efficiency of pine bark may be decreased. Therefore, the
optimal amount of GTMAC is important so that a sufficient number of positively charged sites are obtained in the pine bark and the side reaction is minimized. As the product modified with 0.0134 mol/g GTMAC achieved the same level of vanadium removal efficiency compared to a higher GTMAC dosage (0.0268 and 0.0537 mol/g), the former was selected for subsequent studies. Thus, the optimal product (GPB-opt) was prepared using an initial NaOH concentration of 0.1% (w/v) and a GTMAC dosage of 0.0134 mol/g, which resulted in a GTMAC/NaOH ratio of 10.7.

3.1.2. Effect of modification time
The effect of modification time on the efficiency of GPB is shown in Fig. 2a. Vanadium removal efficiency increased gradually from 62% to 92% with an increasing reaction time from 1 h to 3 h. Subsequently, the removal efficiency decreased with modification times of 4 h and 6 h. This may be attributed to the incomplete reaction under a short modification time, whereas when the reaction time was prolonged, the decomposition of GTMAC and biomass may have occurred, and the hydrolysis of modified pine bark could also have been enhanced, thus leading to the decrease in vanadium removal efficiency. This result is in agreement with earlier studies [27,43]. Therefore, based on the result, 3 h was chosen as the optimal modification time and used in the further steps.

3.1.3. Effect of modification temperature
Fig. 2b shows the effect of modification temperature on the efficiency of GPB. The results reveal that when the modification temperature was 40 °C, the modified pine bark was unable to take vanadium up from the synthetic solution. When modification was carried out at higher temperatures (60 °C and 80 °C), the vanadium removal efficiency was around 91%. This indicates that the modification reaction is favoured by a higher temperature. A desirable temperature can facilitate the nucleophilic addition reaction between biomass and GTMAC [45]. Ren et al. also pointed out that an increased reaction temperature had a favourable effect on the compatibility of the reaction ingredients, the mobility of the reactive molecules and diffusion of the chemical reagent [43]. However, when the reaction temperature was over 80 °C, the biomass is prone to decomposition. The results in this study were consistent with previous studies [43,45]. Therefore, in this study, as the product displayed a similar ability for vanadium removal under modification temperatures of 60 °C and 80 °C, the lower temperature of 60 °C was selected as the optimal temperature with regard to energy savings in large-scale applications.

3.1.4. Effect of modification volume
As discussed in Section 3.1.1, the GTMAC dosage and initial NaOH concentration had a significant effect on the vanadium removal efficiency of GPB. The water content in the reaction system has also been reported to affect the modification process [44]. Thus, a comparison of the modification volume was carried out, firstly with a constant GTMAC/NaOH molar ratio (Fig. 3a) and secondly with a constant initial NaOH concentration (Fig. 3b). As the GTMAC dosage was constant...
in both cases (0.0134 mol/g), the initial NaOH concentration was varied (see Fig. 3a) and then the GTMAC/NaOH ratio was varied, as shown in Fig. 3b.

The three different NaOH solution volumes shown in Fig. 3a, with different initial NaOH concentrations, were as follows: 25 mL (0.2% NaOH), 50 mL (0.1% NaOH) and 100 mL (0.05% NaOH). The results showed that the vanadium removal efficiency was similar (~90%) when the reaction volume was 25 mL and 50 mL, while with a volume of 100 mL, the vanadium removal efficiency decreased to 60%. This result was in good agreement with the results shown in Fig. 1a. This indicated that the success of modification was affected more by the initial NaOH concentration than by the reaction volume or GTMAC/NaOH ratio. Thus, to confirm this assumption, the effect of volume was studied next with a constant initial NaOH concentration.

The initial NaOH concentration was kept constant (0.1% w/v) and the NaOH solution volume was again set to three different levels (25 mL, 50 mL and 100 mL), as shown in Fig. 3b. As the GTMAC dosage was also constant (0.0134 mol/g), the GTMAC/NaOH ratio varied as follows: 5.4 (25 mL), 10.7 (50 mL) and 21.5 (100 mL), respectively. According to the results (Fig. 3b), the vanadium removal efficiency was at the same level (85%-91%), even though the reaction volume and GTMAC/NaOH ratio varied considerably. Therefore, these results confirmed that the studied range of GTMAC/NaOH ratios and NaOH solution volumes were not the determining factors that influenced the success of the modification compared with the initial NaOH concentration when the GTMAC dosage was kept constant. Hence, the initial NaOH concentration should be considered a crucial parameter during the GTMAC modification process.

