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Functionalization of a Natural Biopolymer with Aliphatic Polyamines and its Sorption Properties for Vanadium Removal from Aqueous Solutions

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ABSTRACT

A low-cost natural adsorbent, *Moringa oleifera,* was investigated as a potential alternative for currently costly methods of removing vanadium from contaminated aqueous solutions. The unmodified bark was characterized using techniques such as N_2-BET, SEM, XRD and FTIR spectroscopy, CHNS elemental determination and AA spectroscopy. Results showed a relatively small surface area, motivating surface functionalization to enhance adsorption capacity. Chemical modification was performed using four aliphatic polyamines: ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). The modified bark was characterized and then investigated to determine its efficiency in removing VO_2^+ from aqueous solutions. The bark had a mesoporous amorphous structure and was enriched with N and S groups. FTIR absorption frequencies also revealed that polyamines were indeed immobilized on the adsorbent surface. The polyamine density was calculated and was in the order of EDA > DETA > TETA > TEPA, whereas the adsorption efficiency with VO_2^+ was in the order DETA > EDA > TETA > TEPA. Adsorbent amination was enhanced by up to 26 % and adsorption performance improved by up to 155 %. It was, therefore, concluded that chemical modification of *M. oleifera* using polyamines enhances adsorption of VO_2^+ from aqueous solutions. This can, thus, preconcentrate VO_2^+ in the bark leading to its use as a good water purifier.

KEYWORDS

Adsorption, functionalization, *Moringa oleifera,* polyamine, vanadium.

1. Introduction

Moringa oleifera, a naturally growing plant native to India, Sri-Lanka, Mexico, Middle East and southwestern Africa, has been a subject of research due to its unique nutritional[1], therapeutical[2–4] and water coagulation properties.[5] These properties are attributed to the presence of bioactive chemical constituents such as amino acids and other different types of functional groups in the plant. The *M. oleifera* protein has been isolated and found to have a molecular mass around 6.5 kDa with an iso-electric point[6] above pH 10. The main amino and carboxylic groups present are connected to protein, some fatty acids, carbohydrates and interlinked with lignin units. The adsorptive capacity of *M. oleifera* is highly favoured since most of them contain considerable quantities of cellulose interlinked with lignin in their structure.

Lignin is a complex biopolymeric heterogeneous molecule which is endowed with many different functional groups, including methoxyl, hydroxyl-aliphatic, carboxyl and phenolic,[7] which actively participate in bond formation with metallic species in aqueous solutions. Lignin also has an aromatic, three-dimensional polymer structure[8] and is insoluble in water. This makes lignin rather a most difficult molecule to study, since it is a polyfunctional network polymer with an irregular structure and contains different functional groups.[9] However, the dimensional spatial structure of the macromolecule leads to different accessibilities of functional groups like polyamines. This aroused our interest in studying the functionalization of *M. oleifera* with aliphatic polyamines owing to its high content in lignocellulose.[7] Although such studies do not enable us to predict clearly polyamine interaction with lignin, but prior elemental determination of the percentage nitrogen present in investigated plant material before and after functionalization do provide useful information on the probable elementary reactions of different functional groups with the polyamines.

Due to the cellulosic nature of *M. oleifera,* the potential to explore this property to remove metallic pollutants exists, since lignocellulosic plants have been used to remove a wide range of metals[7–11] from aqueous systems with high removal efficiencies. Lignocellulosics have high sorption capacities,[12,13] which are mainly derived from their constituent polymers, such as extractives, cellulose, hemicelluloses, pectin, lignin and protein.[12] The metal-adsorbent interaction is mainly through binding of the metal ion and cellulose/lignin in the active sites.[14] This can be through binding adjacent functional groups or binding the cellulose units together.[15]

Chemical modifications, especially amine-based, have been applied to remove metal ions from aqueous solutions[16–18] due to the strong chelation properties of the amine functional groups to transitional metal ions,[19] and that the modified biosorbents are usually chemically stable and highly reactive.[16] Polyamines have been used to functionalize silica, polystyrene,[20] cellulose,[21] polyacrylonitrile fiber[22] and poly(glycidyl methacrylate) polymers.[18,23]

