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TECHNICAL ARTICLE

Adsorptive Performance of Surface-Modified Montmorillonite in Vanadium Removal from Mine Water

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Abstract Montmorillonite modified with hexadecyltrimethylammonium bromide was used to remove vanadium (V) from synthetic and real mine water. Fourier transform infrared, X-ray diffraction, and scanning electron microscopy were used to characterise the adsorbent before and after adsorption, while the amount of V adsorbed was determined by ICP-OES. Batch adsorption was evaluated for dissolved V concentrations of 50–320 mg/L and V tailings seepage water from a South African mine. Adsorption capacity was affected by solution pH, temperature, sorbent mass, and the initial concentration. Electrical conductivity of the mine water before and after adsorption was measured to estimate the total dissolved solids. Equilibrium isotherm results revealed that V sorption follows the Freundlich isotherm, indicating that the sorbent surface was heterogeneous. A pseudo-second order kinetic model gave the best fit to the kinetic experimental data. The results of this study allow us to predict uptake efficiency of South African montmorillonite for V removal from mine water. However, the best adsorbent for the uptake of V or other contaminants will depend on the effluent to be treated.

Keywords Batch adsorption · Transition metals · Equilibrium · Kinetics

Introduction

Mining often produces potentially toxic substances that can affect water quality (Wolkersdorfer 2008; Younger et al. 2006). Effluents from mining industries have been found to contain metals such as U, Cd, V, Cu, Al, and Cr, which can pose a serious risk to human and aquatic life depending on their bioavailability (Smith 2009). Among these, vanadium (V), which is used extensively in the steel and petrochemical industries, has been of interest to many researchers because of its toxicity and carcinogenic effects at higher concentrations (Klaassen 2001; Soares et al. 2008). South Africa is a key V producer and the second largest steel maker, and so produces V wastewater in large quantities (Rohrmann 1985). As a result, discharges from these industries find their way into the environment and must be remediated.

Vanadium removal using conventional physical, chemical, and biological wastewater treatment methods is limited due to their cost or performance. For instance, precipitation methods require large amounts of alkaline material and the sludge precipitate needs subsequent treatment (Lynn and Kerry 2005). On the other hand, ion-exchange methods can allow metal recovery, but are expensive and complicated to use and maintain (Srivastava et al. 2006). Amongst wastewater treatment technologies, adsorption has gained a lot of attention as it is capable of removing contaminants even when the relative volatility is high (Douglas 1984). The use

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of adsorption processes in water purification and wastewater treatment is inherently simple and inexpensive and has many applications (Leung et al. 2000). However, the performance of any adsorption process depends on the choice of an appropriate adsorption media.

A number of adsorbent materials have been investigated for removal of V (Kaczala et al. 2009; Mariangela et al. 2012). The most commonly used adsorbents include activated carbon, molecular sieves, polymeric adsorbents and some other low-cost adsorbents (Kurniawan et al. 2006). Even though activated carbon efficiently removes V, it is relatively expensive and non-selective (Lumei et al. 2009). From an economic point of view, high-performing, low-cost treatment technologies are of great importance in developing countries. Clay minerals are good adsorbents for metal ions from aqueous solutions, due to their high ion exchange capacity and high specific surface area due to their small particle sizes (Bleiman and Mishael 2010; Manohar et al. 2005; Wang et al. 2016). In addition, they are abundant and inexpensive. Therefore, they can find application as low-cost, effective materials for the removal of metal ions from various effluents (Abollino et al. 2008).

Montmorillonite $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O]$, a naturally occurring phyllosilicate mineral that is readily available worldwide (Bergaya and Lagaly 2013), has already been investigated in the lab for potential use in V mine water treatment (Fosso-Kankeu and Waanders 2014). However, in its natural form, its effectiveness was very low. We attempted to improve the method by using a surface-modified montmorillonite (SMM) as an adsorbent for V removal from mine water.

Materials and methods

Materials

Chemicals

Montmorillonite, the adsorbent material used in this study, was supplied by Ecca Holding (Pty) Ltd., South Africa. The organic surfactant hexadecyltrimethylammonium bromide (HDTMA-Br, $C_{19}H_{42}BrN$) was purchased from Merck Chemicals Ltd., South Africa. The ammonium metavanadate, acetone, NaOH, NaCl, HNO_3 and HCl were purchased from Sigma Aldrich. All chemicals used were of analytical grade.