3.2. Adsorbent characterization

3.2.1. XPS analyses

The surface element compositions of PB, GPB under different modification conditions, GPB-opt and V-GPB-opt are presented in Table 1. The raw pine bark consisted of C (79.3%), O (20.1%) and N (0.58%). After grafting with quaternary ammonium groups, the elemental content of N increased in all GPB samples. The GPB-opt showed the highest nitrogen content (1.55%). Next came the GPB prepared with a much higher GTMAC dosage (0.0805 mol/g) at 1.52% N, which is at the same level as GPB-opt. In addition, the peak of Cl 2p appeared only in this sample and the Cl content was 0.13%. This may be attributed to the excessive GTMAC dosage in the modification reaction.

The N 1s spectra of PB, GPB-opt and V-GPB-opt are shown in Fig. 4. Raw pine bark only displayed a single nitrogen peak at 400.1 eV (referred to as the N1 component), which was assigned to the nitrogen bound to carbon in amines or amides originating from nitrogen compounds in the raw biomass [46,47]. A new peak at ~402.6 eV (referred to as the N2 component) appeared after GTMAC modification, corresponding to quaternary nitrogen [47], which is responsible for the uptake of anionic pollutants and removal via electrostatic attraction [46]. The result was in good agreement with previous studies [48,49]. The pine bark modified under the optimal conditions (GPB-opt) presented higher total nitrogen (1.55%) compared to other samples, which can explain the highest vanadium removal efficiency achieved by GPB-opt. It should also be noted that GPB modified with 2% NaOH (w/v) gave the highest percentage of quaternary nitrogen (N2) (69% of the total nitrogen). This may be related to the dissolution of pine bark at the higher initial NaOH concentration and may have led to the decrease of nitrogen content (N1) in the biomass matrix, meaning that N2 accounted for the higher percentage of total nitrogen.

After vanadium adsorption, the V 2p spectra presented V 2p3/2 and V 2p1/2 at binding energies of 516.7 eV and 524.3 eV, respectively (Fig. S1), which indicated oxidized vanadium (V5+) on the surface of the material [50]. Thus, there was no valent change for vanadium ions after the adsorption process. It is noteworthy that after modification, the O 1s spectra presented a new peak at 530.9 eV on the GPB-opt (Fig. S2), and the binding energy referred to the C=O bond in quinones [51]. However, further studies would be required to confirm this. The binding energy of the new peak slightly shifted to a lower binding energy (530.5 eV) in the vanadium treated sample (V-GPB-opt), and this was probably related to the V=O bonding at ~530 eV [52]. The C 1s spectra of PB and GPB-opt were fitted to four peaks corresponding to C1: C–C and C–H single bonds at 284.8 eV; C2: C–O and C–N single bonds at 286.4 ± 0.1 eV; C3: carbon having two bonds with oxygen (O=C–O and C=O) at 287.9 ± 0.1 eV, and C4: carboxylic group (O=C=O) at 289.1 eV [51,53]. The C2 (C–O and C–N) increased (Fig. S3) after modification, which is attributed to new C–N bonds from the

Table 1
Surface composition of PB, GPB, GPB-opt and V-GPB-opt.

