



## Influence of organic matter and solute concentration on nitrate sorption in batch and diffusion-cell experiments

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### ABSTRACT

Nitrate sorption potentials of three surface soils (soils-1–3) were evaluated under different solute concentrations, i.e. 1–100 mg L<sup>-1</sup>. Batch and diffusion-cell adsorption experiments were conducted to delineate the diffusion property and maximum specific nitrate adsorption capacity (MSNAC) of the soils. Ho's pseudo-second order model well fitted the batch adsorption kinetics data ( $R^2 > 0.99$ ). Subsequently, the MSNAC was estimated using Langmuir and Freundlich isotherms; however, the best-fit was obtained with Langmuir isotherm. Interestingly, the batch adsorption experiments over-estimated the MSNAC of the soils compared with the diffusion-cell tests. On the other hand, a proportionate increase in the MSNAC was observed with the increase in soil organic matter content (OM) under the batch and diffusion-cell tests. Therefore, increasing the soil OM by the application of natural compost could stop nitrate leaching from agricultural fields and also increase the fertility of soil.

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### 1. Introduction

Nitrate, either formed in soils or supplied as fertilizers, is soluble in water and subject to leaching. Nitrate concentrations of groundwater resources in many countries increased drastically (Chabani et al., 2006; Jaafari et al., 2004) due to an increasing usage of nitrogenous fertilizers or intensive agriculture, high density housing with unsewered sanitation and irrigation of sewage effluent onto land (McLay et al., 2001). Nitrogen loss from irrigated cropland, particularly from sandy soils, significantly contributes to the nitrate contamination of surface water and groundwater sources (Li, 2003; Shukla et al., 1998). The major concern of nitrate contamination is the associated blue-baby syndrome resulting from the conversion of hemoglobin into methemoglobin, which cannot carry oxygen (Ghosh and Bhat, 1998; Golden and Weinstein, 1998). The ability of soil to adsorb ions from aqueous solution has major consequence on both agricultural issues such as soil fertility and remediation of polluted soil, and health concerns (Bradl, 2004).

Several researchers investigated the nitrate transport from non-point source and its concomitant effect, i.e. eutrophication (Davidson et al., 1990; Kinjo and Pratt, 1971; Ndala et al., 2006).

The major processes involved in the nitrogen transformation in soil are nitrogen fixation, ammonification, nitrification, immobilization and denitrification. Nitrate retention, either plant/microbial immobilization or by sorption onto the hydroxides of iron and aluminum has the potential to reduce the leaching of nitrate to the deeper horizons and surface waters. However, the mobility and bioavailability of nitrite in soils are mainly governed by soil properties such as organic matter content (OM), pH, cation-exchange capacity, texture and mineral species especially those constituting the clay fraction (Martinez-Villegas et al., 2004). Nitrogen mineralization is controlled primarily by the dynamics of soil OM because the nitrate utilization by denitrifiers is limited by insufficient supply of oxidizable carbon in the unsaturated zone/aquifer (Singh and Sekhon, 1978). The amount of fertilizer nitrogen leaching as nitrate below the root zone and its stability in the unsaturated zone/aquifer are the factors that determine the extent of nitrate pollution of groundwater.

The adverse impacts of nitrogen overloading from agricultural fields into sensitive eco-systems are increasingly noticeable in the recent decades. Despite the environmental benefits of limiting the nitrogen release, there is a continuous need to supply organics and nutrients including nitrogen for productivity and fertility (Xu et al., 2010). Therefore, the nitrate leaching is an inevitable concomitant of the day-to-day agricultural practice. Although several techniques are available for treating the nitrate contaminated water, i.e. reverse osmosis, electro-dialysis, anion-exchange and biological denitrification, source control of nitrate leaching is the

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most excellent option for better environmental protection. Batch experiments have been used to determine the distribution coefficient ( $K_d$ ) and maximum specific adsorption capacity ( $q_{\max}$ ) of nitrate with various adsorbents (Chabani et al., 2006; Jaafari et al., 2004; Ozturk and Bektas, 2004; Wang et al., 2007). However, the batch experiments could not simulate the actual field conditions for the determination of leaching behavior and maximum adsorption capacity especially in subsurface soil systems due to the difference in pore water solution composition and the soil-solution ratio. On the other hand, diffusion-cell experiments have been employed to investigate the effective diffusion coefficient, retardation factor and effective porosity for tracers (Azzam and Lambarki, 2004; Novakowski and van der Kamp, 1996; Shackelford, 1991).

Many researchers utilized batch or diffusion-cell experiments separately to investigate the adsorption behavior of many pollutants (Hassett and Banwart, 1989; Kumar and Philip, 2006; Martinez-Villegas et al., 2004; Ozturk and Bektas, 2004; Wang et al., 2007). Nevertheless, no researcher has attempted to investigate the difference in adsorption behavior of a pollutant (especially nitrate) under the batch and diffusion-cell experiments. Besides, several studies reported the contamination of groundwater and surface water with nitrate concentration more than  $100 \text{ mg L}^{-1}$  (Jaafari et al., 2004) whereas the maximum contamination level (MCL) of nitrate in drinking water is restricted to  $10 \text{ mg L}^{-1}$  (USEPA, 2000). Therefore, a wide range of nitrate concentration ( $1\text{--}100 \text{ mg L}^{-1}$ ) has to be adopted for both lab-scale batch and diffusion-cell experiments, which can lead to the direct application of the experimental results. Therefore, this study was aimed to scrutinize the nitrate adsorption kinetics in various surface soils under the batch and diffusion-cell tests. In addition, the effect of soil OM in nitrate sorption was investigated.