Given the multi-purpose nature of the plant, various studies have focused on aspects such as its water coagulating, nutritional

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and pharmacological properties and little work has been done to evaluate its biosorption capacity. Moreover, little has been done to understand its bioactive chemical compounds responsible for the removal of metals, the mechanistic pathways involved and the range of metals that can be sequestrated. In our previous work,[15] we reported on the potential use of chemically unmodified bark of *M. oleifera* to remove metals from aqueous solutions and avenues for chemical modification of the bark were identified.

The presence of vanadium in aqueous solutions is undesirable since it is toxic[24] even at low concentrations, bioaccumulates in biota[25] and is refractory. Vanadium may exist in oxidation states +3, +4 and +5 in the environment,[26–30] where the +4 and +5 states dominate in natural waters. The toxicity of vanadium has been found to increase with an increase in the oxidation state, meaning that the +5 oxidation state is the most common,[27] most toxic[24,28] and the most stable in oxic conditions.[29] The bioaccessibility of dissolved vanadium from aqueous solutions depends on pH, redox potential, solubility (which also influences the sediment–water distribution coefficients) and concentration.

In this work, the biopolymeric *M. oleifera* bark was chemically modified using ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). This was done to ascertain whether the different amines could functionalize the adsorbent and what effect this would have on the adsorption performance of the adsorbent. The removal efficiency of the chemically modified bark was evaluated by adsorbing vanadium (VO_2^+) from aqueous solutions. Characterization was performed using a Brunauer Emmett and Tellet (BET) model, Fourier transform infra-red (FT-IR) spectroscopy, scanning electron microscopy (SEM) and a CHNS elemental analyzer.

2. Materials and Methods

2.1. Materials

Moringa oleifera bark samples were collected from the Kwaluseni campus of the University of Swaziland. All chemicals used were of analytical grade. These were procured from Sigma-Aldrich (South Africa). Stock solutions, calibration standards and adsorption experiments were carried out using a 1000 mg L^{-1} vanadium (VO_2^+) standard from Riedel-de Haën (Germany). The polyamines (EDA, DETA, TETA, and TEPA) were used without further modification. Sample filtration was done using a 0.45 μm nylon membrane filter.

2.2. Characteristics of Raw and Modified *M. oleifera* Samples

2.2.1. *Surface Characterization of Samples*

Analysis of the surface characteristics of the raw and modified samples included N_2-BET surface area, micropore volume, pore size distributions and SEM observations. A JEOLJSM 639OLV Scanning Electron Microscope (FIB-SEM) coupled with a Noran Six 200 Energy Dispersive X-ray (EDX) Analyzer were used to characterize the surface morphology of the samples. Samples were adhered onto the conductive tape on the stub and coated with gold-palladium nanoparticles since the samples had irregular surfaces and were charging. The BET specific surface area and micropore volume were determined by the nitrogen adsorption isotherm technique using a Micromeritics ASAP, 2010, N_2-BET analyzer. The nitrogen adsorption was carried out at 77 K.

2.2.2. *Spectrum Analysis*

FTIR was used to characterize the important functional groups for the raw and the amine functionalized samples. The spectra (4000–400 cm^{-1}) were recorded using a Perkin Elmer Spectro65 FT-IR spectrometer, with eight scans and 4 cm^{-1} resolutions. The instrument was coupled to an OptKBr (8000–30 cm^{-1}) beamsplitter and a $LiTaO_3$ (15700–370 cm^{-1}) detector. The data were acquired with the detector set to a strong apodization mode and further normalized after filtration with Savitsky-Golay polynomial-convolution filters to reduce noise.

2.2.3. *CHNS Analysis*

To determine the elemental composition, a CHNS analyzer (NA, Carlo Erba instruments) was used to determine the percentage weight composition of C, H, N and–S. Elemental percentage of O was determined by mass difference.

