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Predictions of nitrate diffusion in sediment using horizontal attenuated total reflection (HATR) by Fourier transform infrared (FTIR) spectrometry

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ABSTRACT

Using a novel and simple method based on horizontal attenuated total reflection (HATR) by Fourier transform infrared (FTIR) spectrometry, the effective diffusion coefficient, D_e , of nitrate in a contaminated anthropogenic sediment was estimated as $7.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This method, which requires as little as 1 mL of sediment sample, was able to measure the D_e of a chemical species with a reproducibility of $\pm 3\%$ in about 5 h. Based on this D_e and a pre-determined nitrate reduction rate, the profiles of nitrate concentration in two sediment columns were satisfactorily predicted from a mathematical model. Results showed that the profile in this aged sediment depended mainly on the diffusion of nitrate and, only to a much lesser degree, the rate of nitrate reduction. Measurements in 55 anthropogenic sediment samples collected from five locations and various depths of a contaminated site further showed that the D_e of nitrate increased linearly with the water content of the sediment, but decreased with the sediment density. The technique demonstrated in this study shall be applicable for the risk assessment of toxic pollutants in contaminated sediments, and for planning the spatial and time intervals of nitrate injection strategy in bioremediation.

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1. Introduction

Recalcitrant water pollutants ultimately settle in sediments, posing a potential threat to the environment. Remediation of the contaminated sediment has thus attracted much concern and interest (Murphy et al., 1999). Although most treatments are conducted *ex situ*, *in situ* processes, especially enhanced intrinsic bioremediation, have become increasingly popular. This technology involves supplementing the sediment with electron acceptors in order to stimulate biodegradation of contaminants by naturally occurring microorganisms. Nitrate has often been added as the terminal electron acceptor in

in situ bioremediation sites contaminated with BTEX (benzene, toluene, ethylbenzene, and xylenes) or polycyclic aromatic hydrocarbons (PAHs) (MacRae and Hall, 1998). The effectiveness of this process depends to a large degree on the diffusion of nitrate, which determines the required nitrate dosage as well as the spatial and time intervals of injections. Thus, the effective diffusion coefficient, D_e , of nitrate in the sediment is a crucial parameter for the planning and execution of nitrate injections in bioremediation.

Traditionally, D_e of a chemical is calculated from its concentration profile at various distances from the injection point several days, or weeks, after the diffusion started. It is

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typically determined by the so-called reservoir (Keneth et al., 1991), half-cell (Krom and Berner, 1980), and radial cell methods (Li and Gregory, 1974). For the reservoir method, a column of sediment is placed underneath a reservoir of water containing a given concentration of target chemical species. After a certain time interval, the concentration profile of the chemical in the sediment column is measured and the D_e is calculated based on the diffusion equation (Krom and Berner, 1980). For the half-cell method, two half-cells are separated by a porous barrier—one contains the sediment as is, and the other contains the sediment dosed with a given concentration of the chemical species. Again, the D_e is calculated from the concentration profile in the first half-cell after a certain time interval. For the radial cell method, a similar methodology was applied for diffusion in the radial direction.

All of these methods are not only time-consuming but also require a relatively large amount of sediment and special setups to conduct the diffusion tests. Consequently, D_e in sediment is, instead of being measured from the concentration profile using these methods, often adjusted from the D_e in pure water taking into account the sediment structure or tortuosity (Ullman and Aller, 1982; Iversen and Jørgensen, 1993). The precision of such estimations is often less than satisfactory (Murphy et al., 1999). A simple method for the measurement of D_e in sediment is thus warranted.

It has been recently demonstrated that the D_e of a chemical species can be estimated using horizontal attenuated total reflection (HATR) by Fourier transform infrared (FTIR) spectroscopy for media such as biofilms (Zhang and Fang, 2005) and polymer films (Elabd et al., 2000). In this study, simple bench experiments were conducted to estimate the D_e of nitrate in an aged anthropogenic sediment using this novel method, as well as the kinetic parameter of nitrate reduction. The estimated D_e and kinetic parameter of nitrate reduction were used to predict nitrate profiles that were subsequently compared with the actual measurements in two columns of sediment. The success of such applications implies that the technique shall be valuable in bioremediation and in estimating the diffusion of toxic contaminants in sediment.

