

Functionalised natural zeolite and its potential for treating drinking water containing excess amount of nitrate

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Abstract

An excess level of nitrate in drinking water is responsible for methemoglobinemia, or 'blue baby' disease. Consequently, management of nitrate in drinking water is universally of public health interest. In this study, clinoptilolite functionalised with cationic surfactant hexadecyltrimethyl ammonium (HDTMA) was used for the removal of nitrate from drinking water. The effects of surfactant loading, adsorbent dosage, pH, coexisting ions, temperature and environmental water quality on the adsorption of nitrate were investigated. It was found that adsorption was optimum when the initial concentration of the functionalising surfactant was 3 000 mg·l⁻¹. An increase in adsorbent dosage raised the percentage removal of nitrate. The valency of the coexisting anion had a major effect on nitrate removal, with the presence of phosphate (a trivalent anion) leading to the lowest removal ability. Temperature and pH had negligible effects on adsorbent performance. Environmental water samples (natural groundwater samples from Limpopo Province, South Africa) were tested and it was found that the World Health Organisation (WHO) regulatory compliance can be achieved even when the initial concentration of nitrate exceeds 300 mg·l⁻¹. Equilibrium data was modelled using the Freundlich and Langmuir isotherms and the data conformed well to the Freundlich isotherm, indicating the heterogeneous nature of the active sites. Kinetically, nitrate adsorption was best described by the pseudo-second rate equation.

Keywords: adsorption, zeolite, nitrate, kinetics, equilibrium

Introduction

A number of rural communities in South Africa use groundwater for drinking purposes. In some cases this water is impure due to high concentrations of nitrates (Schoeman and Steyn, 2003). Pietersen (2005) reported that groundwater in South Africa often has high nitrate values, which exceed 50 mg·l⁻¹, the limit recommended by the world Health Organisation (WHO). Colvin et al. (2008) further noted that South Africa has some of the highest natural nitrate levels in the world (>500 mg·l⁻¹ NO₃-N). Nitrates can spread in the environment either naturally or due to anthropogenic activities (Stadler et al., 2008). It is well recognised that the presence of excess nitrates in drinking water can be detrimental to a variety of living species, including man. A high concentration of nitrate in drinking water leads to production of nitrosamine, which is related to cancer and increases the risk of diseases such as methemoglobinemia in newborn infants (Mažeikienė et al., 2008; Bouwer, 1989; Samatya et al., 2006). Hence, reduction of nitrates in drinking water to permissible levels is mandatory.

A number of physico-chemical technologies, such as reverse osmosis (Bohdziewicz, 1999), ion exchange (Bae et al., 2002; Clifford and Liu, 1993) and chemical precipitation (Ayyasamy et al., 2007) are available for nitrate removal from water (Schoeman and Steyn, 2003). However, some of these methods are either expensive, inefficient or not user-friendly. With the world economic meltdown, no country is spared, and

thus countries are emphasising reducing costs as well as developing technologies which add value to the lives of people. It is therefore necessary to screen techniques to find which ones suit rural communities such as those of South Africa. In doing so, a number of factors that form the basis of a decision framework are considered. These factors include: cost, regulatory compliance and public perception and acceptance. For these reasons, a technique based on adsorption processes is an attractive alternative for rural communities (Onyango and Matsuda, 2006).

The removal of anionic contaminants from water by adsorption methods has been widely studied in recent years. Interest is growing in the use of natural materials, due to their cost implication. One such material is zeolite (Bowman et al., 2000; Ranck, 2005). Zeolites are synthetic or naturally-occurring hydrated aluminosilicates with a cage-like structure, high external cationic exchange capacity and high surface area. The structural framework of zeolite is negatively charged due to isomorphic substitution of aluminium for silicon (Onyango, 2006). Thus, loading anionic contaminants like nitrates onto its surface is only negligibly possible, due to coulombic repulsive forces (Kumar et al., 2006). Therefore, to render the zeolite suitable for anionic contaminant removal from water, its surface charge property must be altered using appropriate charge reversing chemical species (Onyango et al., 2004). While some researchers have utilised synthetic zeolites for water treatment, in this study we exploit the readily available and cheaper natural clinoptilolite from the Western Cape area of South Africa. There is hardly any information in literature on the use of this zeolitic tuff in purifying water containing health-hazardous anions such as nitrate. The study aims to demonstrate the performance of this material in nitrate removal from water, with respect to surfactant loading, adsorbent dosage, pH, coexisting

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Table 1 Summary of adsorption equilibrium and kinetic models		
Model	Equation	No.
Freundlich	$q_e = K_f C_e^{1/n}$	(1)
	$\ln q_e = \ln K_f + 1/n \ln C_e$	(2)
Langmuir	$q_e = q_0 b C_e / (1 + b C_e)$	(3)
	$C_e / q_e = 1/q_0 b + C_e / q_0$	(4)
Pseudo-first order (linear form)	$\ln (q_e - q_t) = \ln q_e - k_1 t$	(5)
Pseudo-second order (linear form)	$t/q_t = 1/k_2 q_e^2 + t/q_e$	(6)