2.2.4. *Metal Analysis*

A Spectro-Arcos ICP-OES (Spectro instruments, South Africa) was calibrated and used to determine concentration differences during adsorption experiments by measuring total vanadium at 311 nm.

2.3. Preparation of Polyamine Functionalized Adsorbents

2.3.1. The unmodified *M. oleifera* bark was carefully washed with water to remove dirt and placed in an oven for 12 h at 100 °C. The bark was then pulverized, sieved using a 0.25 μm mesh size. The sample was then boiled in de-ionized water at 80 °C for 30 min, to dissolve soluble organics, dried in an oven for 12 h at 100 °C. The samples were then stored in glass vials until used.

2.3.2. Amine Functionalization of Adsorbent

The adsorbents were prepared by surface functionalization with 10 mg L^{-1} of EDA, DETA, TETA and TEPA prepared from the commercial polyamines. For each experiment, triplicate analyses were performed wherein 1,4-dioxane was added to 5.00 g pulverized adsorbent in conical flasks. The mixture was degassed with argon gas for 20 min. Then 10 mg L^{-1} of each polyamine was introduced into each flask and then sealed with a silicon rubber. The mixture was then agitated for sufficient time at room temperature (23 ± 2 °C). The adsorbents were then separated by a Buchner funnel, using a 0.45 μm nylon membrane filter and then repeatedly washed with de-ionized water. The amine functionalized adsorbents were then put in a dessicator to dry. Chemically unmodified and the amine functionalized *M. oleifera* adsorbents were then characterized using FTIR, FIB-SEM, elemental analysis and N_2-BET to determine the net effect of surface functionalization using the polyamines.

2.4. Batch Adsorption Studies

The different amine functionalized adsorbents were subjected to batch adsorption experiments with vanadium, as VO_2^+. For all the adsorption experiments, 1.00 g adsorbent was mixed with 50 mL of 1 mg L^{-1} of VO_2^+ in a 250 mL conical flask at room temperature (22–25 °C) and an initial pH maintained at pH 3.3. The mixture was allowed to equilibrate for 1 h with constant agitation. The final and initial concentrations of the system were determined using the Spectro-Arcos ICP-OES. After adsorption, the mixture was separated by filtration using a 0.45 μm nylon membrane filter in a Buchner funnel.

3. Results and Discussion

3.1. Immobilized Amine Content and Polyamine Destiny

The amine content, as percentage nitrogen, immobilized onto the *M. oleifera* bark is presented in Fig. 1.

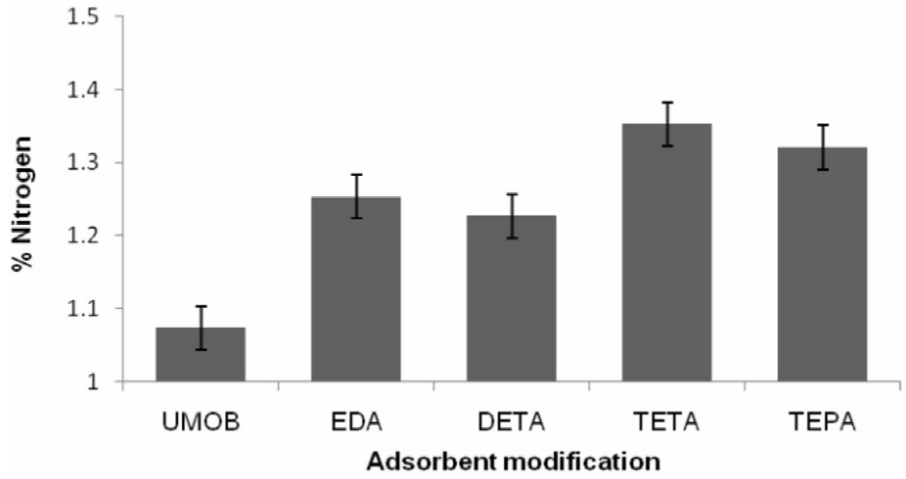

Figure 1 Degree of amination of the *Moringa oleifera* bark with different aliphatic polyamines. UMOB, unmodified *M. oleifera* bark.