2. Materials and method

2.1. Sediment and seawater

In this study, five cores (75 mm diameter) of anthropogenic sediment under 5–6 m of seawater were collected at five sites along the Kai Tak Approach Channel (200 m × 1500 m) of the Victoria Harbor in Hong Kong. For over five decades, municipal sewage and industrial (mainly electroplating) effluent were discharged to this channel. Such practice had been discontinued in the past 8–10 years due to the installation of a new sewage collection system intercepting the discharges. The anthropogenic sediment with a depth of 4–6 m contained organic residues of biodegradation. Sediment in each core was sliced into 250 mm sections for characterization. Those collected from the top 3 m below the interface with seawater were homogeneous with a

toothpaste texture. Some samples collected below 3 m contained sand, rock chips, and shells, all of which, if found, were manually removed prior to the characterization and diffusion tests. The chemical oxygen demand (COD) of sediment samples was measured according to the Standard Methods (APHA, 2001). Water content of each sediment sample was measured from the weight loss in drying at 105 °C to the dry weight of the sample. Seawater filtered through a 0.45 μm membrane (Gelman Science, Ann Arbor, MI) was used to prepare the nitrate solution and the agarose (Sigma-Aldrich) solution. Nitrate concentrations were measured using an ion chromatograph (CDD-6A, Shimadzu, Japan). The seawater had a pH of 8.0 and a nitrate concentration below the detection limit of 1 mgL⁻¹.

A series of bench experiments was conducted to determine the D_e of nitrate in 55 sediment samples, which were collected from various depth levels at five sampling sites in the Kai Tak Approach Channel, to determine the kinetic parameter of nitrate reduction for each sample. Two additional experiments were conducted to measure the nitrate profiles in two columns packed with a selected sediment sample. The nitrate profiles in the columns were then compared with those predicted based on the determined D_e and kinetic parameters.

2.2. Determination of diffusion coefficients by HATR-FTIR

The principle of HATR-FTIR has been described previously (Zhang and Fang, 2005). Based on this method, a 3.23 mm film of sediment was coated on an internal reflection element (IRE) and then covered by seawater containing 50.5 gL⁻¹ potassium nitrate. An infrared (IR) beam entered from one end of the IRE at an angle, reflected within the IRE and exited from the other end. While traveling through the IRE, a fraction of the incident IR was absorbed by nitrate in the sediment at the IRE interface. The nitrate concentration at the interface was measured from the absorbance at 1352 cm⁻¹, the frequency specific to nitrate, based on a pre-established standard curve.

Since the duration of such measurements was normally less than 5 h, the bioactivity of nitrate reduction in the aged sediment sample which contained only biodegradation residues was negligible. The nitrate concentration at the IRE interface was thus strictly dependent on molecular diffusion following Fick's law. As a result, the ratio of the nitrate concentrations at the IRE interface and in the bulk solution is dependent on a dimensionless parameter α , which is defined as

$$\alpha = \frac{tD_e}{L^2}, \quad (1)$$

where t is the diffusion time and L the thickness of sediment coated on the IRE surface. From the concentration of nitrate at the IRE interface, α may be obtained from an established equation using the Microsoft Office Excel 2003 software by trial and error (Zhang and Fang, 2005; Stewart et al., 2000). For a given film thickness, the D_e value may be calculated from the slope of the plot of α vs t . All the diffusion experiments were conducted at 25 °C.