## 2. Methods

### 2.1. Soil samples

Three representative surface soil samples (unpolluted soil samples collected from 0 to 15 cm depth, in the winter season of 2005) were collected from an agricultural field near Aachen, Germany. The soil samples were oven dried at  $50 \text{ }^\circ\text{C}$  for 48 h, sieved through 2 mm sieve and stored in airtight plastic bags. The soils were identified and classified based on sieve analysis and Atterbergs limit analysis. The OM content of the soil was measured by both ignition loss (APHA, 2005) and wet oxidation methods (Kezdi, 1980). When characterizing the OM by ignition loss method it is assumed that the OM particles of the soil in contrast to its mineral constituents are combustible. The soil pH and specific gravity were measured by a direct reading type pH meter and by pycnometer method, respectively. The physicochemical properties of the soil specimen are shown in Table 1.

### 2.2. Chemicals

Reagents and salts used in the experiments were of analytical-grade (Merck, Germany). Sodium nitrate ( $\text{NaNO}_3$ ) (99.5% purity) was used in adsorption experiments. All glassware used in this study (Merck, Germany) were cleaned with distilled water and dried at  $110 \text{ }^\circ\text{C}$  for 5 h prior to use. Batch experiments were carried out in triplicate to ensure the reproducibility of results, and the average values were reported in each case.

### 2.3. Batch adsorption experiments

A set of static adsorption experiment was carried out to determine the adsorption equilibrium and the maximum specific nitrate adsorption capacity (MSNAC). Kinetic studies were conducted in a 500 mL conical flask at a fixed initial nitrate concentration of  $100 \text{ mg L}^{-1}$  and keeping the adsorbent mass as a constant, i.e. 5 g of soil (soil-specimen:solution ratio of 1:20). The sorbent masses were accurate to  $\pm 0.01 \text{ g}$  and solution volumes to  $\pm 0.5 \text{ mL}$ . Throughout the study, the contents of the conical flask were agitated using an orbital shaker at 150 rpm for a period of 24 h at room temperature ( $28 \pm 2 \text{ }^\circ\text{C}$ ). At various time intervals, the samples were collected from the conical flasks, centrifuged at 5000 rpm for 15 min and the supernatant was analyzed for residual nitrate concentration in a HP-790 Ion Chromatograph (98% accuracy).

On the other hand, the equilibrium studies were carried out under varying initial nitrate ion concentrations, i.e. 0.5, 1.5, 10, 15, 20, 25, 50 and  $100 \text{ mg L}^{-1}$ , and keeping the other conditions as similar as the kinetic study. The experiments were conducted for a period equal to the equilibrium time obtained from the kinetic study. At the end of this period, samples were collected, centrifuged at 5000 rpm for 15 min and the supernatant was analyzed for residual nitrate concentration. The equilibrium nitrate concentration ( $q_e$ ) retained on the soil was calculated by the mass balance between the initial and the final states.

#### 2.3.1. Data appraisal

In order to examine the controlling mechanisms of adsorption process, kinetic models were used to test the experimental data. The kinetic rates were estimated by Lagergreen pseudo first-order model (1898) and Ho's pseudo second-order model (1995) given in Eqs. (1) and (2), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where  $q_e$  and  $q_t$  are the amounts of nitrate adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively.  $k_1$  and  $k_2$  are the rate constants of first-order and second-order adsorption, respectively.

**Table 1**  
Characteristics of soil specimen.

Soil properties	Soil-1	Soil-2	Soil-3
Sand (%)	79	75	77
Silt (%)	10	14	13
Clay (%)	11	12	10
Type of soil	Loamy sand	Sandy loam	Sandy loam
pH	5.85	4.71	6.80
Water content (% wet wt basis)	16.01	17.75	14.17
Organic matter content (%)	3.43	6.76	9.42
Density ( $\text{g cc}^{-1}$ )	2.64	2.23	2.10
Total dissolved solids (ppm)	28.81	28.41	24.39
Anion exchange capacity ( $\text{cmol kg}^{-1}$ )	0.24	0.58	0.82
Soil nitrate-N ( $\text{mg g}^{-1}$ )	0.018	0.032	0.025

The fit of these models was checked from their linear plots, i.e.  $\log(q_e - q_t)$  versus  $t$  and  $(t/q_t)$  versus  $t$ , respectively (Ozturk and Bektas, 2004). Subsequently, the data obtained from equilibrium study were fitted with Langmuir (1918) and Freundlich (1926) isotherms shown in Eqs. (3) and (4), respectively.

