

Synthesis and characterization of hydrophobic zeolite for the treatment of hydrocarbon contaminated ground water

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ABSTRACT

Hydrophobic zeolite was synthesized, modified and characterized for its suitability as a permeable reactive barrier (PRB) material for treatment of hydrocarbons in groundwater. Batch sorption tests were performed along with a number of standard characterization techniques. High and low ionic strength and pH tests were also conducted to determine their impact on hydrocarbon uptake. Further ion exchange tests were conducted to determine the potential for the zeolite to act as both a hydrocarbon capture material and nutrient a delivery system for bioremediation.

The zeolite was coated with octadecyltrichlorosilane (C18) to change its surface properties. The results of the surface characterization tests showed that the underlying zeolite structure was largely unaffected by the coating. TGA measurements showed a reactive carbon content of 1–2%. Hydrocarbon (*o*-xylene and naphthalene) sorption isotherms results compared well with the behaviour of similar materials investigated by other researchers. Ionic strength and pH had little effect on hydrocarbon sorption and the treated zeolite had an ion exchange capacity of 0.3 mequiv./g, indicating it could be utilised as a nutrient source in PRBs. Recycle tests indicated that the zeolite could be used cleaned and reused at least three times without significant reduction in treatment effectiveness.

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1. Introduction

Permeable reactive barriers (PRBs) have been developed and successfully used to treat soil and ground water contaminated by various toxic substances [1,2]. Their use provides a passive in situ approach for treatment of contaminated ground water, over the more energy intensive dig-and-haul techniques. Typically a PRB is located perpendicular to the path of a migrating plume so that the contaminated water flows through the reactive zone. The barrier is filled with reactive materials that result in the capture, treatment or stabilization of the contaminants and a resulting improvement in ground water quality. There are several technologies available for the construction of permeable reactive barriers for ground water remediation [3–5] depending on the contaminant and the nature of the site. One of the largest expenses concerns the purchase, transport and installation of the reactive media. Therefore significant cost savings can be made by the development of materials which can perform multiple roles, such as combining hydrocarbon capture, as well as delivery of nutrients

for the growth of microorganisms responsible for bioremediation.

The aim of this research is to develop materials which will be suitable for capture and biodegradation of hydrocarbons in groundwater. Development and evaluation of new materials for the sorption of fuel-based contaminants is an expanding area for applications in water treatment and PRBs. These materials typically have to fulfil conflicting requirements of being granular enough to enable good hydraulic conductivity, whilst having large enough surface area to offer sufficient sorption sites. The adsorption of hydrocarbons by various media such as soil [6], hydrophobic zeolite [7–9], peat moss [6], humic substances [10], GAC [6,11,12] and polymeric sorbents [13] is well documented. Surface modification of some of these materials to improve adsorption properties has been reported [7,11,13–15].

Zeolite, is typically used for adsorption of cations and is not considered to be suitable for sorption of anions and organics. However, the properties of zeolites can be altered by surface modification. Investigators have looked at the use of natural zeolites and clays modified by cationic surfactants [16,17]. High-molecular-weight quaternary amines such as hexadecyltrimethylammonium (HDTMA) may be sorbed to the zeolite [18]. Whilst natural zeolites have a net negative charge, treatment with a cationic surfactant

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Table 1
Experimental conditions for the Z-C18 synthesis (batches 1–5).

Batch	<i>m</i> (zeolite): <i>V</i> (toluene): <i>m</i> (C18)	Reflux time (h)
1	50.056 g:500 mL:50.0 g	4
2	50.094 g:500 mL:50.032 g	7
3	50.053 g:500 mL:50.085 g	7
4	50.068 g:500 mL:50.014 g	7
5	100.03 g:10,000 mL:100.62 g	7

reduces or reverses that charge. This leads to anions being retained through ion exchange and non-polar organics partitioning to the surfactant coating [18]. This approach to zeolite surface modification has been studied extensively and has been shown to be effective at removal of trace soluble hydrocarbons from groundwater [2,16,19]. In a review of the state of surfactant modified zeolites for groundwater remediation [2] one of the most significant challenges identified was the need to improve the stability of the surface coating from long term leaching effects. Studies by Li and Bowman [16,19] have shown that surfactant modified zeolite surface coatings are affected by low ionic concentration solutions and effects of counter ions. Another approach is to attach a chlorosilane hydrocarbon molecule to the surface of the zeolite in order to make it hydrophobic [20]. Chlorosilanes are reactive chemical compounds that contain up to three non-polar aliphatic or aromatic moieties which can be covalently grafted to the silanol groups on the surface of the zeolite. As described by Huttenloch et al. [20], this forms a much more stable covalent chemical linkage and the risk of the hydrophobic coating being removed by further sorption reactions is significantly reduced.