2.3. Determination of nitrate reduction kinetics

A series of bench experiments were conducted in duplicate at 25 °C to evaluate the nitrate reduction kinetics of the sediment. In each experiment, 5 g (dry weight) of sediment sample was mixed with 100 mL of nitrate solution of either 2500 or 1250 mgL⁻¹, in a 150 mL serum bottle. After purging with helium, each bottle was placed on a shaker table for incubation at ambient temperature. Nitrate concentration in bulk solution of each bottle was measured in duplicate over time by an ion chromatograph. The kinetics of nitrate reduction was then analyzed based on the time profile of nitrate concentration.

2.4. Concentration profile of nitrate in sediment columns

Experiments of nitrate diffusion were conducted in two sediment columns over 20 days at 25 °C. The sediment was packed in polyethylene tubes (2.9 cm ID and 50 cm in length) to the depth of 28 cm each. In one tube, the sediment was pre-sterilized in an autoclave for 30 min at 121 °C in order to ensure the absence of bioactivity during the test so that the nitrate profile depended strictly on molecular diffusion only. In the other column, the sediment was used unchanged, in which case the nitrate profile depended not just on diffusion but on nitrate reduction as well. In each experiment, the sediment was overlaid with 15 cm of seawater solution, which contained 88 gL⁻¹ of potassium nitrate, and was replenished daily. After 20 days, the sediment column was frozen at -20 °C and sliced into segments of 0.50–0.95 cm length. The sediment sections were then thawed and centrifuged at 4000 rpm (Centrifuge 5810R, Eppendorf, Germany). The nitrate concentration in the supernatant was measured by an ion chromatograph, and the resulting measured nitrate concentration profile was compared with the predicted profile based on the measured D_e and kinetic parameters.

3. Results and discussions

3.1. D_e of nitrate in agarose gel

Although the validity of D_e estimation of HATR-FTIR has been demonstrated so far against molecular species, such as glucose (Zhang and Fang, 2005) and acetonitrile (Elabd et al., 2000), it was uncertain whether the same methodology is applicable to the estimation of D_e for an ionic species, such as nitrate. In order to confirm the validity of the HATR-FTIR method for nitrate, three diffusion tests were first conducted in agarose (1% by weight) films (Zhang and Fang, 2005). The films were prepared by dissolving agarose in boiling seawater with gentle mixing for 10–15 min. The mixed solution was then decanted on IRE surface to form a film with a thickness of 3.23 ± 0.03 mm. After 60 min of solidification, the film was covered with 50 mL of 50.5 mgL⁻¹ potassium nitrate solution. The nitrate concentration at the IRE interface was monitored, based on the IR absorbance, over time.

Fig. 1 shows that α increased linearly with time, as expected from Eq. (1). From the slopes and the agarose film thickness, the D_e of nitrate in 1% (weight) agarose was calculated.

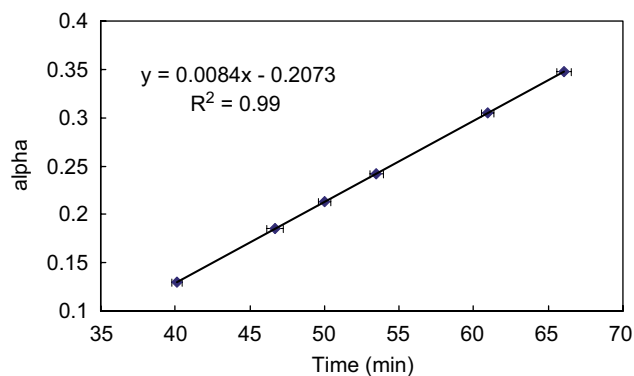


Fig. 1 – Variations of α as a function of time for three diffusion tests of nitrate in agarose film.

According to the three separated tests, the D_e of nitrate was estimated as $14.6 \pm 0.31 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is 14.3% less than the $17.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ of D_e in seawater (Westrin and Axelsson, 1991). The reduction of D_e of nitrate in agarose was similar to those of other chemicals, such as fluorescein (14%) (Wolfaardt et al., 1993) and glucose (10.7%) (Zhang and Fang, 2005).