| Samples    | Modification conditions | Atomic percentage of the elements |
|------------|-------------------------|----------------------------------|
|            | NaOH w/v% | GTMAC mol/g | GTMAC/NaOH ratio | Mod. Temp. | C % | O % | N (N1:N2) % |
| PB         | ~          | ~           | ~               | ~           | 79.3 | 20.1 | 0.58 (-)    |
| GPB        | 0.01%      | 0.0134      | 107.3           | 60 °C       | 78.2 | 21.0 | 0.77 (44%-56%) |
| GPB        | 2%         | 0.0134      | 0.5             | 60 °C       | 70.6 | 28.4 | 0.99 (31%-69%) |
| GPB        | 0.1%       | 0.0067      | 5.3             | 60 °C       | 77.9 | 21.9 | 1.06 (47%-53%) |
| GPB*       | 0.1%       | 0.0085      | 80.5            | 60 °C       | 81.8 | 16.6 | 1.52 (49%-51%) |
| GPB        | 0.1%       | 0.0134      | 10.7            | 40 °C       | 78.5 | 20.4 | 1.11 (56%-64%) |
| GPB-opt    | 0.1%       | 0.0134      | 10.7            | 60 °C       | 76.5 | 22.0 | 1.55 (44%-56%) |
| V-GPB-opt**| 0.1%       | 0.0134      | 10.7            | 60 °C       | 75.1 | 23.2 | 1.48 (49%-51%) |

Note: GPB* contained 0.13 atomic % of chlorine; V-GPB-opt** contained 0.30 atomic % of vanadium.
grafted quaternary ammonium group. In addition, it was also observed that the C3 (O––C–O and C–O) increased after modification, indicating some structural changes in the pine bark. The N1:N2 ratio was 1:1.25 for GPB-opt (based on the peak area), while the ratio changed to 1:1.04 after vanadium adsorption. This supported the finding that quaternary nitrogen compounds were involved in the adsorption of vanadium.

3.2.2. Surface area, pore size and pore volume
The surface area and pore characteristics of PB and GPB-opt are shown in Table 2. The BET specific surface area was 0.4075 m²/g for raw pine bark and increased slightly to 0.4340 m²/g after GTMAC modification. The average pore diameter increased from 30.9 nm to 42.2 nm. De Lima et al. also observed a minor increase in the BET surface area of quaternized coconut shell fiber [54]. On the other hand, Thamilarasi et al. found that the BET surface area of the quaternized palm fruit husk was lower than that of the raw material [55]. The difference between the results may be due to the different properties and composition of the materials concerned.

3.2.3. Elemental composition
As shown in Table 3, the total nitrogen content increased from 0.47% in PB to 1.16% in GPB-opt, which proved that quaternary ammonium groups had been successfully grafted onto the pine bark. Similar results have been reported for other quaternized adsorbents. Gogoi et al. reported that the nitrogen content of peat slightly increased from 2.2% to 3.3% in GTMAC-modified peat [48]. Keränen et al. observed that, after grafting quaternary ammonium onto raw sawdust, the nitrogen increased from 0.27% to the range of 1.1–2.7% in the modified sawdust [56].

3.3. Vanadium removal with optimized GTMAC-modified pine bark
3.3.1. Effect of solution pH
Fig. 5 shows the effect of solution pH on vanadium removal by GPB-opt. The solution pH had a significant influence on the vanadium removal efficiency. Low vanadium removal efficiency was observed at pH 2. Maximum removal efficiency (95%) was achieved at pH 3, followed by a slight drop to 88% at pH 4. With the increase in pH from 5 to 9, the vanadium removal efficiency decreased from 31% to 13%. A similar result was reported by Thamilarasi et al. in that higher vanadium removal efficiency was achieved in the pH range of 3–4 for quaternary ammonium-modified palm fruit husk [55]. A strong acidic pH is not
suitable in real applications, therefore pH 4 was chosen for further experiments.

In the aqueous solution, vanadium in the oxidation state of +5 occurs in cationic form (VO$_2^+$) at pH 2 [3], and the lower vanadium removal efficiency was probably due to the repulsive force between the cationic vanadium species and the positively charged pine bark surface. When the pH was above 3, vanadium existed in anionic form and thus the positively charged pine bark could bind anionic vanadium species effectively. At a high pH, competition between OH$^-$ and anionic vanadium species for the available sites on GPB-opt might have occurred. The speciation of vanadium is greatly affected by the pH and vanadium concentration. Based on different calculations, the predominant species at pH 3–4 could be $\text{V}_6\text{O}_{27}\text{(OH)}^{5-}$ [57] or $\text{H}_3\text{V}_2\text{O}_7^-$ [58].