In this study hydrophobic zeolite was synthesized by covalently bonding a chlorosilane (in this case octadecyltrichlorosilane, or C18) to the surface of the zeolite. The following sections describe the laboratory scale synthesis methodology, as well as the surface and adsorption characterization experiments.

2. Experimental section

2.1. Synthesis of hydrophobic zeolite

The raw zeolite material was a clinoptilolite obtained from St Cloud's Mine, Winston, USA. This was surface coated with octadecyltrichlorosilane (C18). The zeolite was refluxed for 4–7 h with toluene and C18 at a 1:10:1 ratio. Following reflux, the mixture was cooled overnight to room temperature, washed with toluene and methanol, filtered and dried under vacuum at room temperature. Five batches in total were synthesized, with the first three batches being analysed for surface characteristics. Batches 2–5 were also used in all sorption/ion exchange experiments (Table 1).

The amount of C18 that bonded to the zeolite surface was confirmed by various tests, as discussed in Sections 2.2 and 3.1–3.3. These tests showed that functionalisation of the zeolite surface with C18 was successful and that reflux should be conducted at 7 h to optimise surface functionalisation.

2.2. Surface characterization

The modified zeolite was analysed using the following techniques:

- Fourier transform-infrared spectroscopy (FT-IR).
- Thermogravimetric analysis (TGA).
- X-ray diffraction (XRD).

TGA measurements were performed on a TGA/SDTA851 (Mettler Toledo) to determine the carbon content of the zeolite and surface

modified zeolite (Z-C18). The starting temperature was 25 °C and samples were heated up in an oxygen atmosphere to a maximum temperature of 1000 °C with a heating rate of 25 °C/min.

FT-IR spectroscopy was used to determine the reactive functional groups on the surface of the Z-C18. Measurements were conducted with samples of plain zeolite, C18 and Z-C18. The samples were ground to a fine powder before mixing with powdered potassium bromide crystals (Wako Chemicals) in a 0.001 g sample: 0.1 g KBr ratio and pressed into thin discs. These discs were analysed using a Jasco FT/IR-680 Plus spectrophotometer.

X-ray diffraction spectra were obtained for the treated and untreated zeolite on oriented samples using a Rigaku Rint 2200 series diffractometer with monochromatised CuK α radiation at 40 kV and 40 mA.

2.3. Reagents for sorption tests

Unless otherwise stated, reagent-grade chemicals were used and all were used as received without further purification. High purity water for all experiments was provided by a MilliQ purification System (Millipore Corp.). *o*-Xylene (Acros Organics) was chosen as a typical aromatic hydrocarbon and has a water solubility of 175 mg L⁻¹. Naphthalene (Sigma–Aldrich), which has a relatively low solubility in water of 30 mg L⁻¹, was chosen to represent the group of polyaromatic hydrocarbons [20].

2.4. Analysis of dissolved hydrocarbons

Gas chromatography (GC) was used to determine the sorption efficiency of the hydrophobic zeolite for *o*-xylene and naphthalene. The analysis was performed using a HitachiG-6000 Gas Chromatograph with a PorapakQ 80/100 mesh in 3 mm \times 1.0 m glass column and a flame ionization detector. The flow rate was of the carrier gas (H₂) was 30 mm/min. The *o*-xylene or naphthalene was extracted into acetonitrile, with a 1 mg L⁻¹ butoxyethanol internal standard for *o*-xylene and nitrobenzene internal standard for naphthalene. The sample injection volume was 0.2 μ L and the temperature was 90 °C. The GC was calibrated for the measurement of *o*-xylene and naphthalene by testing solutions of each component dissolved in acetonitrile (0–30 mg L⁻¹ *o*-xylene and 0–20 mg L⁻¹ naphthalene). A linear calibration curve was fitted to the mass of hydrocarbon versus the peak area ratio with *R*² values of 0.98 or greater for all components.