Note: K_f and b are Freundlich and Langmuir constants, respectively, q_e is the uptake at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), C_e is the equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$), q_0 is the theoretical adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), $1/n$ is the heterogeneity coefficient, k_1 ($\text{L}\cdot\text{min}^{-1}$) is the pseudo-first order rate constant, k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the pseudo-second order rate constant, q_t ($\text{mg}\cdot\text{g}^{-1}$) is the amount of nitrate adsorbed at time t (min).

ions, temperature and environmental water quality. The nitrate percentage removal and the ability to meet the local regulatory compliance are used as performance indicators. Equilibrium and kinetic modelling are done to estimate important capacity and rate parameters which can aid in system design.

Equilibrium and kinetic models

The analysis and design of an adsorption process requires information on the equilibrium adsorption isotherms and rate data. Moreover, the evaluation of the equilibrium data also helps in the investigation of mechanisms involved in nitrate-zeolite interaction. In this work, the 2 adsorption equilibrium models used are the Freundlich and Langmuir isotherms. Altin et al. (1998) indicated that the Langmuir and the Freundlich adsorption isotherms are the most widely used mathematical models, owing to their simplicity and ability to describe liquid-phase equilibrium data in a wide range of concentrations. For brevity, a summary of the isotherm models are given in Table 1. The theoretical basis of these isotherms is readily available in the literature.

Theoretically, an adsorbing species may occupy 1 or 2 adsorption sites. The kinetics of the former sorbate-sorbent interaction is described by the Lagergren pseudo-first order model (Uysal and Ar, 2007) while the latter is described by the Ho pseudo-second order model (Ho and McKay, 1999). Table 1 summarises the linearised pseudo-first order model (Eq. (5)) and pseudo-second order model (Eq. (6)) used in interpreting the kinetic data.

Experimental

Preparation of surfactant-modified natural zeolite.

The natural zeolite used in this study was clinoptilolite supplied by Interscan Company, South Africa. The material was thoroughly washed with deionised water to remove dirt. Washed zeolite was then allowed to dry. To convert the zeolite to a final homoionic or near homoionic state, 20 g of the natural zeolite was treated with 2 M NaCl solution at room temperature over a period of 3 d. The solution was kept under agitation on a shaker operated at 200 $\text{r}\cdot\text{min}^{-1}$. After 3 d the solution was vacuum filtered and the conditioned zeolite prepared as such

was double-washed with deionised water to remove excess sodium chloride. The conditioned zeolite (Na form) was then dried at 105°C for 24 h.

Hexadecyltrimethyl ammonium bromide (HDTMABr) from Sigma Aldrich, South Africa, was used for surface modification. A pre-weighed quantity of conditioned zeolite sample was mixed with HDTMABr solution in 1:100 (solid: liquid) ratio. The concentrations of HDTMABr used for the preparation of surfactant modified zeolite (SMZ) were 1 $\text{g}\cdot\text{L}^{-1}$, 2 $\text{g}\cdot\text{L}^{-1}$, 3 $\text{g}\cdot\text{L}^{-1}$ and 4 $\text{g}\cdot\text{L}^{-1}$. The zeolite and surface-modifying solution were contacted in a batch reactor for 3 d. Finally, the solution was vacuum filtered, and the solid residue was double-washed with deionised water and air dried. The materials prepared in this manner are hereafter referred to as SMZ1 (for 1 $\text{g}\cdot\text{L}^{-1}$ HDTMABr), SMZ2 (for 2 $\text{g}\cdot\text{L}^{-1}$ HDTMABr), SMZ3 (for 3 $\text{g}\cdot\text{L}^{-1}$ HDTMABr) and SMZ4 (for 4 $\text{g}\cdot\text{L}^{-1}$ HDTMABr).

Adsorption media characterisation

Fourier transform infrared (FTIR) spectroscopy analyses were undertaken on a Perkin Elmer Spectrum 100 spectrophotometer. The FTIR spectrum of the solid sample dispersed in KBr disk was obtained to determine the functional groups in the surfactant-modified zeolite (SMZ) and HDTMA. The spectrum was recorded in the region from 500 to 4 000 cm^{-1} with a spectra resolution of 4 cm^{-1} .