The results in Fig. 1 show that the amine content (presented as percentage nitrogen) was improved after the addition of different polyamines of varying chain lengths at diverse degrees of functionality and under the same conditions. The degree of amination of the adsorbent is in the order: TETA>TEPA>EDA>DETA. The results indicate that the use of polyamines with a high amine content can increase the overall amine (as nitrogen) content immobilized on the adsorbent. Table 1 shows the amine contents (reported as percentage nitrogen) for each group and the ratio thereof.

Polyamine density is defined as the number of polyamine molecules immobilized on the adsorbent per unit area.[13] Results of polyamine density immobilized onto the adsorbent are presented in Table 1. It was observed that increasing the molecular chain of the polyamines results in corresponding increases in the polyamine density on the adsorbent in the order; TEPA>TETA>DETA>EDA (Table 1). Theoretically, this is to be expected as the chemical compositions of the polyamines depict the number of amine groups as 2, 3, 4 and 5 for EDA, DETA, TETA and TEPA, respectively. The question, therefore, is the ease of reactivity of the polyamines with the adsorbent and the accessibility of the active sites of the adsorbent for bond formation with the polyamines.

3.2. Surface Characterization Analysis

FIB-SEM images showing the surface morphology of the *M. oleifera* bark at different degrees of amination are shown in Fig. 2. The images show the distribution of the polyamines on the surface of the adsorbent. It is noticed that the polyamine density seems to be highest for the DETA and TEPA-functionalized adsorbents (Fig. 2c,e) than for EDA and TETA-functionalized adsorbents (Fig. 2b,d).

3.3. Spectral Analysis

FTIR spectra of the unmodified and amine modified *M. oleifera* samples (EDA, DETA. TETA, TEPA) are presented in Fig. 3. As the degree of amination increases in the order UMOB<DETA<EDA<TETA, an absorption peak emerges at 3500 cm^{-1} and increases in intensity in that specific order. This peak emergence shows the introduction of acidic phenolic and alcohol functional groups, which probably are due to the effect of the 1,4-dioxane,[30] which was added to activate the adsorption sites before the modification process. This means that the washing step was not effective in removing the activation agent; hence it became part of the intermediate step prior to the desired MOB-amine complex reaction.

Of note is that this region (~3500 cm^{-1}) represents the stretching frequencies for N-H amides. Therefore, addition of amines of increasing chain length and hence amine density also improves the surface functionality of the adsorbent. In contrast with the UMOB, there is also a steady increase and magnification of a peak at 1635 cm^{-1}, which is also observed to increase in the order; DETA<EDA and TETA. This increase is due to the introduction of N-H primary amines to the surface of the adsorbent, which then reacts with the cellulose to form cellulosic amine-crosslinked[16] biopolymers.

There are no observed differences in peak formation or magnification in TEPA functionalized adsorbent, both at 3500 cm^{-1} and 1635 cm^{-1}, even though TEPA contains the highest amine chain. Correlation coefficients calculated for the adsorbent-amine reaction were low for the TEPA functionalized adsorbent (Table 1), implying lower reactivity between TEPA and the adsorbent.

3.4. Vanadium Adsorption Performance

After VO_2^+ adsorption on the modified adsorbent, the amine

Table 1 N_2-BET and elemental analysis of polyamine functionalized *Moringa oleifera* adsorbent.

Parameter	EDA	DETA	TETA	TEPA
Amine content /% wt [a]	1.23	1.25	1.35	1.32
Ratio of amine content [b]	1	1	1.1	1.1
Surface area /m^2 g^{-1} [c]	7.23	7.07	5.56	1.11
Surface area increase /% [d]	304	295	211	–38
Polyamine density /mmol g^{-1} [e]	0.17	0.18	0.24	1.19
Correlation coefficients[f]	0.80	0.91	0.88	0.78

[a]determined from CHN analysis; [b]EDA/polyamine; [c]BET surface area; [d]determined from surface area for unmodified bark; [e]amine content/surface area; [f]calculated from FT-IR data.