For the pH dependence, ionic strength and recycle tests, high performance liquid chromatography (HPLC) was used to determine the concentrations of the solutions before and after the adsorption equilibrium was reached as previously reported [21]. The analysis was performed using a Waters Symmetry[®] C₁₈ 5 μ m, 3.9 mm \times 150 mm column in a HPLC system (Waters Corporation) under the following chromatographic conditions: an acetonitrile (HiPerSolv for HPLC, BDH) and water mixture with a ratio of 60:40 (v/v) and a flow rate of 1 mL min⁻¹ as the mobile phase; room temperature (20 °C); sample injection volume 200 μ L, isocratic elution mode, run time of 10 min for *o*-xylene and naphthalene. Detection was performed at a wavelength of 254 nm.

The HPLC was calibrated for measurement of toluene, *o*-xylene and naphthalene by testing a solution of each component dissolved in acetonitrile (30 mg L⁻¹ *o*-xylene and 20 mg L⁻¹ naphthalene) at sample injection volumes between 20 and 200 μ L. A linear calibration curve was fitted to the mass of hydrocarbon versus the integrated peak area with *R*² values of 0.96 or greater for all components. In order to determine potential loss of sample due to volatilization, five consecutive tests were conducted on samples of known concentration at sample injection volumes of 200 μ L. These were analysed for variation in peak area over time and the change in concentration was found to be less than 1%.

2.5. Batch equilibrium tests

Adsorption isotherms for different components on Z-C18 were obtained via batch equilibrium experiments that were conducted using the hydrocarbon solution with nominal concentrations of 20 mg L⁻¹ for naphthalene and 30 mg L⁻¹ for o-xylene. These experiments were performed at 20 °C using different masses of Z-C18 (0.3–6 g) placed in centrifuge tubes. 50 mL of the organic component dissolved in water was added to the tube. One sample was prepared without any sorbent to accurately determine the initial concentration of the solution and account for any losses due to the volatility of the hydrocarbons. The tubes were sealed with Teflon lined septa and shaken for 24 h at 120 rpm on a Ratek platform mixer. Kinetic experiments were performed to confirm that 24 h was sufficient for equilibrium to be achieved in the samples. The samples were then centrifuged for 5 min in a Beckman GS-15R centrifuge at 3000 rpm. For the GC experiments; the aqueous samples from the batch equilibrium tests were extracted into acetonitrile, then run through the GC as described in Section 2.4. For the further pH dependence and ionic strength experiments, 4 mL aliquots were taken of each sample and tested using HPLC as discussed in Section 2.4.

2.6. Effect of ionic strength and pH on sorption stability

To determine whether the sorption would vary for Z-C18 under conditions of high ionic strength and pH extremes, more batch equilibrium tests were conducted. For analysing the effect of ionic strength on hydrocarbon removal, triplicate samples containing 3 g of Z-C18 were prepared. These were contacted with o-xylene and naphthalene solutions containing 1.0 M CaCl₂ (calcium chloride dried, Ajax Finechem). The samples were prepared and analysed as described in Section 2.5.

For the pH tests, the Z-C18 was contacted with o-xylene and naphthalene solutions at pH 3 and 10. The low pH was obtained by adding 0.1 M hydrochloric acid drop-wise to the stock solution and the high pH obtained by adding 0.1 M sodium hydroxide solution. pH values were measured using an Activon CyberScan 500 pH-meter.

2.7. Ion exchange experiments

The aim of the ion exchange experiments was to determine whether the Z-C18 had any ion exchange potential and so could be loaded with a nutrient source such as ammonium ions. For the ion exchange capacity and isotherms the hydrophobic zeolite was first conditioned by contacting 30 g of Z-C18 with 500 mL of 2 M ammonium chloride solution for 72 h. The ammonium chloride solution was replaced twice during this period. The zeolite was then washed with distilled water to remove excess ammonium chloride, filtered and dried overnight in an oven at 40 °C.

For the ion exchange equilibrium isotherms, 0.5–6 g of ammonium loaded zeolite was contacted with 100 mL KCl solution (0.05 and 1 M) for 72 h. The aqueous phase was separated by filtration using disposable syringes fitted with a 0.45 μm filter. The concentration of ammonium ions in the aqueous phase was measured using a Cary IE UV-vis spectrophotometer. The UV-vis apparatus was pre-calibrated by measuring a number of ammonium chloride solutions of known concentration (0–40 mg/L), with the data fitted with a linear calibration curve with R² value of 0.99.