3.2. D_e of nitrate in sediments by HATR-FTIR

In HATR-FTIR diffusion tests of nitrate, the nitrate absorbance at the sediment-IRE interface increased with time and gradually leveled off to about 60–80% of the absorbance of nitrate in the bulk solution, depending on the sediment. This was due to the fact that only a fraction of the IRE interface was covered by the pore water in the sediment. The remaining fraction of the interface was covered by particulates in the sediment, resulting in a reduction of IR absorption. Thus, a normalization factor was determined for each sediment sample in order to accurately measure the nitrate concentration at the IRE interface. The reproducibility of D_e measurement by this method was $\pm 3\%$, based on data of HATR-FTIR diffusion tests of seven sediment samples.

3.3. Mathematical model for nitrate diffusion

With a zero-order nitrate reduction, the diffusion model of nitrate may be described by the following differential equation:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - k \quad (2)$$

with the conditions of $C = 0$ at $t = 0$, and $C = C_0$ at $x = 0$, where C represents the nitrate concentration, t the diffusion time, x the diffusion distance, and k the rate constant of nitrate reduction. For the sterilized sediment, k equals zero because of the absence of nitrate-reducing activity. By letting $C = W - kt$ and $t^* = tD_e$, the above partial differential equation and conditions become

$$\frac{\partial W}{\partial t^*} = \frac{\partial^2 W}{\partial x^2} \quad (3)$$

with the conditions of $W = 0$ at $t^* = 0$, and $W = C_0 + kt^*/D_e$ at $x = 0$.

The solution for the above equation and conditions is as follows:

$$C(x, t) = (C_0 + kt) \frac{x}{\sqrt{4\pi D_e}} \int_0^t \frac{e^{(-x^2/4\tau D_e)}}{\tau^{3/2}} d\tau - k \frac{x}{\sqrt{4\pi D_e}} \int_0^t \frac{\tau e^{(-x^2/4\tau D_e)}}{\tau^{3/2}} d\tau - kt, \quad (4)$$

which may also be expressed as

$$C(x, t) = (C_0 + kt) \frac{2}{\sqrt{\pi}} \int_{x/\sqrt{4tD_e}}^{\infty} e^{-\eta^2} d\eta - \frac{k}{4D_e} \frac{2}{\sqrt{\pi}} \int_{x/\sqrt{4tD_e}}^{\infty} \left(\frac{x}{\eta}\right)^2 e^{-\eta^2} d\eta - kt. \quad (5)$$

The nitrate profile in the sediment column depended on molecular diffusion (D_e) as well as the rate constant of nitrate reduction (k). From this equation, the nitrate profile in the sediment column at any given time may be predicted. For recalcitrant contaminants, the degradation rates of which are negligible as compared with molecular diffusion, Eq. (4) or (5) may be simplified, assuming $k = 0$, as

$$C(x, t) = C_0 \frac{x}{\sqrt{4\pi D_e}} \int_0^t \frac{e^{(-x^2/4\tau D_e)}}{\tau^{3/2}} d\tau \quad (6)$$

or

$$C(x, t) = C_0 \operatorname{erfc}\left(\frac{x}{\sqrt{4tD_e}}\right). \quad (7)$$

3.4. Rate of nitrate reduction

Tests of nitrate reduction were conducted for a selected sediment for two initial nitrate concentrations for over 5 days. Results in Fig. 2 illustrate that the nitrate concentration decreased linearly over time for nitrate concentrations ranging from 300 to 2600 mg L⁻¹. The linearity shows that nitrate reduction in the sediment was of zero order, the slope being rate constant. The average rate, as illustrated in Fig. 2, was 2.25×10^{-3} mg L⁻¹ s⁻¹, independent of nitrate concentration in the sediment. This implies that nitrate reduction of the tested sediment had a low half-rate constant of the Monod equation (Monod, 1949), as compared with the concentration of nitrate (ranging 300–2600 mg L⁻¹) in the sediment.