As the leaching of organic compounds from biomass-based adsorbents may increase the COD of the treated water, the COD was measured for both pine bark and optimized pine bark treated water (adsorbent dosage 2 g/L; pH 4; contact time 24 h; initial vanadium concentration 20 mg/L). The results revealed that the COD was significantly lower in the GPB-opt-treated water ($38.2 \pm 2.3$ mg/L) than in the PB-treated water ($363.5 \pm 2.1$ mg/L). Another study has also reported a decrease in COD after modification of pine bark with NaOH (from 1820 mg/L to 35 mg/L) [12].

### 3.3.2. Adsorption kinetics

Vanadium removal efficiency reached 38% in the first hour, then gradually increased to the maximum (85%) in 24 h. A study of adsorption kinetics by three different models, pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich, is shown in Fig. 6 and the parameters obtained are given in Table 4. As shown in Table 4, the equilibrium adsorption capacity ($q_e$) from the pseudo-first-order and second-order models are close to the experimental data. Of these three models, the Elovich model gave the best fit to the experimental data as this model provided the highest correlation coefficient ($R^2$) and lowest chi-square value ($\chi^2$). The Elovich equation is generally used to describe chemisorption (with new chemical bonds) [35].

To further interpret the adsorption phenomenon, the intra-particle diffusion model was applied. The linearized plot of $q_t$ versus $t^{0.5}$ is shown in Fig. 7 and the parameters calculated are summarized in

### Table 5

Parameters of adsorption isotherms for GPB-opt under different temperatures.

| Models          | Parameters       | Parameters       | Temperature |
|-----------------|------------------|------------------|-------------|
|                 |                  | $20 \, ^\circ \text{C}$ | $15 \, ^\circ \text{C}$ | $5 \, ^\circ \text{C}$ |
| Langmuir        | $Q_{max}$ (mg/g) | 34.639           | 37.078       | 36.740       |
|                 | $K_L$ (L/mg)     | 0.040            | 0.018        | 0.014        |
|                 | $R^2$            | 0.935            | 0.935        | 0.942        |
|                 | $\chi^2$         | 9.299            | 11.692       | 12.905       |
| Freundlich      | $K_F$ (mg/g)/(mg/L)$^n$ | 6.709         | 5.594       | 4.549       |
|                 | $n$              | 0.283            | 0.298        | 0.324        |
|                 | $R^2$            | 0.944            | 0.983        | 0.964        |
|                 | $\chi^2$         | 4.430            | 0.986        | 1.137        |
| Redlich-Peterson| $K_{RP}$ (L/g)   | 3.692            | 4.841        | 5.301        |
|                 | $a$              | 0.304            | 0.663        | 0.959        |
|                 | $g$              | 0.819            | 0.744        | 0.706        |
|                 | $R^2$            | 0.969            | 0.967        | 0.965        |
|                 | $\chi^2$         | 2.449            | 1.004        | 1.273        |
| Dubinin-Radushkevich | $q_0$ (mg/g) | 28.460            | 29.980       | 28.881       |
|                 | $K_D$ (mol$^2$/kJ$^2$) | 2.28E-5        | 1.43E-4     | 2.41E-4     |
|                 | $E$ (kJ/mol)     | 148.072          | 58.974       | 45.542       |
|                 | $R^2$            | 0.712            | 0.751        | 0.775        |
|                 | $\chi^2$         | 4.07E+6          | 2.01E+17     | 2.73E+21     |

Fig. 7. Intra-particle diffusion (a) and Boyd model (b) for vanadium adsorption by GPB-opt (dosage 2 g/L; solution pH 4; initial vanadium concentration 20 mg/L; temperature 20 °C; error bars represent the range of two repeats).