Nitrate adsorption experiments

The nitrate adsorption experiments were conducted using environmental water from Limpopo Province and assimilated water samples of known initial concentration prepared by dissolution of an appropriate amount of KNO_3 (analytical grade) and performance of the necessary dilution. Batch experimental mode was adopted due to its simplicity. In the 1st set of experiments, 50 ml nitrate solutions contained in 100 ml plastic bottles were contacted with 0.5 g of unmodified natural zeolite and SMZ samples. The sealed bottles containing 50 $\text{mg}\cdot\text{L}^{-1}$ nitrate solution were placed in a thermostatic shaker operated at 200 $\text{r}\cdot\text{min}^{-1}$ for 24 h at 20°C. After 24 h the samples were filtered through a Whatman Filter Paper No. 41. The filtrate was then analysed for residual nitrate concentration. The nitrate percentage removal was calculated from:

$$\% \text{removal} = 100 \frac{(C_o - C_e)}{C_o} \quad (7)$$

where C_o ($\text{mg}\cdot\text{L}^{-1}$) is the initial nitrate concentration and C_e ($\text{mg}\cdot\text{L}^{-1}$) is the concentration of nitrate at equilibrium. In a 2nd set of experiments, the effects of pH and temperature on nitrate removal from water were explored by varying the initial solution pH from 1.66 to 11 and temperature from 20 to 60°C. The other experimental conditions were unchanged. Meanwhile the adsorption isotherm data were generated by contacting SMZ (0.5 g each) with nitrate solution in the concentration range from 10 to 300 $\text{mg}\cdot\text{L}^{-1}$ (50 ml each) for 24 h in a thermostatic shaker operated at 200 $\text{r}\cdot\text{min}^{-1}$. The equilibrium adsorption capacity was obtained by:

$$q_e = (C_o - C_e)V/m \quad (8)$$

where q_e ($\text{mg}\cdot\text{g}^{-1}$) is the equilibrium adsorption capacity, V (L) is the volume of the solution and m (g) is the mass of the SMZ. Since natural water contains different anions in different concentrations, which may compete with nitrates for the

available active sites, it is therefore imperative to study their effect on nitrate removal from water. The effects of the presence of sulphate, fluoride, phosphate and chloride on nitrate adsorption were studied. Tests were conducted in the presence of 10 mg·L⁻¹ of nitrate and 10 mg·L⁻¹ each of the co-existing ions. The adsorbent mass was fixed at 0.1 g per 50 ml solution. The experimental procedure was similar to that described previously. In the kinetic experiments, the effect of particle size on nitrate adsorption was studied. The particle sizes used were: <75 μm, 150-300 μm and 300-600 μm. The sorbent was contacted with nitrate-containing (100 mg·L⁻¹) aqueous solution for a period between 0 and 60 min. A final set of experiments involved the use of natural groundwater samples collected from various locations of Limpopo Province. The samples were analysed for nitrate levels before contacting them with different masses of sorbents. The equilibrium nitrate concentration was determined after 24 h.

Analysis of nitrate

The determination of nitrate in the filtrate followed the salicylate method (Monteiro et al., 2003). The absorbance of the solutions was measured at 410 nm using a UV visible spectrophotometer (Hach DR/3000).

Results and discussion

Zeolite characterisation

The raw zeolite used in this study was first conditioned with Na⁺ salt with the aim of removing certain cations from the structure and locating more easily removable ones, prior to any ion exchange application. It has been shown that the final homoionic or near homoionic state after conditioning zeolite improves the effective exchange capacity (Hui et al., 2005; Inglezakis, 2005; Athanasiadis and Helmreich, 2005). An FTIR study was used to explore changes in chemical stability and composition of the zeolite following conditioning and functionalisation. The FTIR patterns of raw, conditioned, surfactant-modified and nitrate-containing zeolites are shown in Fig. 1a. The raw zeolite and the zeolite in homoionic state (conditioned) show characteristic peaks at wave-numbers 624, 808, 993 and 1 594 cm⁻¹. Upon functionalisation of zeolite, new bands are observed at 1 461, 2 848 and 2 915 cm⁻¹, which can be attributed to HDTMA sorbed on the external surface of the zeolite, as the corresponding peaks are also observed in the FTIR pattern of HDTMA (see Fig. 1b). Nitrate adsorption on functionalised zeolite caused the bands at positions 1 461, 2 848 and 2 915 cm⁻¹ to decrease in intensity suggesting that the active sites created by HDTMA were responsible for nitrate removal from water. This observation corroborated the fact that the nitrate adsorption was of a physical nature, probably due to electrostatic forces between positively charged surfactant-modified zeolite and anionic nitrates. Most band positions did not change following modification and adsorption, suggesting that the basic zeolite structure did not collapse.

Optimising surfactant loading on zeolite with respect to nitrate adsorption

Nitrate is an outer-sphere complex-forming species and therefore its ample removal from water by adsorption is a challenge. In order to apply conventional adsorption media, their surfaces need to be modified to induce functional groups that can attract and adsorb nitrate ions. Recently, surfactants have been widely

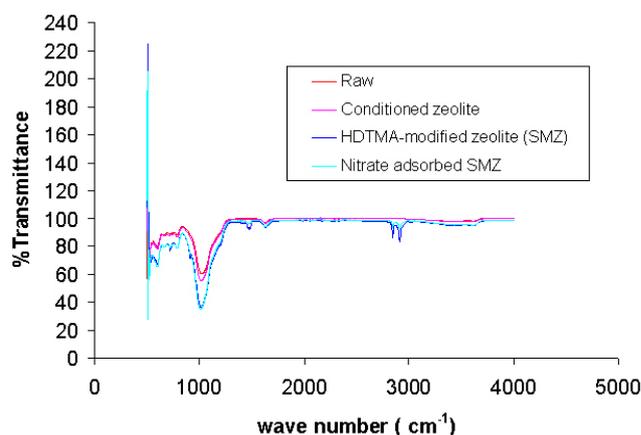


Figure 1a
The FTIR spectra of raw, conditioned, modified, and nitrate-adsorbed zeolites