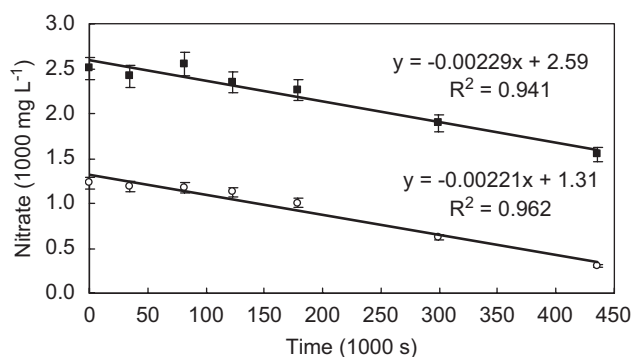


Fig. 2 – Decrease in nitrate concentrations over time in a sediment mixed with a 2600 mg L⁻¹ (squares) and a 1250 mg L⁻¹ (circles) nitrate solution.

3.5. Comparison of measured and predicted nitrate profiles in sediment columns

To determine whether the nitrate-reducing activity had any effect on D_e measurement, two HATR-FTIR tests were conducted in parallel for a given sediment sample: one using the sediment as-is and the other after sterilization by autoclaving. Results of two D_e measurements showed a deviation of less than 1.5%, suggesting that the effect was insignificant.

Diffusion tests of nitrate were then conducted in two columns: one packed with the as-is sediment sample and the other packed with the same sample after autoclave sterilization. The D_e of nitrate in this sterilized sediment was measured as 7.34×10^{-6} cm² s⁻¹ by HATR-FTIR. The nitrate profile in the column of sterilized sediment was presumably governed by molecular diffusion alone, whereas the profile in the as-is column was affected by diffusion as well as nitrate reduction. The profiles of nitrate concentration are compared with the calculated profiles in columns packed with sterilized sediment (Fig. 3a) and as-is sediment (Fig. 3b), using the D_e value (7.34×10^{-6} cm² s⁻¹) estimated from HATR-FTIR.

Results in Fig. 3a show that the D_e value of 7.34×10^{-6} cm² s⁻¹ estimated from the HATR-FTIR is satisfactory to predict the molecular diffusion of nitrate in sediment in the absence of nitrate reduction. The best-fit D_e for the measured nitrate profile was 7.76×10^{-6} cm² s⁻¹, which is only 5% higher than the one estimated by HATR-FTIR.

Fig. 3b compares the measured nitrate profile in the as-is sediment column, and three predicted profiles: one assuming

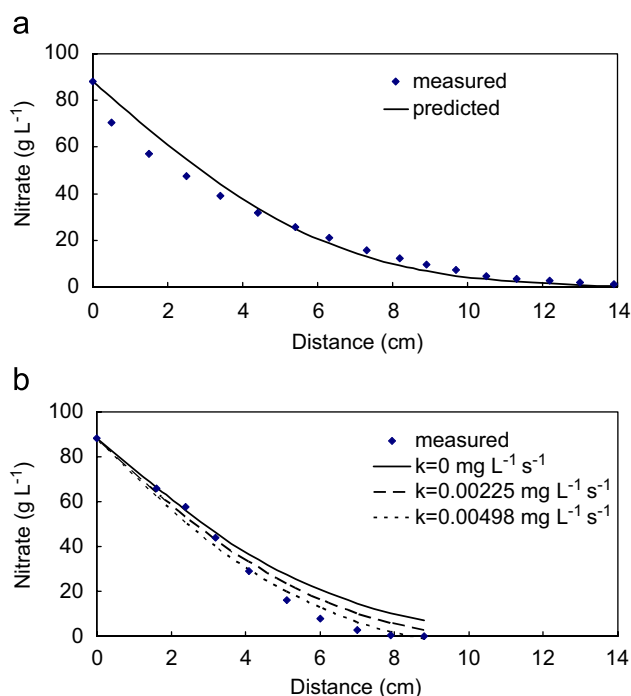


Fig. 3 – Measured (symbols) and predicted (lines) nitrate concentration profiles after 20 days in laboratory sediment columns: (a) sterilized sediment and (b) as-is sediment.