Preparation of Synthetic V Wastewater

Soluble V exists mainly in the +3, +4, and +5 oxidation states in aqueous solution (Hem 1985). Generally, 12 vanadium species can coexist in solution and can be categorized as cationic species $[VO_2^{+}]$, neutral species $[VO(OH)_3]$ and anionic species (Naeem et al. 2007). Anionic V species can be divided into two subclasses, decavanadate species, $V_{10}O_{27}(OH)^{-5}$, and mono or polyvanadate species, $VO_2(OH)^{2-}$, which are most stable in aqueous solution. In general, it was reported that a solution of V prepared in deionised water was stable in the pH range of 2–9 (Okamura et al. 2001). By contrast, a solution of V(IV) was only completely stable at pH 2. At pH 5.6, it gradually oxidizes and fully transforms into V(V) within 3 min (Krystyna and Tomasz 2004). Therefore, preparation of synthetic V wastewater involves decomposition of ammonium metavanadate in deionised water at around 200 °C (Crans 2005). Using this method, 2.2960 g (1.96×10^{-2} mol) of ammonium metavanadate were added to 200 mL of distilled water and the mixtures were placed on a hot plate for 10 min at 200 °C. Afterwards, the V concentrate obtained was diluted with 800 mL of distilled water in a 1000 mL volumetric flask. The pH of the solution was then adjusted with 0.1 M NaOH or 0.1 M HCl to the desired pH values, mostly between 2 and 9, which was reported stable in aqueous solution.

South African Mine Water

Mine water was obtained from a V mining operation in the North West province of South Africa that is one of the world's most prominent producers of V. The sample was stored in a cold room below 5 °C without further preservation to keep its chemical composition as close as possible to the original.

Surface Modification of Montmorillonite

Details of the montmorillonite modification procedure are described elsewhere (Onyango et al. 2012). All particles were washed with distilled water to remove dirt and impurities and allowed to dry for 24 h; particle sizes between 75 and 150 µm were selected for the adsorption process. Thereafter, the dried montmorillonite was transformed into a near homoinic state through a conditioning process using a NaCl solution. To generate hydrophobic properties on the Montmorillonite surface, the conditioned montmorillonite was then modified. Preliminary modification tests were performed to determine the best surfactant loading: 10 g of conditioned montmorillonite was separately added to 5 different batch reactors containing surfactant solutions of 1, 2, 3, 4, and 5 g/L HDTMA-Br concentrations. The mixtures were stirred at 300 rpm (rotations per min) for 72 h. Finally, the mixtures were vacuum filtered and the solid residue obtained was double washed with distilled water and air dried to produce the SMM.

Characterization of the Montmorillonite Sorption Material

Functional groups, mineralogical properties and elemental composition of the sorption material were determined using Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS) analyses. The composition of the montmorillonite was analysed before and after treatment with the HDTMA-Br to ascertain if there were changes in chemical stability.

Fourier transform infrared spectroscopy (FT-IR) analysis was done using a Perkin Elmer Spectrum 100 spectrometer with the spectra recorded in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. The XRD results were recorded on a Bruker-AXS D8 advance diffractometer, using a quartz sample holder, with Cu K α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA and an increment of 0.01°). The morphology and composition of the sorption media were characterized by SEM/EDX using a JEOL JSM-7600F field emission SEM, running at an accelerating voltage of 2 kV. To avoid charging effects during observation, an ion-sputtering device was used for fine gold coating of the samples.

Batch Experiments

Sorption Equilibrium

The best modification regimes for V removal were first investigated using sorption equilibrium. An amount of 0.1 g of sorption media prepared in different modification regimes was added separately to 50 mL of synthetic V wastewater in 100 mL sample bottles with a concentration of 100 mg/L and a pH of 5.20. The mixtures were shaken in a thermostatic bath shaker for 24 h at a speed of 200 rpm. The as-prepared 2 g/L HDTMA-Br sorption media performed better than the other regimes and was subsequently used for characterization and sorption experiments.

Adsorption of V by the SMM was assessed to determine the effect of different variables. First, the effect of solution pH was studied to determine the optimum pH for the process. Using either NaOH (0.1 M) or HCl (0.1 M), the initial pH was adjusted from 2 to 10 and 0.1 g of SMM was added to 100 mL plastic bottles containing 50 mL solution of synthetic and real mine water with initial V concentrations of 100 and 119 mg/L, respectively. Thereafter, the bottles were placed in a thermostatic shaker at 200 rpm for 24 h. At the end of the contact period, the samples were filtered using Whatman filter paper No. 42 and the filtrate analysed by inductive coupled plasma (ICP-OES) at a wavelength of 292.4 nm to determine the V concentration. The above procedure was repeated to determine how the sorbent mass, initial concentration and temperature affected the amount of V adsorbed. The effect of sorbent loading was explored by varying the mass of the sorbent from 0.01 to 0.2 g while the effect of concentration was explored by varying the concentration of the V synthetic solution from 20 to 200 mg/L. Finally, the effect of temperature was determined varying the temperature range between 25 and 45 °C, with a 50 mg/L V solution at a pH of 5.20. The sorbent mass was fixed at 0.15 g for the latter experiments. The percentage removal of V (efficiency) R_t (%) was calculated using Eq. 1 and the equilibrium uptake q_e (mg/g) with Eq. 2:

$$R_t = \frac{C_o - C_e}{C_o} \cdot 100 \tag{1}$$

$$q_e = \frac{C_o - C_e}{m} \cdot V \tag{2}$$

where C_0 (mg/L) is the initial V concentration, C_e (mg/L) is the concentration of V at equilibrium, V is the volume of the sample (L), m the mass of the adsorbent (g), and R_t is the percentage removal.

Sorption Kinetics

Sorption kinetic experiments were conducted using a batch reactor, varying synthetic V initial concentrations between 50 and 100 mg/L at room temperature using a stirring speed of 300 rpm. A mass of 2 g of the SMM was added to the reactor containing 1 L of synthetic V wastewater. At predetermined time intervals, 10 mL samples were withdrawn from the reactor using a syringe. Each sample was immediately filtered using a Whatman Filter paper No. 42 and the filtrates were analysed by ICP-OES to determine the residual concentration of V. Using Eq. 1, the amount of V removed at any given time was calculated.

Results and Discussion

Characterization of the Montmorillonite Material

Fourier Transform Infra-Red (FT-IR) Spectroscopy

FT-IR spectra of raw montmorillonite (RMM), SMM, after adsorption montmorillonite (AMM), and HDTMA-Br had bands at 1006–980 cm^{-1}, which is due to Si-O-Si and Si-O-Al vibrations (Fig. 1). Bands at 3388–3624 and 1634 cm^{-1} are attributed to stretching vibrations of molecular water and the H–O–H deformation vibration bands appear at 1629 cm^{-1} (Mozgawa et al. 2011). As can be seen, the bands shifted to higher wavelengths in the SMM owing to its interaction with HDTMA-Br. Two additional peaks show up in the SMM in the

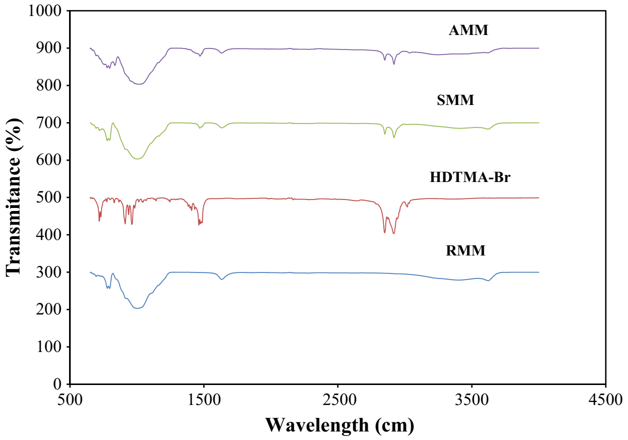

Fig. 1 FT-IR Spectra of montmorillonite (RMM), modified montmorillonite (SMM), HDTMA-Br and after-adsorption form (AMM)

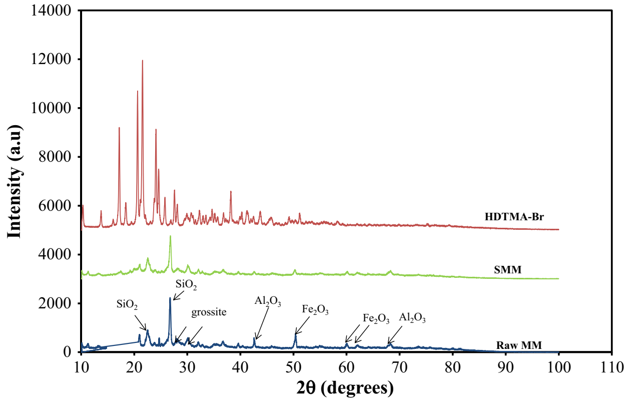

Fig. 2 XRD pattern of raw montmorillonite, modified montmorillonite and HDTMA-Br

2851–2919 cm^{-1} region and can be assigned to the anti-symmetric and symmetric CH_2 stretching. Furthermore, the peak at 3018 cm^{-1} is assigned to the anti-symmetric and symmetric stretching of CH_3-N in the trimethylammonium group (Ma et al. 2010). The first vibration was attributed to symmetric (*vs.* CH_2) and the second asymmetric (*vs.* CH_2) stretching vibrations of CH_2 in the alkyl chain that was derived from the cationic surfactant HDTMA-Br.