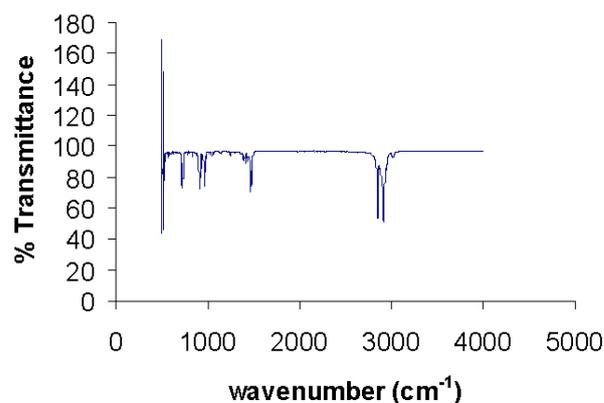


Figure 1b
The FTIR spectrum of HDTMA

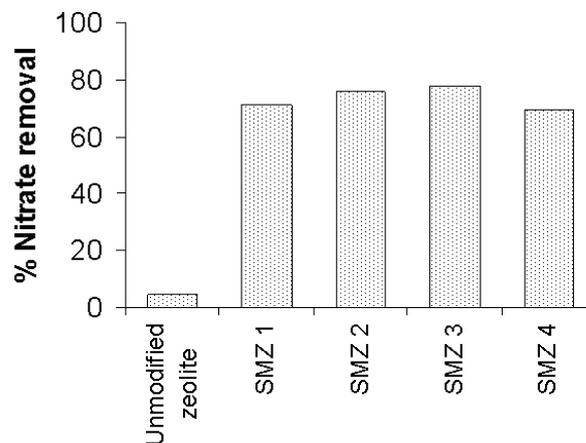


Figure 2
Sorption of nitrate on raw and surfactant modified zeolites. Initial nitrate concentration = 50 mg/L; sorbent mass = 0.5 g; particle size = 150-300 μm; equilibrium time = 24 h

reported to aid adsorption of anions. Consequently, this study considers the use of positively-charged HDTMA as the surface-modifying surfactant. Several studies have been reported on the use of HDTMA in modifying different kinds of adsorption media (Zhou et al., 2008; Wingenfelder et al., 2006; Yusof et al., 2009). Figure 2 shows the application of unmodified zeolite and surfactant-modified zeolites in nitrate removal from water.

The results clearly show that unmodified zeolite has very little adsorption capacity for nitrates. This observation concurs well with those of previous researchers (Schick et al., 2010; Mažeikienė et al., 2008; Li and Bowman, 2001). Zeolites are not good candidates for removal of anions from water because of their inherently negatively-charged surfaces that increase coulombic repulsion between the adsorbing anionic species and active sites. When the zeolite was functionalised with HDTMA (SMZ1, SMZ2, SMZ3, SZM4), a remarkable nitrate removal was observed. Surfactant modification of zeolite (clinoptilolite in this case) changes its surface charge from a net negative to a positive charge. Thus, electrostatic forces exist between the positively-charged zeolite and the nitrates in solution, which enhance nitrate adsorption. The nitrate removal increases with an increase in the concentration of the functionalising HDTMA and a value of 3 g HDTMA·ℓ⁻¹ gives the best performance. Further increase of HDTMA concentration to 4 g·ℓ⁻¹ results in a decline in removal of nitrates. This may be due to the fact that 4 g·ℓ⁻¹ exceeds the surfactant critical micelle concentration; thus the micelles attach to the external surface of the zeolite and rearrange to form a bi-layer that tends to impart anionic characteristics (Bowman et al., 2000). Therefore, zeolite treated with an initial concentration of 3 g·ℓ⁻¹ (SMZ3) of the surfactant appears to give optimal results and was used in all subsequent experiments.

Effect of co-existing anions

In reality the nitrate-contaminated water contains several other anions which can compete for the same adsorption sites. In order to explore the effect of interfering anions on the nitrate removal ability of the SMZ3, binary component systems were adopted in which nitrate removal in the presence of another anionic species was studied. The anions considered in this study included; phosphate, sulphate, chloride and fluoride. These anions represent both inner-sphere (phosphate and fluoride) and outer-sphere (sulphate and chloride) complex-forming species. The nitrate percentage removal of SMZ3 for single component (nitrate only) and in the presence of other anions is shown in Fig. 3. In the NO₃⁻ single component system, the nitrate percentage removal is 99%. This value reduces to 90% in the NO₃⁻/PO₄³⁻ binary component system. The binary systems involving sulphate, chloride and fluoride give 95%, 98% and 99% nitrate removal, respectively. Similar observations were recently reported by Saad et al. (2007) and Öztürk and Bektaş (2004). The trend in nitrate removal in the presence of coexisting anions seems to be related to the valence of the coexisting anions. Trivalent phosphate has the largest effect while monovalent anions give the least effect. These results suggest that electrostatic coulombic interaction plays a major role in nitrate uptake.