without nitrate reducing activity (i.e. $k = 0$), the other assuming the rate of nitrate reduction being the same as in the serum bottle tests ($k = 2.25 \times 10^{-3} \text{mgL}^{-1} \text{s}^{-1}$), and the last using the best-fit rate constant of nitrate reduction ($k = 4.98 \times 10^{-3} \text{mgL}^{-1} \text{s}^{-1}$). The D_e of $7.34 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ estimated from HATR-FTIR was used for all predicted profiles.

Fig. 3b shows that the nitrate profile based on the pre-determined D_e and k values matches the measurements very satisfactorily. The profile may be better matched by using the pre-determined D_e and a best-fit k of $4.98 \times 10^{-3} \text{mgL}^{-1} \text{s}^{-1}$. This suggests that the rate of nitrate reduction was underestimated from the serum bottle tests, probably due to their lower biomass concentrations. On the other hand, Fig. 3b also shows that the profile assuming negligible nitrate-reducing activity deviates only slightly more from the measurements. This indicates that the nitrate concentration profile in the sediment depended mainly on molecular diffusion, and was affected by nitrate reduction activity only to a much lesser degree.

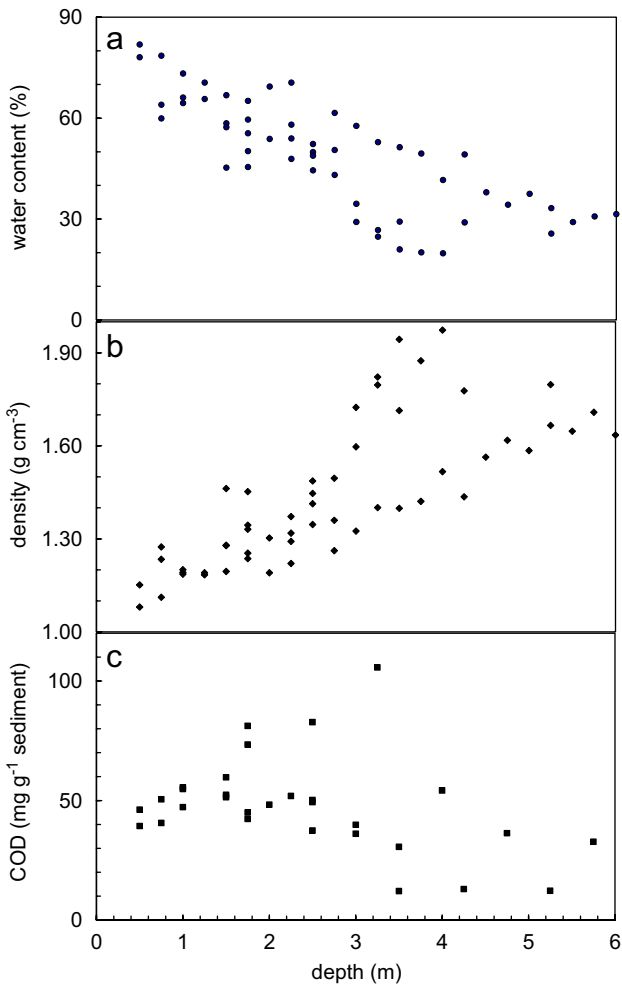


Fig. 4 – Variation of sediment characteristics with the depth level: (a) water content, (b) density, and (c) chemical oxygen demand.