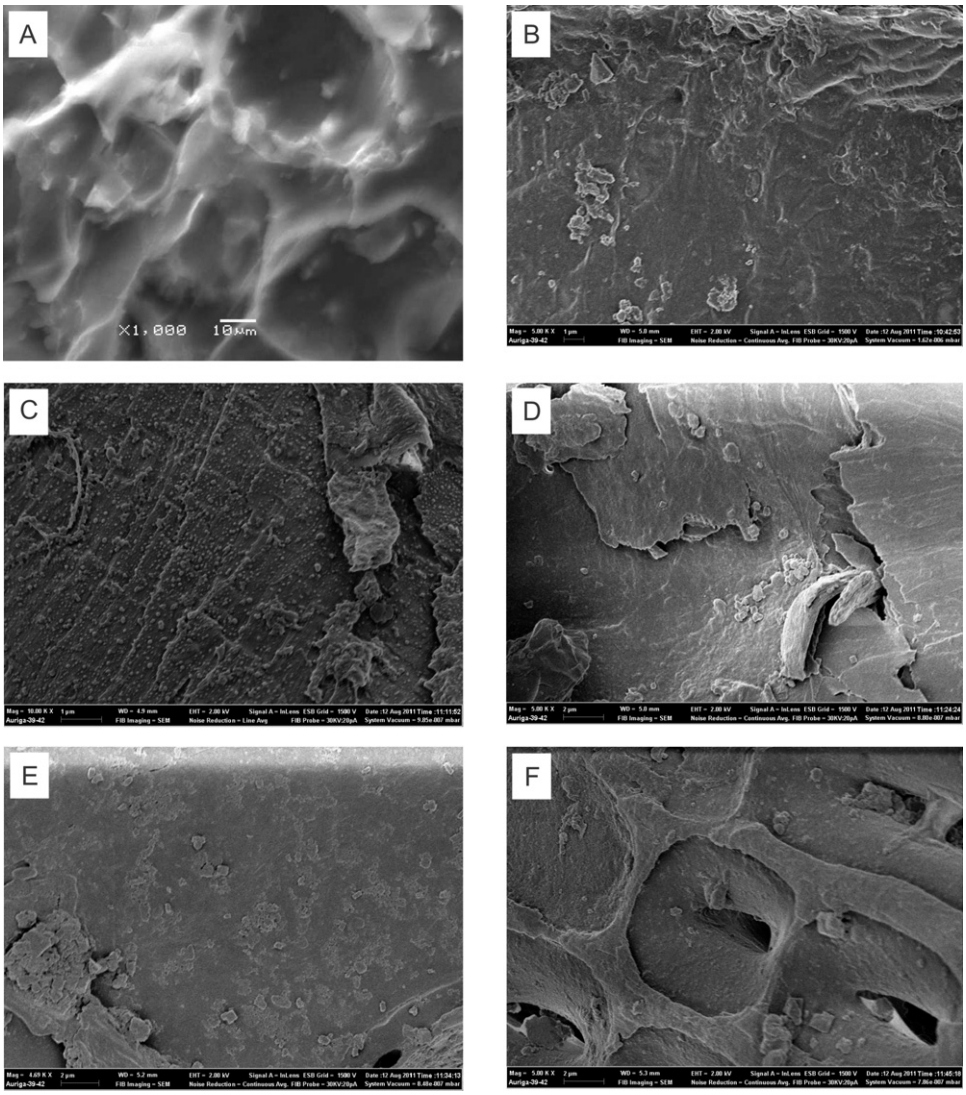

Figure 2 FIB-SEM images showing the surface morphology of the *Moringa oleifera* bark at different stages of functionalization; (**A**) unmodified, (**B**) EDA-functionalized, (**C**) DETA-functionalized, (**D**) TETA-functionalized, (**E**) TEPA-functionalized and (**F**) a closer morphology of the active sites and how the adsorbate adsorbs itself on the surface of the adsorbent.