Effect of adsorbent mass

The number of active sites relates to adsorbent mass and hence sorption performance. The effect of adsorbent mass on the nitrate percentage removal is shown in Fig. 4. It is clear that an increase in adsorbent mass resulted in an increase in the removal of nitrates from water. Specifically, nitrate removal increases from 25% when the sorbent mass is 0.1 g·(50 mL)⁻¹ to 100% when the sorbent mass is 1.5 g·(50 mL)⁻¹, due to an increase in available sorption sites. However, it is observed that the increase in nitrate percentage removal is not directly proportional to adsorbent mass. One plausible reason could be due

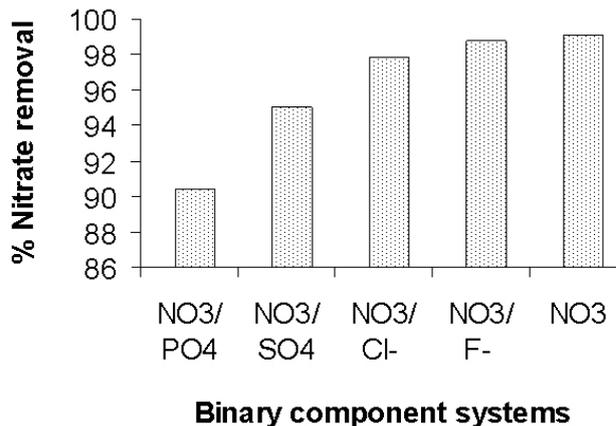


Figure 3

Effect of coexisting anions on nitrate removal from water. Sorbent mass = 0.1 g; initial nitrate concentration = 10 mg/ℓ; particle size = 150-300 μm; equilibrium time = 24 h

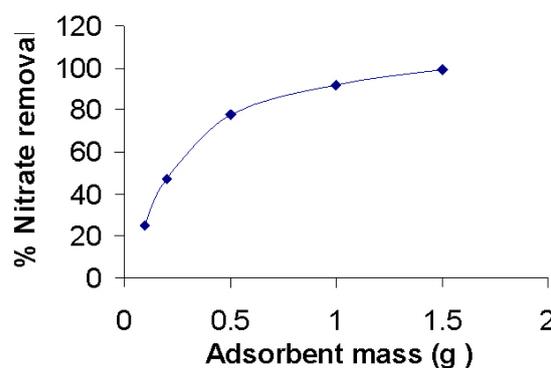


Figure 4

Effect of adsorbent mass on nitrate removal by SMZ3. Initial nitrate concentration = 50 mg/ℓ; particle size = 150-300 μm; equilibrium time = 24 h

to overlap of active sites at higher adsorbent masses resulting in reduced effective surface area required for sorption.

Effect of pH

Solution pH is one of the factors that have been found to significantly affect the sorption process (Onyango et al., 2006). A study was therefore undertaken to ascertain to what extent pH affected the sorption of nitrate. Table 2 summarises the effects of initial solution pH (1.6-11) on the removal of nitrate from water. The system (solution–solid) pH at equilibrium is also included. Results reveal that nitrate removal from water is marginally affected by pH. With no electrokinetic data at this stage, it can only be hypothesised that the surface charge on the SMZ3 was not significantly affected by pH changes. A confirmation is required to ascertain this. The slight decrease in nitrate adsorption with increase in pH could be due to interaction during passive transport in the pores and competition between OH⁻ and NO₃⁻ anions for active sites. One disadvantage of using adsorption processes in removal of anionic contaminants from water inheres in most sorption media's inability to perform adequately at higher pH. Indeed several researchers have reported a significant reduction in media performance in nitrate removal from water at near neutral and alkaline pH (6.5-8.5), the pH range typical of natural systems such as

Initial pH	Final pH	Removal (%)
1.66	2.04	100
4.66	6.71	99.2
6.56	7.23	98.2
8.47	7.61	96.0
11.0	9.87	96.0

groundwater (Chatterjee et al., 2009; Chatterjee and Woo, 2009; Cengeloglu et al., 2006). A media, such as SMZ3 used in this study, whose performance does not deteriorate with pH changes is desirable for water treatment. Meanwhile the pH of the system (solution-solid) after sorption was found to increase when the initial pH was acidic and to decrease when the initial pH was alkaline. This is due to the buffering effect of the zeolite. Sorbents normally shift solution pH towards their natural pHs or their point-of-zero charge (pH_{pzc}) (Onyango, 2006).