The peaks at 1468, 2851, and 2919 cm^{-1} are attributed to HDTMA sorbed on the external surface of the montmorillonite, since these corresponding peaks are also observed in the FT-IR pattern of HDTMA only. The vibrations at 3100–3600 cm^{-1}, due to H-bonded water molecules, become broader in AMM, indicating increased H-bonding in the SMM (Ama et al. 2015; Ma et al. 2010).

X-ray Diffraction (XRD) Analysis

The XRD pattern of the RMM shows peaks of major intensity corresponding to SiO_2 and other species present in small quantities: calcium oxide, aluminium oxide, iron oxide, grossite ($CaAl_4O_7$), and quartz (Fig. 2). The reduction and disappearance of major peaks in the XRD pattern of SMM indicates reduced crystallinity after the modification of the montmorillonite. For instance, SiO_2 and Al_2O_3 peaks reduced in intensity, and the peak at 50° (2θ), which is attributed to Fe_2O_3, disappeared in the SMM XRD pattern. A similar interaction between HDTMA-Br with clay was reported by Pablo et al. (2015), whereby little or no substantial changes could be observed in the XRD patterns before and after modification.

Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy

SEM analysis revealed information about the morphology of the RMM, SMM, and AMM. The laminar crystals of RMM (Fig. 3a) are not as clear as those for the SMM (Fig. 3b, c) due to the HDTMA-Br adsorbed on the external surface of the modified montmorillonite. The use of cationic surfactants to modify the negatively charged RMM occurs through cation exchange and hydrophobic interactions and leads to the formation of a stable, organic-rich coating on the external surfaces of the RMM. The charge-balancing cations present on the RMM (typically Na^+, K^+, Ca^{2+} and Mg^{2+}) are replaced by the high molecular weight quaternary amines. These quaternary amines exchange quantitatively with cations on the external surface of the montmorillonite (Riza Putra et al. 2013; Slimani et al. 2005). The shapes of the particles on the surface of raw montmorillonite are irregular, whereas its modification with HDTMA-Br results in an onset of regularity in shape. The AMM form is more regularly shaped. Generally, the particles are clustered, as observed in the SEM images. Energy spectroscopy results revealed that O, Si, Al, Fe, Ca, Mg K, Na, and Ti are the principal constituents of the montmorillonite used in this study (supplementary Table 1), which agrees with the information obtained from the montmorillonite material data sheet. The AMM elemental composition shows the presence of V sorbed on the surface, an indication of the chemical interaction between SMM and V. Furthermore, the high percentage of carbon on the surface of RMM and AMM shows the successful coating of the samples with HDTMA-Br. Finally, the observed differences in chemical composition between SMM and AMM are due to the various constituents present in the