Fig. 8. Regeneration studies of GPB-opt (Adsorption: dosage 2 g/L; solution pH 4; contact time 24 h. Desorption: dosage 5 g/L; contact time 30 min. Temperature 20 °C; error bars represent the range of two repeats).
3.3.3. Adsorption isotherms

The maximum adsorption capacity for vanadium was found to be 34.3 mg/g, 35.0 mg/g and 32.3 mg/g at 20 °C, 15 °C and 5 °C respectively, indicating that the temperature has a minor effect on the adsorption capacity in the selected temperature range. The obtained capacity is at a satisfactory level considering the simplicity of the modification and the low-cost raw material. Vanadium adsorption capacity is also at a similar level to that obtained for other adsorbents, such as 22.1 mg/g with quaternized palm fruit husk [55], 16 mg/g with iron-modified peat [4] and 15 mg/g with kaolin-supported zerovalent iron [5].

The experimental data was applied to the non-linear Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich models. The parameters evaluated from these four models are shown in Table 5 and the fitting curves are presented in Fig. S4. Of these four models, the Freundlich and Redlich-Peterson gave better fits as a higher R² and lower χ² were obtained. This refers to the fact that the adsorption occurred at a heterogenous surface [35]. However, the adsorption capacity obtained from the Langmuir model at equilibrium was close to the experimental capacity although it provided a lower R² and higher χ² compared to the Freundlich and Redlich-Peterson models.

The Dubinin-Radushkevich isotherm is generally applied to estimate adsorption energy (E). The E magnitude may provide useful information about the type of adsorption reaction, i.e. physical adsorption (E < 8 kJ/mol), ion exchange (8 < E < 16 kJ/mol) and chemical adsorption (E > 16 kJ/mol) [60]. The E values obtained in this study were all over 16 kJ/mol, which could be categorized as chemical adsorption [60]. However, it should be noted that the Dubinin-Radushkevich isotherm did not provide a good fit as the R² was low (0.721–0.775) and the χ² was relatively high (a high χ² value was induced by the lowest vanadium concentration in this study).

3.3.4. Batch regeneration experiments

Regeneration is an important factor in evaluating the performance of the adsorbent used in practical applications. The results of the adsorption and desorption cycles in the batch tests are shown in Fig. 8. In the first cycle, the vanadium removal efficiency of GPB-opt was 89% and the desorption efficiency reached 87%. In the second and third cycles, the adsorption and desorption both decreased slightly. The adsorption efficiency dropped to 85% in cycle 2 and cycle 3. As for the desorption cycles, the efficiency decreased to 79% and 78% in cycle 2 and cycle 3, respectively. The regeneration mechanism was probably an ion-exchange reaction, in which Cl⁻ from NaCl replaced anionic vanadium ions on the GPB-opt. The studies demonstrated that GPB-opt can be repeatedly used as an efficient adsorbent for vanadium removal from aqueous solution in batch mode.

3.3.5. Column adsorption and regeneration

The results of the three adsorption and regeneration cycles in column mode are shown in Fig. 9. As mentioned above, the vanadium adsorption of GPB-opt was significantly affected by the pH of the solution. As the breakthrough point was observed already after feeding with 300 mL of vanadium solution in cycle 1 (solution pH 3.9), the decision was made to decrease the pH of the vanadium solution slightly. Then for cycle 2 and cycle 3 (solution pH 3.5) the breakthrough point was observed much later, i.e. after treating with 1150 mL and 900 mL of solution, respectively. Moreover, in the adsorption stage of cycle 2 and cycle 3, the vanadium concentration in the eluent increased sharply after the breakthrough point, which is different compared to the slow increase in the adsorption stage of cycle 1. Sodium chloride efficiently desorbed vanadium. For all three cycles, the desorption efficiency reached over 80%. However, a higher efficiency might be achieved by decreasing the desorption flow rate in practical applications.