2.8. Recycle test

The aim of the recycle tests was to determine whether the material could be used multiple times without significant reduction in hydrocarbon sorption efficiency. The tests were performed by con-

Table 2

Results of TGA experiments, mass loss and f_{OC} .

Sample	Mass loss (%)	f_{OC}^a
Untreated zeolite	10.14	–
Z-C18 batch 1	11.13	0.0099
Z-C18 batch 2	11.88	0.017

^a f_{OC} (fraction of organic carbon) is equivalent to mg C18/mg Z-C18. Hence a f_{OC} of 0.0099 means the C18 comprises 1 wt% of the Z-C18.

tacting a fresh sample of hydrophobic zeolite (15 g) with 40 mL of pure o-xylene for 20 min. A portion of the sample was then washed in distilled water, to remove excess o-xylene and filtered. The o-xylene was then removed by drying in a vacuum oven at 60 °C for 24 h. A second portion of the sample was washed in distilled water, followed by methanol and then distilled water again. This sample was also dried for 24 h. The regenerated Z-C18 was then used in an o-xylene sorption test, as described in Section 2.5. The o-xylene sorption results were compared for the two regeneration methods. The Z-C18 was regenerated and the o-xylene sorption tests repeated three times in total.

3. Results and discussion

3.1. Thermogravimetric analysis

The results of the TGA (Table 2) indicate that a similar amount of material from the untreated zeolite and Z-C18 was lost upon heating, most of which can be attributed to water evaporating from the zeolite structure. Ouki and Kavannah [22] found that for clinoptilolite the average weight reduction due to water loss upon heating to high temperatures is approximately 10%, which is confirmed by the results in Table 2. The fractional organic carbon contents f_{OC} can be found by

$$f_{OC} = \frac{M_{OC}}{M_{Total}} \quad (1)$$

where M_{OC} is the difference between the initial and final mass of the zeolite during the TGA test (i.e. mass of carbon burned off the surface of the zeolite) and M_{Total} is total mass of sorbent material. f_{OC} was calculated for Z-C18 batches 1 and 2 and is shown in Table 2. As untreated zeolite does not contain carbonaceous components, no value for f_{OC} was determined.

The TGA results indicate an increase of approximately 1% and 1.7% of the total weight loss at 1000 °C for batches 1 and 2 respectively following surface modification. This is an indication of the presence of C18 in the treated samples and the higher wt% (mg C18/mg surface modified zeolite) of C18 in batch 2 is consistent with a longer reflux time, suggesting that surface modification may be significantly improved by increasing the reflux period. The difference in wt% also suggested that hydrocarbon sorption would likely be higher for batches 2–5 and hence all batch sorption tests were carried out on samples prepared using a 7 h reflux time.

3.2. XRD analysis

The XRD spectrum for untreated clinoptilolite and Z-C18 is shown in Fig. 1. Comparison with a typical XRD spectrum [23] for clinoptilolite-rich zeolites suggests that the clinoptilolite structure is undisrupted with surface modification. The batch 1 spectrum has two new peaks which appear at 20.8 and 42.6, whereas these are not present in the spectrum for batch 2. This may be an indication of a partial or incomplete reaction of the C18 with the surface of the zeolite due to the shorter reflux time for batch 1.

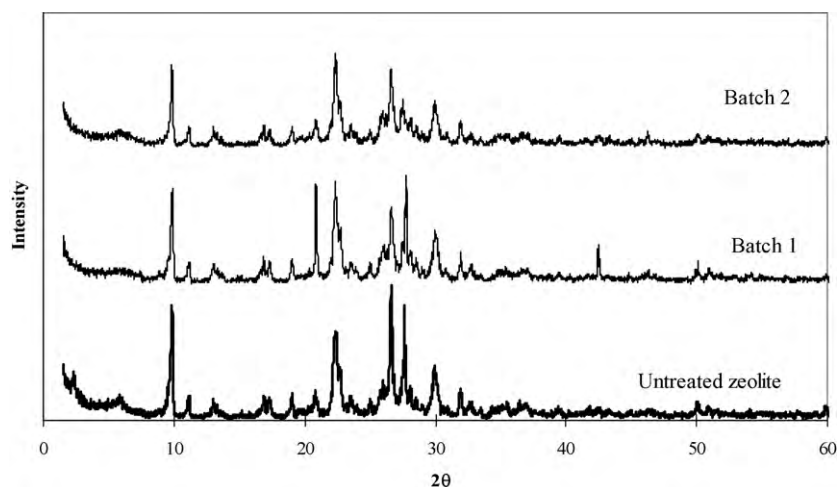


Fig. 1. XRD spectra of clinoptilolite and Z-C18 (batches 1 and 2).