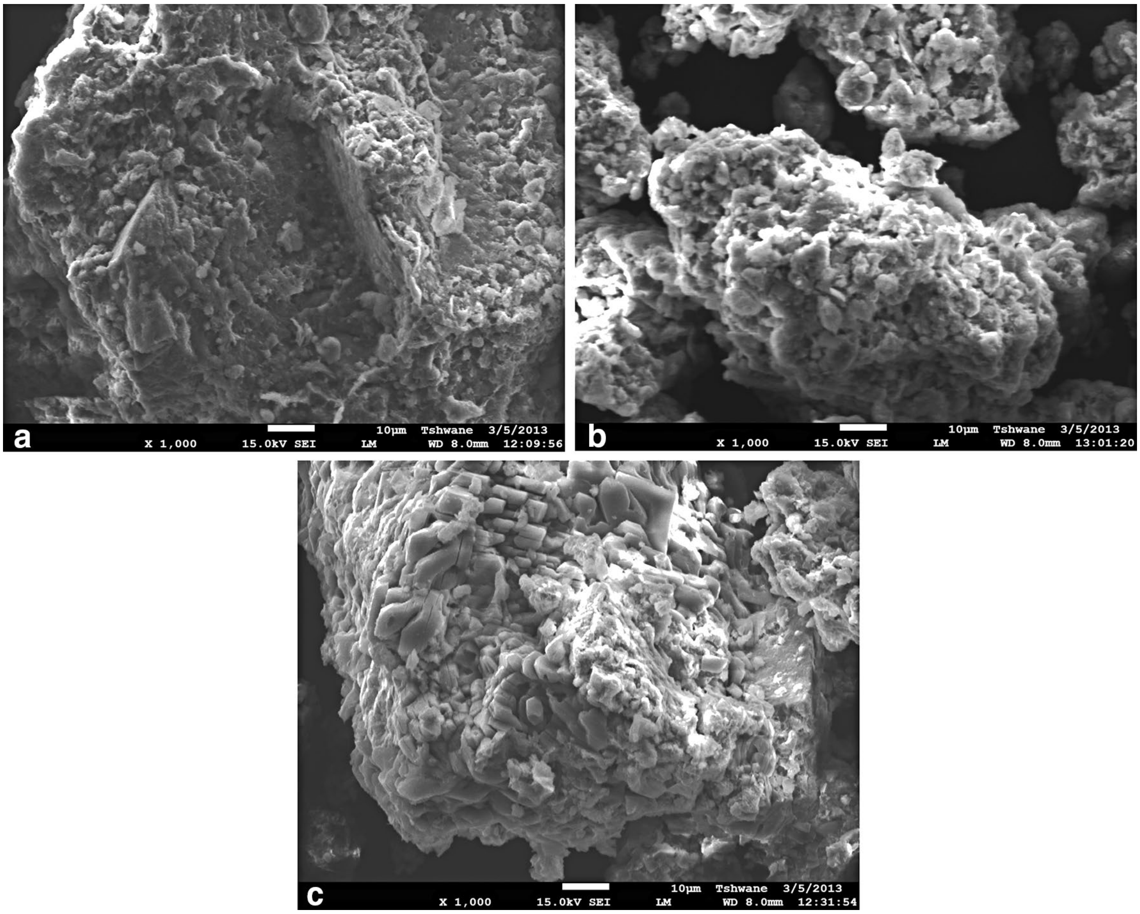

Fig. 3 SEM Images of **a** raw montmorillonite **b** modified montmorillonite and **c** after use form montmorillonite EDS

mine water used and the formation of bicarbonate in the higher pH-waters due to reactions of atmospheric CO_2 with the mine water.

Effect of the Quantity of Surfactant used in Surface Modification of Montmorillonite

RMM is not suitable for the separation and pre-concentration of V as it has a negative surface charge over the entire pH range and therefore cannot adsorb the anionic V species predominant at pH values above 6 (Fosso-Kankeu and Waanders 2014). Consequently, this results in a relatively low adsorption capacity, as also shown by dos Anjos et al. (2014). For this reason, an attempt was made to increase the montmorillonite adsorption capacity by conditioning the surface of the montmorillonite with NaCl and then modifying it with HDTMA-Br to create a surface with hydrophobic properties and partially neutralized negative charges (Fig. 4).

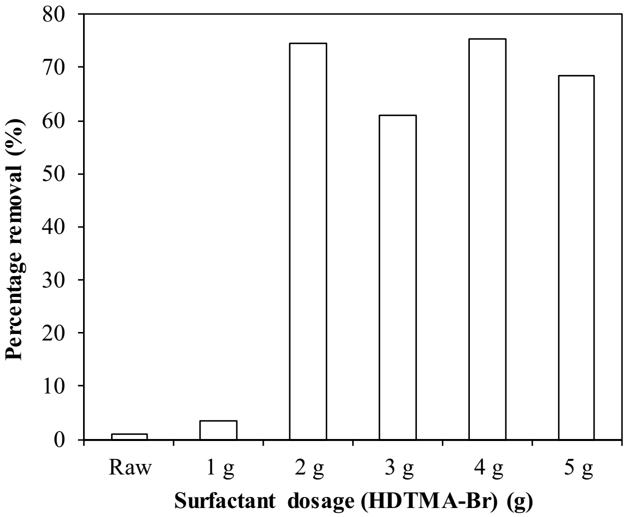

Fig. 4 Effect of surfactants dosage onto montmorillonite on vanadium adsorption (initial concentration 100 mg/L, pH 5.2, Temp. 25 °C, duration 24 h)

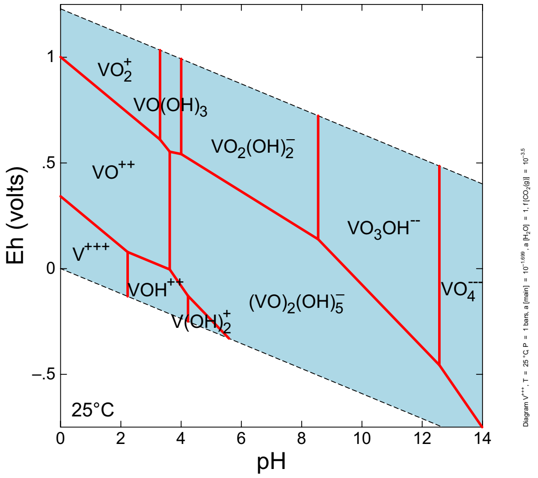

Fig. 5 Vanadium speciation diagram (made with Geochemist's Workbench 10×)