4. Conclusions

Quaternary ammonium-modified pine bark can be effectively used for vanadium removal. The modification conditions significantly affected the vanadium adsorption ability and the optimal modification parameters were as follows: an initial NaOH concentration of 0.1% (w/v), a GTMAC dosage of 0.0134 mol/g, a modification time of 3 h and a modification temperature of 60 °C. The results also revealed that the initial NaOH concentration was more of a determining factor affecting vanadium adsorption ability than the modification volume and GTMAC/NaOH ratio, when the GTMAC dosage was kept constant. XPS studies revealed that the content of quaternary nitrogen groups was closely related to the vanadium adsorption ability of modified pine bark. Adsorption was favoured by a lower pH (3–4) and vanadium removal efficiency was also dependent on the contact time (equilibrium reached after 24 h). The column adsorption and regeneration studies indicated that modified pine bark could be considered a potential adsorbent for use in real industrial applications for vanadium removal.
the quaternized products were efficient in removing different anionic pollutants from aqueous solutions, other potential applications for this modified pine bark include nutrient recovery (nitrate and phosphate) and arsenic and chromium removal.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

[1] J.R. Peterson, D.B. Smathers, Vanadium: an overview of industrial capacity and other factors, J. Nucl. Mater. 141–143 (1986) 1113–1116, https://doi.org/10.1016/0027-2757(86)90150-1.
[2] A. Naem, P. Westerhoff, S. Mustafa, Vanadium removal by metal (hydr)oxide adsorbents, Water Res. 41 (2007) 1596–1602, https://doi.org/10.1016/j.watres.2007.01.002.
[3] C.L. Peacock, D.M. Sherman, Vanadium(V) adsorption onto goethite (α-FeOOH) at pH 1.5 to 12: a surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy, Geochim. Cosmochim. Acta 68 (2004) 1723–1733.
[4] R. Zhang, T. Leiviskä, J. Tanskanen, B. Gao, Q. Yue, Utilization of ferric ground-water treatment residuals for inorganic-organic hybrid biosorbent preparation and its use for vanadium removal, Chem. Eng. J. 361 (2019) 680–689, https://doi.org/10.1016/j.cej.2018.10.068.
[5] A. Bello, T. Leiviskä, R. Zhang, J. Tanskanen, P. Maziarz, J. Matusik, A. Bhatnagar, Synthesis of zerovalent iron from water treatment residue as a conjugate with kaolinite and its application for vanadium removal, J. Hazard. Mater. 374 (2019) 372–381, https://doi.org/10.1016/j.jhazmat.2019.04.056.
[6] F. Kaczala, M. Marques, W. Hogland, Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto Pinus sylvestris sawdust, Biosor. Technol. 100 (2019) 235–243, https://doi.org/10.1016/j.biotechbioeng.2018.05.055.
[7] T.S. Anirudhan, P.G. Radhakrishnan, Adsorptive performance of an amine-functionalized poly(hydroxyethylmethacrylate)-grafted tamarind fruit shell for vanadium(V) removal from aqueous solutions, Chem. Eng. J. 165 (2010) 142–150, https://doi.org/10.1016/j.cej.2010.09.005.
[8] A. Bhatnagar, A.K. M inoha, D. Pudasainee, H.K. Chung, S.H. Kim, H.S. Kim, G. Lee, B. Min, B.H. Jeon, Vanadium removal from waste water by metal sludge and cement immobilization, J. Chem. Eng. J. 144 (2008) 197–204, https://doi.org/10.1016/j.cej.2008.01.021.
[9] E. Nehrenheim, J.P. Gustafsson, Kinetic sorption modelling of Cu, Ni, Zn, Pb and Cr ions to pine bark and blast furnace slag by using batch experiments, Biosor. Technol. 99 (2018) 1571–1577, https://doi.org/10.1016/j.biotechbioeng.2017.04.017.
[10] S. Al-Asheh, Z. Duvnjak, Sorption of cadmium and other heavy metals by pine bark, Desalination 249 (2009) 519–527, https://doi.org/10.1016/j.desal.2009.01.020.
[11] S. Souza, P. Jimenez-Guerrero, A. Ruiz, N. Ratsola, A. Alves, Organochlorine pesticides removal from aqueous solution by pine bark adsorbent, Desalination 234 (2009) 143–149, https://doi.org/10.1016/j.desal.2008.10.036.
[12] S. Sousa, P. Jimenez-Guerrero, A. Ruiz, N. Ratsola, A. Alves, Characterization of a pine bark adsorbent, Int. J. Environ. Sci. 63 (2006) 59–66, https://doi.org/10.1080/09593330.2006.1101014.