Effect of temperature

The effect of temperature was investigated in a range of 20–60°C and is shown in Fig. 5. It was observed that an increase in temperature resulted in a minor decrease in nitrate uptake by SMZ3. This clearly indicates that the adsorption process was exothermic. Similar observations in which adsorption decreased with an increase in temperature were recently reported by Chatterjee and Woo (2009) for nitrate adsorption by chitosan hydrogel beads. Temperature may or may not have a significant effect on adsorption depending on whether the process is chemical or physical in nature. When the process is chemical in nature, a higher energy barrier has to be overcome and hence temperature changes result in a significant (either a large increase or large decrease in adsorption) effect on adsorption. Conversely, a minor effect is normally observed when the process is physical in nature. The results of this study therefore reveal further that the nitrate adsorption process is physical in nature, involving coulombic electrostatic forces between the positively-charged SMZ3 surface and negatively-charged nitrate ion.

Adsorption isotherm

The design of an adsorption system requires equilibrium isotherm data. This study considers the application of the 2 most commonly-used isotherms: the Freundlich (Eq. (1) and linear form Eq. (2) and Langmuir (Eq. (3) and linear form Eq. (4)) models. The Langmuir isotherm is based on the premise that all active sites have identical energy strength. Figure 6 shows a typical fit of linearised Langmuir isotherm (see Table 1, Eq. (4)) for the experimental data (at 20°C) presented in Fig. 5. There is a deviation from linearity in the low concentration range. The regression coefficient (R^2) is 0.973. The R^2 values for other temperatures, 45°C and 60°C, are 0.957 and 0.913, respectively, which, for physico-chemical process like adsorption, are not very high. The Langmuir parameters, q_0 and b , were determined from the slope and intercept of the plots, and are 12.35 $mg \cdot g^{-1}$ and 0.048 $l \cdot mg^{-1}$, respectively. The Langmuir parameters for other temperatures are summarised in Table 3. The q_0 value is sufficiently high for a class of low-cost natural materials but lower than that of high-cost synthetic materials (Chatterjee

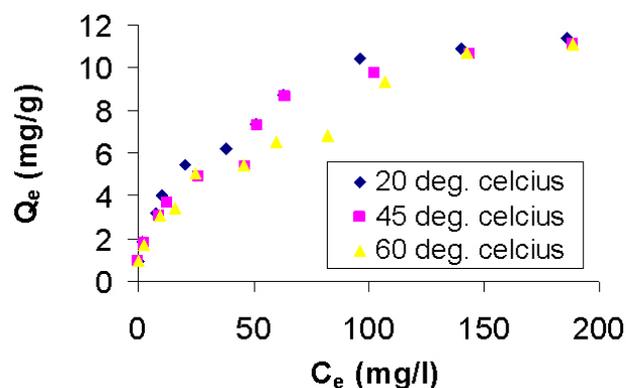


Figure 5
Effect of temperature on nitrate removal by SMZ3

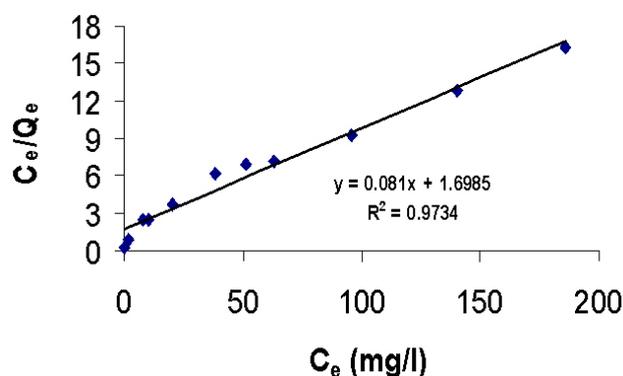


Figure 6
Linearised Langmuir isotherm (Eq. (4)) for nitrate adsorption onto SMZ3. Temp. = 20°C; pH= 6.6; adsorbent dose = 0.5 g; particle size = 150–300 μm

and Woo, 2009; Chatterjee et al., 2009). The feasibility of the Langmuir isotherm was assessed using dimensionless constant separation factor, R_L , defined by:

$$R_L = 1/(1+bC_0) \quad (9)$$

where b is the Langmuir constant and C_0 is the initial nitrate concentration ($mg \cdot l^{-1}$). The value of R_L indicates whether the isotherm is irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). R_L values between 0 and 1 were obtained suggesting the present sorption system is favourable.