content was determined to be in the same order (TETA>EDA> DETA) as with the amination step (Fig. 4) for the low chain polyamine functionalized adsorbent. A direct proportionality was observed in the amine content before and after VO_2^+ adsorption with the adsorption performance, and following the same order. However, there is no significant change in amine content for the TEPA-functionalized adsorbent after VO_2^+ adsorption. This suggests that the N-based functional groups

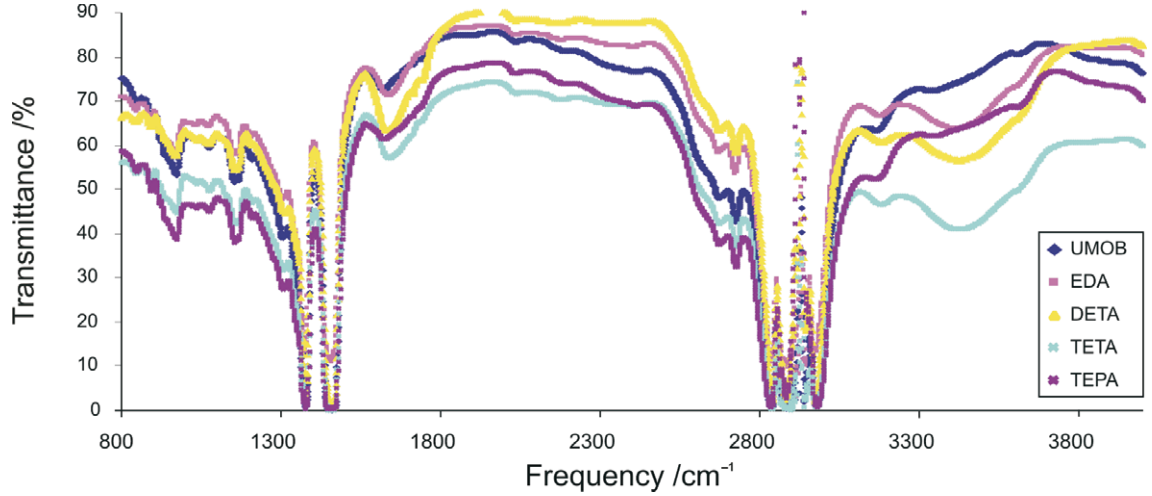

Figure 3 FTIR spectra of *Moringa oleifera* bark (UMOB) before and after chemical modification with polyamines (EDA, DETA, TETA and TEPA).

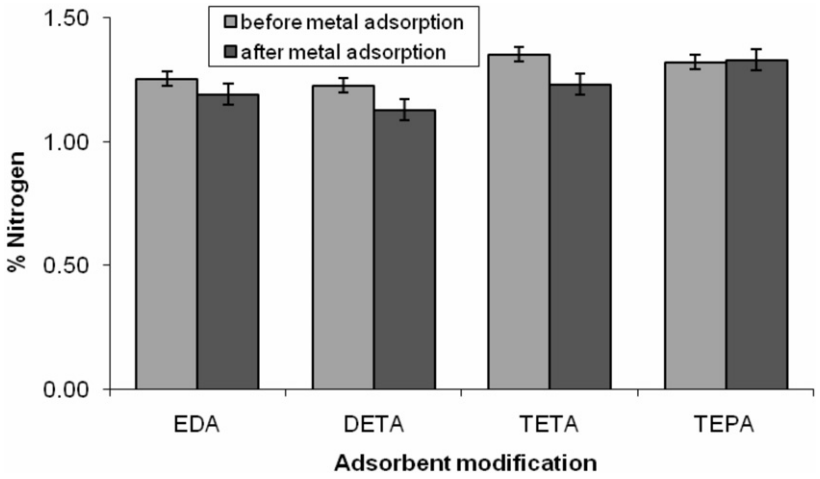

Figure 4 Percentage nitrogen levels in the modified adsorbent before and after vanadium adsorption.