3.3. FT-IR analysis

Comparison of the FT-IR spectrum of untreated zeolite, C18 and Z-C18 indicate the presence of C18 in the treated sample. Characteristic peaks at 2855 and 2930 cm^{-1} can be seen in both C18 and Z-C18 (Fig. 2). Such peaks for the untreated zeolite in the range of 400–1800 cm^{-1} also indicate that the structure of the zeolite following treatment is intact. An FT-IR study of HDTMA

modified zeolite by Majdan et al. [24] showed that characteristic peaks for zeolite in the range 400–1200 cm^{-1} represent the aluminium–silicon tetragonal bond arrangement, whilst peaks in the 1640–1650 and 3000–4000 cm^{-1} range result from the deformation and stretching vibrations of water molecules. These peaks can be clearly identified in the unmodified zeolite sample seen in Fig. 2. Majdan et al. [24] also identified the characteristics peaks for the surfactant both in pure form and on the surface of the zeolite

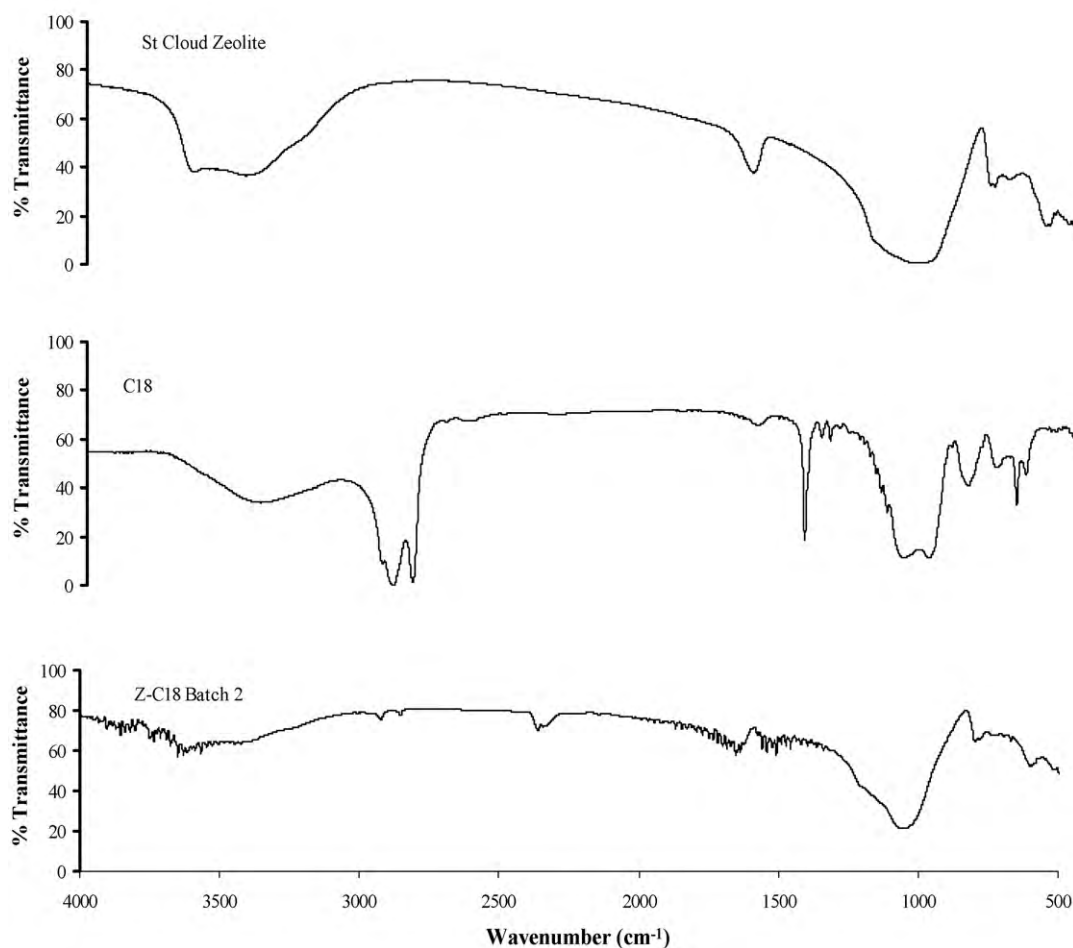


Fig. 2. FT-IR spectra of untreated zeolite, C18 and Z-C18.

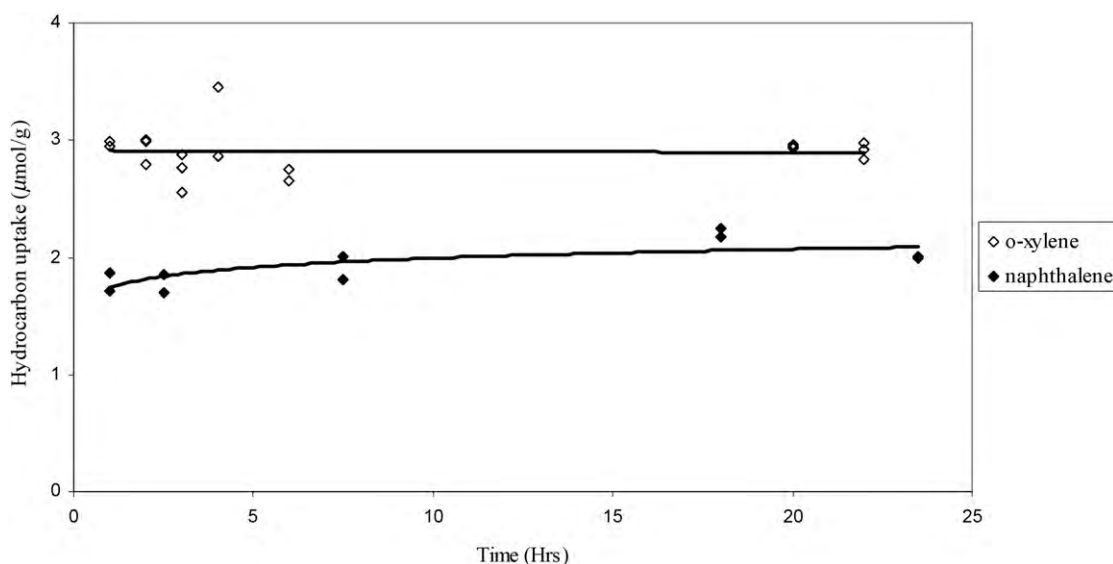


Fig. 3. Kinetic tests for o-xylene and naphthalene uptake onto Z-C18. 20 mg L⁻¹ naphthalene and 30 mg L⁻¹ o-xylene. Experiments at 20 °C with 0.3–6 g of Z-C18 and 50 mL of the organic component dissolved in water.

at 2853 and 2921 cm⁻¹, which are almost identical to the identified peaks in this study. A study by Li and Gallus [25], of HDTMA modified kaolinite also indicated the characteristic peaks for the surfactant were most evident at 2850 and 2920 cm⁻¹. FT-IR measurements conducted on batches 1–3 indicated similar results.

3.4. Adsorption behaviour of sorbent materials

Kinetic tests were conducted on the sorption of o-xylene using 2.5 g samples of Z-C18. Samples were shaken at room temperature between 2 and 24 h prior to measurement by gas chromatography. Results were varied, showing no significant trends in the sorption kinetics over time (Fig. 3) and indicating that the time to achieve equilibrium for the o-xylene system is relatively quick. Further kinetic tests were conducted for naphthalene sorption, with 1.5 g samples of Z-C18. The amount of naphthalene sorbed over a 24-h period is shown in Fig. 3, which indicates that the majority of naphthalene adsorption occurs in the first 8 h.