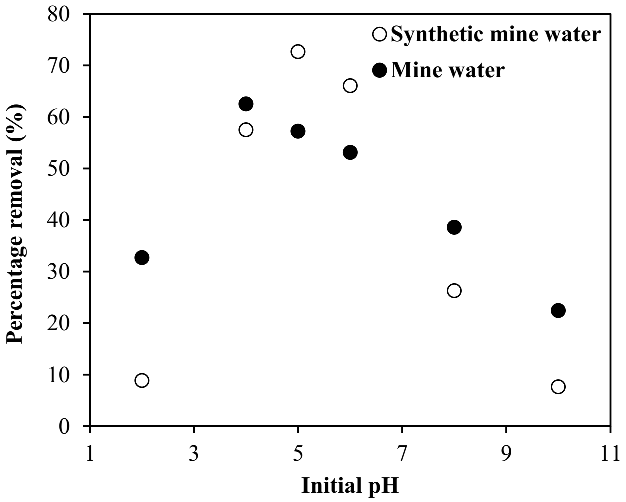

Fig. 6 Effect of solution pH in vanadium synthetic water and mine water by surface modified montmorillonite (SMM) (Temp. 25 °C, duration 24 h, initial concentrations 100, 119 mg/L respectively)

Effect of Initial Solution pH

The sorbent removed very little V at extreme pH values (pH 2 and 10). A gradual increase in V uptake was observed with an increase in pH up to 5.20 and 4.20 for the synthetic and real mine water, respectively, indicative of the interaction of the anionic V species with the hydrophobic surface of the modified montmorillonite. At low pH, positively charged V species predominate (Figs. 5, 6). The surface of the modified montmorillonite is also positively charged within this pH range, as the surfactant used during the modification process changed the surface from hydrophilic to hydrophobic. Multiple mechanisms could be involved in the V sorption, including hydrophobic interactions and hydrogen bonding, which are the major mechanisms in inorganic sorption (Mohana et al. 2009). At pH 4–6, anionic V species predominate (Crans 2005) and this could explain the higher removal rates at pH 5.20 and 4.20. It can be observed from Table 2 that the pH after adsorption increased by almost a pH unit in all cases, which is indicative of V ion protonation in the mine water. Crans (2005) reported that a higher pH causes a higher degree of protonation and polymerisation of V ions, which could limit removal of anionic V species, even at optimum pH. The adsorption of V onto montmorillonite was dependent on the pH that the interaction occurred at via the hydrophobic surface of montmorillonite and the anionic V group.

In addition to chemical and biological parameters, industrial water treated for agriculture and industrial reuse must meet certain TDS criteria. TDS was calculated from the electrical conductivity, using a conversion factor of 0.65, which was based on data from Hubert and Wolkersdorfer (2015), which complies with the conversion factor recommended by the Department of Water Affairs and Forestry (1996). Consequently, the highest TDS value was 217 mg/L, which is within the requirement for industrial reuse (Table 1).

Effect of Sorbent Mass

The effect of SMM mass on the V uptake efficiency shows that the percentage of V removed increased with an

Table 1 Solution pH and electrical conductivity for TDS determination

Sample treated	pH before adsorption	pH after adsorption	Initial electrical conductivity (µS/cm)	Electrical conductivity after adsorption (µS/cm)	TDS (mg/L)
pH2	2.20	2.94	727	551	114
pH4	4.20	4.90	727	863	88
pH5	5.20	5.60	727	807	52
pH6	6.10	6.19	727	791	42
pH8	8.20	6.32	727	866	90
pH10	10.1	8.42	727	1061	217

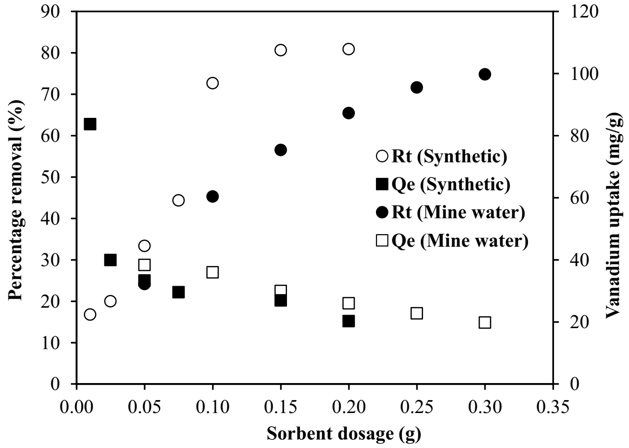

Fig. 7 Effect of adsorbent dosage on vanadium adsorption (synthetic water; initial conc. 100 mg/L and pH 5.2, mine water; 119 mg/L and pH 4.2. Temp. 25 °C, duration 24 h)

increase in the adsorbent dosage (Fig. 7). This is because active sites available for V sorption are proportional to the adsorbent mass.