The Freundlich isotherm, which describes sorption on sites of different affinity for sorbate, was applied in the linear form

Parameters	20°C	45°C	60°C
Langmuir isotherm			
q_0 ($mg \cdot g^{-1}$)	12.35	12.09	12.21
b ($l \cdot mg^{-1}$)	0.0477	0.0366	0.0298
R^2	0.97	0.95	0.91
Freundlich isotherm			
K_f	1.59	1.44	1.12
n	2.55	3.05	2.31
R^2	0.99	>0.98	0.98

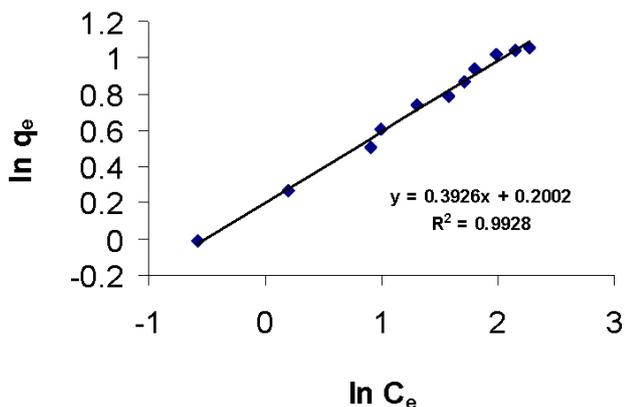


Figure 7
Linearised Freundlich isotherm (Eq. (2)) for nitrate adsorption onto SMZ3. Temp. = 20°C; pH = 6.6; adsorbent dose = 0.5 g; particle size = 150-300 μm

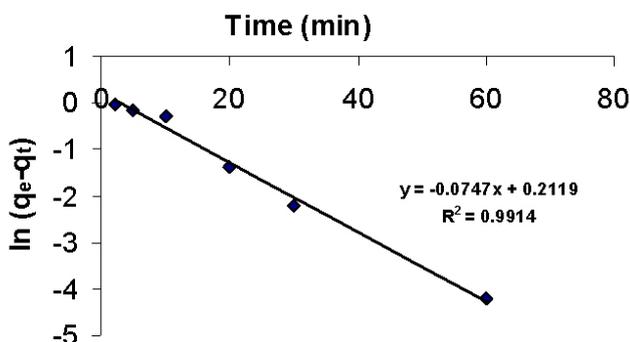


Figure 8
Fit of experimental data according to pseudo-first order kinetic model

expressed by Eq. (2) and is presented in Fig. 7. Linear plots were obtained with R^2 in the range 0.98-0.99, suggesting a good description of isotherm data by this model. In a study of nitrate removal from water by ion exchange resin, Chabani et al. (2006) also found the Freundlich isotherm to give the best description of the equilibrium data. The Freundlich constants, K_f and n , calculated at 20°C from this investigation, are 1.59 and 2.55, respectively. Values of n greater than 1 indicate favourable adsorption (Chabani et al., 2006). The Freundlich parameters for all the temperatures investigated are summarised in Table 3.

Adsorption kinetics

To apply an adsorption process for large-scale treatment of water, a clear understanding and determination of the rate parameters is a prerequisite. Kinetic data can be used to determine the time required for sorption to go to equilibrium and to develop predictive models that can aid in system design. Two kinetic models summarised in Table 1 were used to fit the experimental data. The first was the Lagergren pseudo-first order model (Eq. (5)). A plot of $\ln(q_e - q_t)$ versus t according to Eq. (5) should be linear if the adsorption process follows the first order kinetics. The equilibrium uptake in this case was used as a fitting parameter. For 150-300 μm sorbent size, the fitting value of $q_e = 11.53 \text{ mg}\cdot\text{g}^{-1}$ was used. A typical plot according to Eq. (5) is presented in Fig. 8 for particle size

Parameters	<75 μm	150-300 μm	300-600 μm
Pseudo-first order kinetics			
k_1 (min^{-1})	0.075	0.075	0.025
q_e ($\text{mg}\cdot\text{g}^{-1}$)	1.475	1.236	3.934
R^2	0.945	0.991	0.828
Pseudo-second order kinetics			
k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.174	0.183	0.048
q_e ($\text{mg}\cdot\text{g}^{-1}$)	11.40	11.43	10.48
R^2	>0.999	>0.999	>0.999

150-300 μm . The curve is linear with regression coefficient $R^2 > 0.99$. From the linear curve a rate constant k_1 was determined from the slope and is 0.075 min^{-1} . The first order rate constant, k_1 , is in the same order of magnitude for sorbent size <75 μm and 150-300 μm (see Table 4), but significantly lower in magnitude for sorbent size 300-600 μm . The latter is attributed to reduced external surface area for reaction and at the same time may be due to the increased diffusion path – a species has to travel a longer distance to reach an active site. Apparently, in adsorption, diffusive transport has an effect on the overall kinetics of the process. The nitrate uptake at equilibrium was determined from the intercept and is only $1.236 \text{ mg}\cdot\text{g}^{-1}$. The q_e extracted from the intercept is extremely low and does not match the one used as fitting parameter. Hence the pseudo-first order model is not applicable to the present sorption system.