3.6. Effect of sediment water content and density on D_e

The D_e of nitrate in 55 anthropogenic sediment samples collected at various depths (up to 6 m) of the five sites along a contaminated marine channel were measured using the HATR-FTIR method. Fig. 4 illustrates that in general (a) the water content in sediment (20–81%) decreased with depth, (b) density ($1.1\text{--}2.0 \text{g mL}^{-1}$) increased with depth, and (c) chemical oxygen demand ($11\text{--}106 \text{mg g}^{-1}$) slightly decreased with depth. Fig. 5 illustrates that the D_e of nitrate increased linearly with the water content of the sediment, but decreased with the sediment density. This is in agreement with a previous study (Sweerts et al., 1991), which reported that D_e of $^3\text{H}_2\text{O}$ increased with the porosity, which is directly proportional to the water content of the sediment. The established relationship between the D_e and the water content or density of sediment is a useful tool to estimate the diffusion of nitrate in the sediment, and thus shall be valuable in bioremediation.

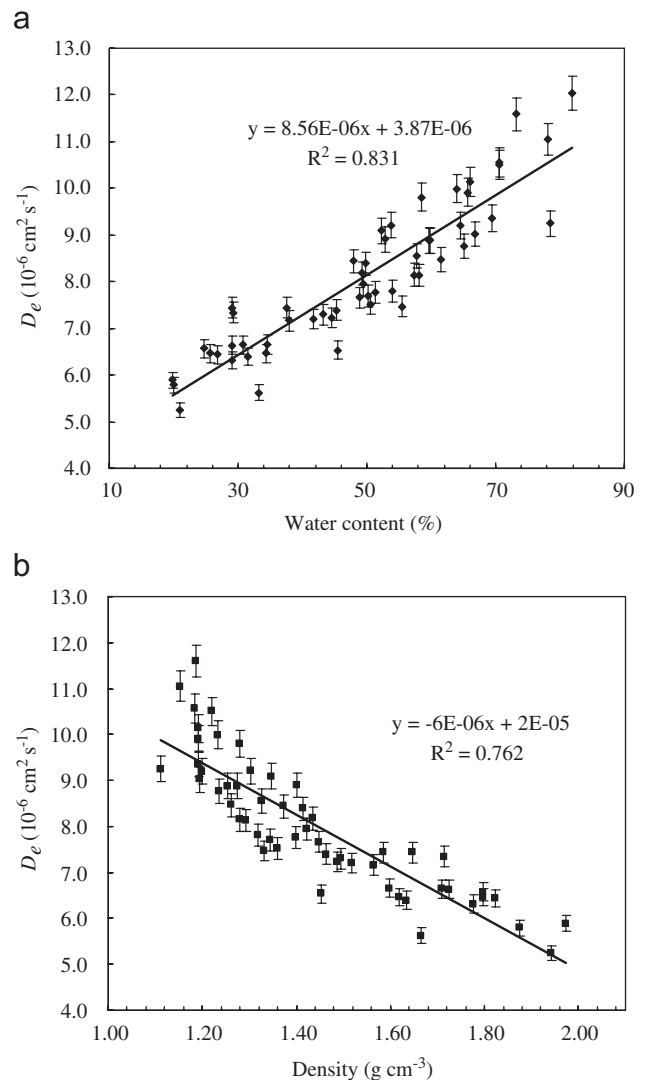


Fig. 5 – Correlation between D_e of nitrate and (a) water content and (b) sediment dry bulk density.

3.7. Advantage of HATR-FTIR method

The HATR-FTIR method, as demonstrated in this study, is an effective technique for the estimation of diffused molecular and ionic species, like nitrate, in sediments. Compared with the conventional D_e determining methods, this one is easy and rapid to operate, and requires as little as 1 mL of sediment sample. This method shall be applicable for the risk assessment of toxic pollutants in contaminated sediments, and for planning the spatial and chronological nitrate dosing strategy in bioremediation.

4. Conclusion

This study demonstrates that the effective diffusion coefficient, D_e , of a chemical species in sediment can be estimated using a novel and simple method based on HATR-FTIR. The D_e of nitrate in a contaminated sediment was accordingly estimated as $7.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Based on this D_e and the measured nitrate reduction rate, the profiles of nitrate concentration in two sediment columns were satisfactorily predicted from a mathematical model. This technique shall be useful for the study of pollutant diffusion in sediment and for remediation by denitrification.

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