Sorption Isotherms

The temperature dependence of V sorption from synthetic and real mine water was explored by varying the temperature from 25 to 45 °C (supplementary Fig. 1). It was observed that an increase in equilibrium concentration increased the V equilibrium uptake. Moreover, the adsorption capacity increased as the temperature rose, indicating that V sorption on montmorillonite is temperature dependent. The enhanced sorption at higher temperatures may have been due to a decrease in the thickness of the boundary layer surrounding the SMM. There is also a possibility that the increased movement of the molecules as the temperature rose increased the uptake. The data provided from sorption equilibrium are used to describe the interaction between adsorbate and adsorbent for effective design of an adsorption process. Furthermore, sorption equilibrium data are used in comparing the performance of different media for a given sorption process. Consequently, the experimental data were analysed using Langmuir and Freundlich models (Table 2).

The linear form of the Langmuir and Freundlich adsorption isotherm equations are given in Eq. (3) and Eq. (4), respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where C_e (mg/L) is the concentration of V at equilibrium, q_e (mg/g) the V equilibrium uptake, b is the Langmuir constant and q_o is the adsorption capacity of the monolayer; K_F and n are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively.

The Langmuir isotherm parameter q_o, which measures the monolayer capacity of the adsorbent, increased with an increase in temperature, as did the predicted K_F values from the Freundlich isotherm; an inconsistent pattern was noted for the Langmuir constant b. K_F is related to the sorption capacity, and its increase matched the enhanced sorption (Table 2). Comparing the Langmuir and Freundlich adsorption isotherm correlation values (R^2), the Freundlich isotherm described the V removal better, indicating a heterogeneous phase of SMM and multilayer adsorption, which also was reported by Ramesh et al.

Table 2 Isotherms parameters for vanadium synthetic and mine water adsorption onto MM

Temperature °C	Langmuir isotherm parameters					
	Synthetic water			Mine water		
	q_m (mg/g)	b (L/mg)	R^2	q_m (mg/g)	b (L/mg)	R^2
25 °C	38.8	3.3×10^{-2}	0.934	40.0	5.4×10^{-1}	0.987
35 °C	42.5	3.6×10^{-2}	0.995	47.6	4.1×10^{-2}	0.988
45 °C	58.8	1.0×10^{-2}	0.942	59.6	2.2×10^{-1}	0.992
	Freundlich isotherm parameters					
	Synthetic water			Mine water		
	K_F (L/g)	$1/n$	R^2	K_F (L/g)	$1/n$	R^2
25 °C	1.01	0.60	0.999	14.4	0.22	0.993
35 °C	1.02	0.67	0.999	18.4	0.21	0.995
45 °C	1.07	0.73	0.999	25.7	0.17	0.999

Table 3 Comparison of the adsorption capacity of SMM and other adsorbents for V removal at 25 °C

Adsorbent	q_m (mg/g) or R_t (%)	References
$ZnCl_2$ activated carbon	24.4	Namasivayam and Sangeetha (2006)
Metal-hydroxide (EE-33; seven trents)	25.06	Naeem et al. (2007)
Metal sludge	24.8	Naeem et al. (2007)
Montmorillonite	78%	dos Anjos et al. (2014)
Surface modified montmorillonite (V synthetic water) (90%)	38.8	This study
Surface modified montmorillonite (South African V mine water) (99%)	40.0	This study

(2007). A comparison of adsorption capacities of other adsorbents and SMM for V removal from wastewater is provided in Table 3.

Sorption Kinetics

Designing an adsorption process from a laboratory experiment to an industrial practice requires a thorough understanding of sorption kinetics. This can be influenced by many factors including stirring speed, the size of adsorbent particles and their concentration in suspension, and the residence time between adsorbate and adsorbents (Bhatnagar et al. 2008). In this study, batch kinetic experiments explored the effects of varying initial concentration. The process was very rapid in the initial phase of up to 20 min when the driving force was fast, due to the excess availability of active sites, but later slowed down; a constant removal capacity was observed beyond 20 min, which means there were no more active adsorption sites (Fig. 8). A similar short reaction time has been reported earlier by Madona et al. (2014).