The linear form of Ho pseudo-second order model, Eq. (6), was tested as a plot of t/q_t versus t and is shown in Fig. 9. From the value of the regression coefficient, $R^2 > 0.99$, it can be concluded that the pseudo-second order model describes the nitrate kinetic data. This observation is in total agreement with that of previous researchers (Öztürk and Bektas, 2004). The calculated values of q_e and k_2 are $11.43 \text{ mg}\cdot\text{g}^{-1}$ and $0.183 (\text{g}\cdot\text{min}^{-1}\cdot\text{mg}^{-1})$, respectively. In this case, the calculated q_e value is almost the same as the experimental value and only marginally decreases with sorbent size. This observation is not surprising as sorption active sites are not normally dependent on sorbent size. As a rule, the pseudo-second order kinetic model describes sufficiently the nitrate adsorption kinetic data. As with the case of pseudo-first order kinetics, the rate constant, k_2 , is in the same order of magnitude for sorbent size <75 μm and 150-300 μm (see Table 4), but is significantly lower in magnitude for sorbent size 300-600 μm .

Application of SMZ to nitrate removal from groundwater

Many rural communities in South Africa use groundwater for drinking purposes. With increased spells of drought leading to water scarcity, groundwater may form a major source of potable water in the near future. However, nitrate concentrations in some of the groundwater sources used for drinking purposes are above the limit of $50 \text{ mg}\cdot\text{l}^{-1}$ (see Fig. 10), the maximum recommended by WHO. In this study, ability of SMZ3 to remove nitrate from environmental water (groundwater) was explored. The water samples were collected from 3 areas, Tshiozwi, Lesodi Motlala and Sekhokho, all in Limpopo Province. The residual nitrate concentration for the 3 water samples as a function of sorbent mass is shown in Fig. 10. First, an increase in sorbent mass resulted in an increased removal of nitrate

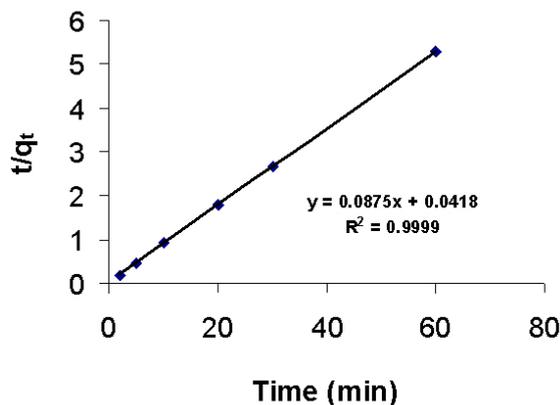


Figure 9
Fit of experimental data according to pseudo-second order kinetic model

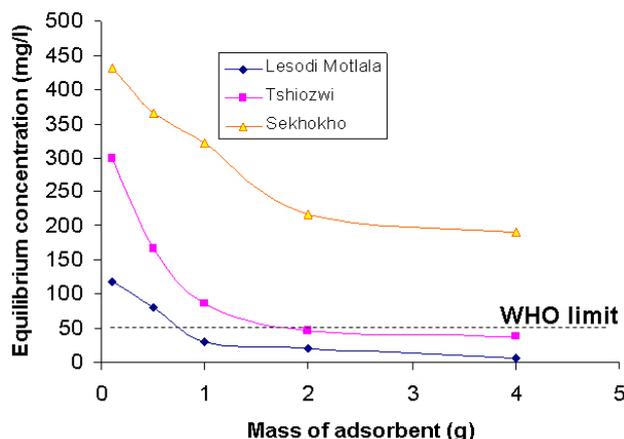


Figure 10
Effect of sorbent mass on nitrate removal from South African groundwater samples

from groundwater samples. This is attributed to increased sorption sites in the media. Second, at sorbent mass above 2 g, the residual concentration of nitrate in Chiozi and Lesodi Mottlala water samples was below $50 \text{ mg}\cdot\text{L}^{-1}$, while the nitrate level in Sekhokho water was still above the maximum allowable concentration (MAC) value. The latter is attributed to the extremely high level of initial concentration. Such high levels of nitrate in water may require combined systems for effective removal.

Conclusions

HDTMA was successfully used to functionalise clinoptilolite and it was demonstrated that the latter is a low-cost and robust media for nitrate removal from water. The functionalised zeolite (SMZ) exhibited a nitrate maximum adsorption capacity of around $11.4 \text{ mg}\cdot\text{g}^{-1}$, which is sufficiently high for this class of natural media. The SMZ can be efficiently used over a wide range of temperature and pH without a significant change in performance. Hence, nitrate-SMZ interaction seems to be physical in nature, probably involving coulombic electrostatic forces. In binary component systems, nitrate sorption was marginally affected by the presence of co-ions. Meanwhile the equilibrium data were satisfactorily described by the Freundlich isotherm while the kinetic data fitted well to the

pseudo-second order kinetic model. Results from application of SMZ to treatment of environmental water suggest that the maximum allowable concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ is achievable even when the initial nitrate concentration exceeds $300 \text{ mg}\cdot\text{L}^{-1}$. With South Africa being a water-stressed society, groundwater use is expected to increase with time. To ameliorate problems related to high levels of nitrate, low-cost technologies will be required. One such technology based on adsorption using SMZ could be appropriate. Further studies will, however, be required to scale-up and optimise process variables.

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