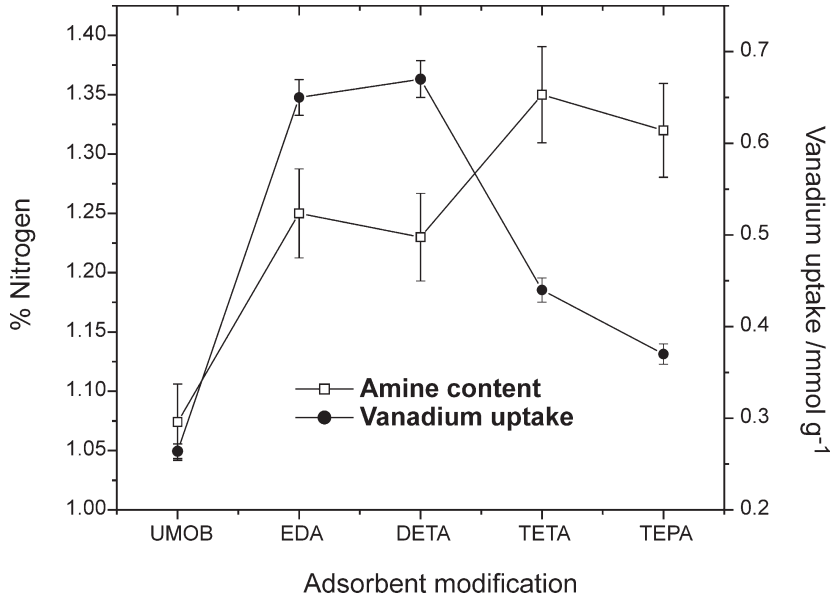

Figure 5 Effect of amination on the adsorption performance of the adsorbent at different degrees of modification.

did not participate in the formation of the V-adsorbent complex. It would seem that there was also poor adsorption/reaction between the adsorbent and TEPA (Fig. 1 and Table 1). Calculated amination correlation coefficients were found to be low for the *M. oleifera*-TEPA mixture than with the other combinations (Table 1).

The low amine content for the TEPA-functionalized adsorbent can be further explained by the size of the longer chain polyamines which lead to steric effects, wherein the size of the molecule prevents more long chain polyamines from accessing and reacting with the functional groups on the surface of the adsorbent.[20] The long chain polyamines also have a tendency of reacting with more terminal functional groups on the adsorbent surface, due to its many functional groups contained, thus consuming more of the available active sites. This is evidenced by low surface areas where chemical modification was performed using the longer chain polyamines, especially TEPA (Table 1).

Figure 5 shows that the adsorption of vanadium by the modified adsorbents was enhanced in the order: DETA>EDA> TETA>TEPA, representing percentage increases of 155, 146, 67 and 42, respectively. Evidently, TEPA functionalized adsorbent recorded the lowest adsorption potential probably due to the poor amination recorded in earlier experiments (Figs 1, 3 and 4).

4. Conclusion

The success of the study was in showing that chemical functionality of *M. oleifera* bark was improved by immobilizing different aliphatic polyamines (EDA, DETA, TETA and TEPA) on its surface. Subsequently, the vanadium adsorption capacity of the adsorbent was greatly improved. The chain length of the chemical modifiers was found to have an effect on the degree of amination, as the amine content increased from EDA to TEPA. However, *M. oleifera* modification using the long chain polyamines (TETA and TEPA) resulted in relatively lower adsorption capacities due to steric effects as well as the possibility of each molecule occupying more than one reaction site on the adsorbent. Hence, the adsorption performance and percentage increases were found to be in the order; DETA (155 %) >EDA (146 %) >TETA (67 %) >TEPA (42 %), implying that there is a threshold degree of chemical modification that *M. oleifera* can accommodate for maximum improvement in chemical reactivity for metal removal.

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