Whilst both Langmuir and Freundlich isotherms are commonly used to describe the behaviour of many sorption systems [18,20], linear isotherms are often observed for hydrocarbon sorption at low concentration levels [20]. This implies that sorption is not dependent on the initial hydrocarbon concentration of the aqueous solutions. The linear sorption behaviour may be described by the equation

$$C_S = K_d \cdot C_W \quad (2)$$

where C_S (moles adsorbate/mass sorbent) and C_W (moles/volume) stand for the equilibrium surface and solution concentration respectively and K_d (L g⁻¹) is the distribution coefficient. The distribution coefficient is often normalized by the sorbent's fractional organic carbon content f_{OC} to reflect the dominant influence of the surface coating on the sorption of organic solutes. The resulting parameter K_{OC} is the organic carbon-based partition coefficient [26]:

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (3)$$

The adsorption isotherms of o-xylene and naphthalene onto Z-C18 at 20 °C (Fig. 4) indicate that adsorption for naphthalene is more favourable than that of o-xylene. This result is in agreement with a study by Huttenloch et al. [20] that investigated naphthalene

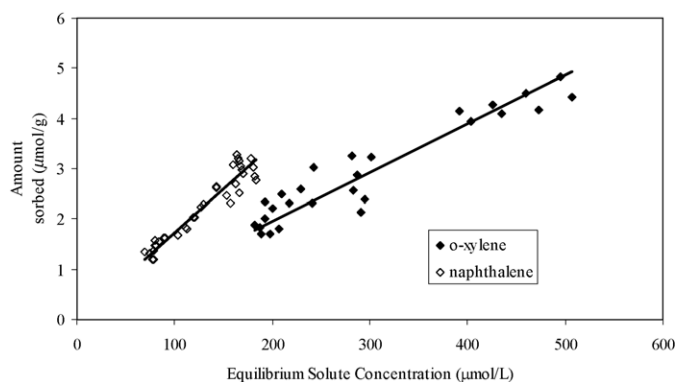


Fig. 4. Adsorption isotherms of o-xylene and naphthalene onto Z-C18. 20 mg L⁻¹ naphthalene and 30 mg L⁻¹ o-xylene. Experiments at 20 °C with 0.3–6 g of Z-C18 and 50 mL of the organic component dissolved in water.

and o-xylene uptake onto a clinoptilolite surface modified with dimethyloctadecylchlorosilane. The isotherms for adsorption onto Z-C18 can be well described by linear adsorption behaviour. Table 3 summarizes the resulting values for K_d , K_{OC} and $\log K_{OC}$ for the adsorption of naphthalene and o-xylene on Z-C18 (f_{OC} from batch 2 has been used for calculations, see Table 2), as well as comparative values with a study conducted by Hornig et al. [21] on hydrocarbon sorption onto surfactant modified zeolite (SMZ). The K_{OC} values indicate that the Z-C18 has a good affinity for hydrocarbons. However, the HDTMA surface modified zeolite investigated by Li et al. [17] has a higher affinity for hydrocarbon sorption than Z-C18. The benefit of Z-C18 over HDTMA coatings is the chlorosilane that is covalently bonded and hence less likely to be leached off from the surface of the zeolite [27].

Table 3

Distribution coefficients, K_d , organic carbon-based partition coefficients, K_{OC} (L kg⁻¹), for sorption of naphthalene, o-xylene and toluene on SMZ.

Hydrocarbon	Z-C18				SMZ [7]
	K_d	K_{OC}	$\log K_{OC}$	R^2	$\log K_{OC}$
Naphthalene	17.3	1018	3.0	0.92	4.3
o-Xylene	9.7	571	2.8	0.89	3.5

Table 4
o-Xylene and naphthalene sorbed ($\mu\text{mol g}^{-1}$) onto Z-C18 under high and low ionic strength as a function of pH.

Hydrocarbon	0 M CaCl ₂ No pH control ($\mu\text{mol/g}$)	1 M CaCl ₂ ($\mu\text{mol/g}$)	Reduced performance (%)	pH 3 ($\mu\text{mol/g}$)	Reduced performance (%)	pH 10 ($\mu\text{mol/g}$)	Reduced performance (%)
o-Xylene	1.62 (0.03)	1.07 (0.26)	34	1.52 (0.09)	6	1.02 (0.05)	37
Naphthalene	1.69 (0.06)	1.70 (0.02)	0	1.42 (0.02)	16	1.41 (0.00)	16

Numbers in brackets are the standard deviation for three samples tested.