As concentrations were increased from 50 to 100 mg/L, the predicted removal capacity increased steadily from 5.89 to 22.6 and 19.61 to 26.32 mg/g in the pseudo-first order and pseudo-second order models, respectively (Table 4), and the rate constants k_1 and k_2 decreased at greater concentrations. The values of the Elovich parameters a and b also changed with initial concentration. Thus, as the initial V concentration increased from 50 to 100 mg/L, the value of a also increased from 1.5×10^{-2} to 2.84×10^{-6} mg/g/min. Thus, the pseudo second order sorption mechanism was predominated, with high correlation factors of 0.999 in almost all cases. Therefore, this model satisfactory describes the kinetics of the experimental data, compared to the Elovich and first-order models, and the overall rate of the V uptake was controlled by chemisorption. An operational application of this adsorbent was reported in a continuous adsorption process (Mahadevaiah et al. 2008).

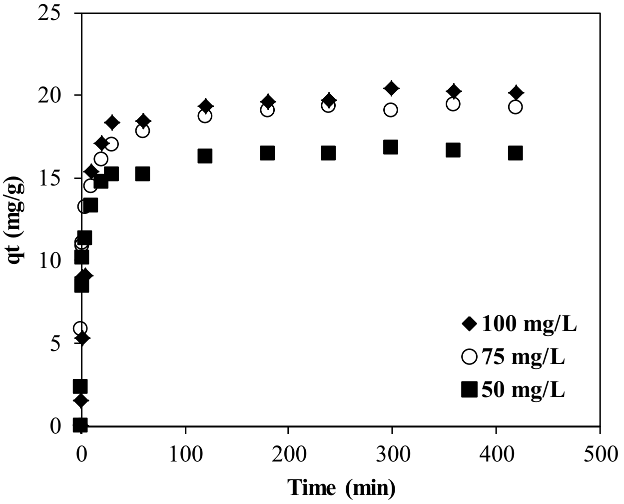

Fig. 8 Sorption kinetic of vanadium onto SMM at varying concentration (sorbent dose 2 g/L, Temp. 25 °C, particle size 0.15–0.30 mm and speed 300 rpm)

Conclusions

Generally, it can be concluded from this study that the surface modification of montmorillonite with HDTMA-Br enhanced its sorption capacity for V removal from synthetic and real mine water. On this note, surface modification of montmorillonite with other cationic surfactants is highly recommended for further investigations. The extent of adsorption was found to be controlled primarily by pH and temperature. A pH of 5.20 and pH 4.20 were found to be favourable for the sorption of V from synthetic solution and a South African mine water, respectively, which is consistent with the chemical interaction between the hydrophobic surface of SMM and the strongly anionic V species. It was also observed that a dosage in the range of 0.01–0.2 g of SMM with a particle size between 75 and 150 μm was required for 90% removal of V from an initial concentration of 100 mg/L at pH 5.20 and 99% removal of V from an initial concentration of 119 mg/L at pH 4.20. The adsorbents exhibited excellent adsorption properties for V found in fresh water and mine water in concentrations ranging from 10 to 200 mg/L and the maximum allowable concentration (1.0 mg/L) for discharge was achieved. The SMM-V interaction was found to be endothermic in nature, which was confirmed by the positive value of the enthalpy. The adsorption equilibrium was described by the Freundlich adsorption isotherm, which revealed that the surface of the adsorbent material is heterogeneous. The sorption kinetics

Table 4 Kinetics parameters of vanadium adsorption onto surfactant modified montmorillonite

C_o (mg/L)	Pseudo-first-order model			Pseudo-second-order model			Elovich model		
	k_1 (L/min)	q_e (mg/g)	R^2	k_2 (g.mg/min)	q_e	R^2	α	β	R^2
50	6.01×10^{-3}	5.89	0.629	20.8×10^{-2}	19.61	0.999	1.5	0.591	0.629
75	5.24×10^{-3}	6.72	0.768	12.9×10^{-2}	20.41	0.998	2.23	0.581	0.768
100	5.14×10^{-3}	22.26	0.935	7.0×10^{-3}	26.32	0.999	2.84	0.559	0.935

was well described by the pseudo-second order model. A similar operational application was reported in the literature for a continuous adsorption process; therefore, industrial application using this adsorbent media is highly feasible. Given the low cost of natural montmorillonite and the competitive sorption capacity achieved through functionalization, this material can be considered as a potential candidate for treatment of V contaminated water.

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