3.5. Effect of ionic strength and pH extremes

The Z-C18 showed only minor changes in the naphthalene sorption behaviour when exposed to extremes in pH and ionic strength (Table 4). The sorption of o-xylene was affected by high ionic strength and high pH, with a reduction in performance of up to 34% when exposed to a solution of 1 M CaCO₃ and reduced performance of up to 37% at pH 10. The results showed better naphthalene uptake at high ionic strength than that for o-xylene. Similarly naphthalene uptake was less affected by high pH, however low pH did not affect sorption of either hydrocarbon to any great extent.

3.6. Ion exchange tests

A typical nutrient delivery system used for PRBs is to load an ion exchange material with ammonium ions, which are then released into the PRB via exchange with a dissolved ion such as potassium [28]. In this investigation, the ion exchange capacity of the Z-C18 for the ammonium-potassium system was found to be 0.3 mequiv./g (Fig. 5). The capacity for this same system using untreated zeolite is about 0.8 mequiv./g [28]. Hence after treatment Z-C18 has retained some ion exchange capacity for ammonium ions making it possible for this material to also be utilised for nutrient delivery.

3.7. Recycle tests

The results for the recycle tests for o-xylene uptake onto regenerated Z-C18 are shown in Table 5. The results for hydrocarbon uptake for two methods of regeneration (washed in MilliQ water only and methanol followed by a MilliQ wash) were compared with an unused sample of Z-C18 in each case. For the first regeneration test, there is a significant difference between the fresh Z-18 sample and the regenerated samples, indicating that the regeneration was possibly incomplete. For runs 2 and 3, the regeneration process appeared more successful, with the o-xylene uptake only slightly

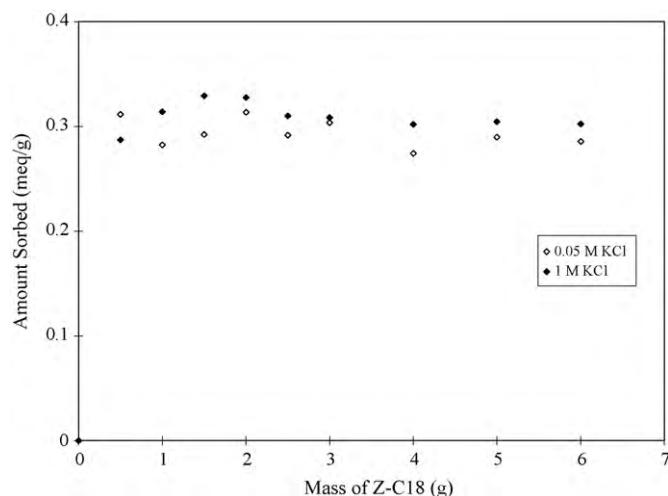


Fig. 5. Ion exchange capacity for the NH₄-K system on Z-C18.

Table 5
Recycle test for o-xylene uptake onto Z-C18.

Sample	Sorption (mg L^{-1})		
	Run 1	Run 2	Run 3
Z-C18, unused	16.07	14.31	14.54
Z-C18, MilliQ water wash and oven dry	9.36	13.84	13.85
Z-C18, MilliQ water and methanol wash, and oven dry	10.10	14.54	14.63

less for the MilliQ water wash regenerated sample compared to the unused methanol/MilliQ regenerated samples. Hence the Z-C18 has the potential to be used and regenerated at least three times with no discernable reduction in performance.

4. Conclusions

Surface characterization of covalently bonded C18 onto the surface of a clinoptilolite-rich zeolite showed that it was possible to get a good surface coating of around 2% with no change to the underlying zeolite structure. From the results of hydrocarbon sorption tests it is clear that Z-C18 has capacity for removal of dissolved phase xylene and naphthalene from water. Isotherms showed linear sorption behaviour over the concentration ranges investigated. Stability tests showed that hydrocarbon removal from water is not significantly affected by extremes in pH and ionic strength. It was found that the Z-C18 can be successfully regenerated and reused for hydrocarbon sorption at least three times.

In addition to the hydrocarbon capture it is possible to utilise at least some of the natural ion exchange capability of the zeolite for exchange of ammonium ions as part of a PRB nutrient delivery system for bioremediation. In this investigation it was found that the Z-C18 retained an ion exchange capacity of 0.3 mequiv./g for the K-NH₄ system.

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