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (3)$$

$$q_e = K_f C_e^{1/n} \quad (4)$$

where  $C_e$  is the equilibrium concentration of nitrate in the solution ( $\text{mg L}^{-1}$ );  $q_{\max}$  is the maximum amount of adsorbed nitrate ( $\text{mg g}^{-1}$ );  $b$  is Langmuir's constant related to the energy of adsorption;  $K_f$  is Freundlich's proportionality constant, which is indicative of bond strength, and  $n$  is a dimensionless exponent related to bond energies between nitrate ion and adsorbents.

#### 2.4. Diffusion-cell test

The diffusion-cell test was carried out to determine the diffusive mass flow, leaching behavior and sorption characteristics. The schematic diagram of the diffusion-cell experimental setup is shown in Fig. 1. Prior to the test, soil specimens were compacted to a dry density of  $1.7 \text{ g cm}^{-3}$ , and saturated to minimize the mass transport by suction, which was done by exposing the bottom of the specimen to distilled water (to reduce the possible disturbance to the soil structure). After saturation, the water in the top reservoir was replaced by nitrate solution of known concentration ( $C_s$ ). In order to exclude the hydraulic gradient, i.e. advection transport, the levels of nitrate solution and distilled water in the storage vessels were kept constant (Fig. 1). Subsequently, the nitrate solution and the distilled water were pumped through the upper and lower parts of the diffusion-cell, respectively. The pump speed was adjusted in such a way that the cell contents have been completely exchanged once in a day. The whole diffusion-cell tests were performed at ambient temperature ranging from 20 to 23 °C (Shackelford et al., 1989). The samples collected in the collection reservoirs from the upper-cell area and lower-cell area were analyzed for nitrate concentrations ( $C_L$  and  $C_w$ , respectively) and mass flux curves were plotted. After reaching a stationary condition, i.e. mass flux input equals mass flux output, the total nitrate sorption capacity ( $S$ ) and total nitrate sorbed ( $G$ ) in the soil specimen were determined through integration (Eq. (5)) and mass balance methods (Eq. (6)), respectively (Azzam and Lambarki, 2004).

$$S = \int_0^{t_E} (J_{in} - J_{out}) dt \quad (5)$$

$$G = M_{in} - M_{out} + \Delta m = \sum_t ((C_s V_{L_{in}} - C_L V_{L_{out}}) - C_w V_w + \Delta m) \quad (6)$$

where  $J_{in}$  and  $J_{out}$  are the input and output mass flux ( $\text{mg m}^{-2} \text{ d}^{-1}$ ) obtained from the input and output mass flux curves, respectively.  $t_E$  is the time for attainment of stationary condition.  $M_{in}$  and  $M_{out}$  are the masses (mg) diffused-in and -out, respectively.  $\Delta m$  is the quantity taken for analysis.  $V_{L_{in}}$  and  $V_{L_{out}}$  are the input and output volumes of nitrate solution from the upper-cell area, and  $V_w$  is the output volume of the solution from lower-cell area at any particular time. A statistical program XACT was used to obtain the area under the mass flux curve required for the integration method. The diffusion-coefficient ( $D_e$ ,  $\text{m}^2 \text{ s}^{-1}$ ) is determined by Eq. (7).

$$D_e = \left( \frac{\Delta Q}{A \Delta t} \right) / \left( \frac{\delta c}{\delta x} \right) = \frac{J_{out} d}{C_w} \quad (7)$$

where  $\Delta Q$  is the quantity of substance transported by unit time  $\Delta t$  through the effective diffusion area ( $A$ ) of soil sample ( $78.5 \text{ cm}^2$ ),  $\delta c / \delta x$  is the change in concentration per unit length and  $d$  is the thickness of the soil sample ( $m$ ) used for the diffusion-cell test. The parameter time-lag ( $t_e$ ) can be obtained from the plot between cumulative output mass flux and time and it is linked to the apparent diffusion-coefficient ( $D_{app}$ )  $\psi$  as shown in Eq. (8).

$$t_e = \frac{d^2}{6D_{app}} \quad (8)$$

Subsequently, the impedance factor or apparent tortuosity ( $\gamma$ ) and the retardation factor ( $R_d$ )  $\psi$  are determined using the effective and apparent diffusion-coefficients as shown in Eqs. (9) and (10), respectively.

$$D_e = D_o \gamma \quad (9)$$

$$D_{app} = \frac{D_e}{R_d} = \frac{D_o \gamma}{R_d} \quad (10)$$

For calculating the apparent tortuosity, the diffusion-coefficient of nitrate ( $D_o$ ) in free solution was assumed as  $1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  based on the earlier reports. A detailed calculation related to the nitrate sorption, diffusion-coefficients, apparent tortuosity and retardation factor in various soils under the diffusion-cell test are given as a Supplementary data.

### 3. Results and discussion

The physico-chemical properties of soils are shown in Table 1. All soils were slightly acidic and the sand contents were more than 75%. A wide variation in soil OM was observed between the soils specimens (3.43–9.42%), whereas the other characteristics were almost similar.

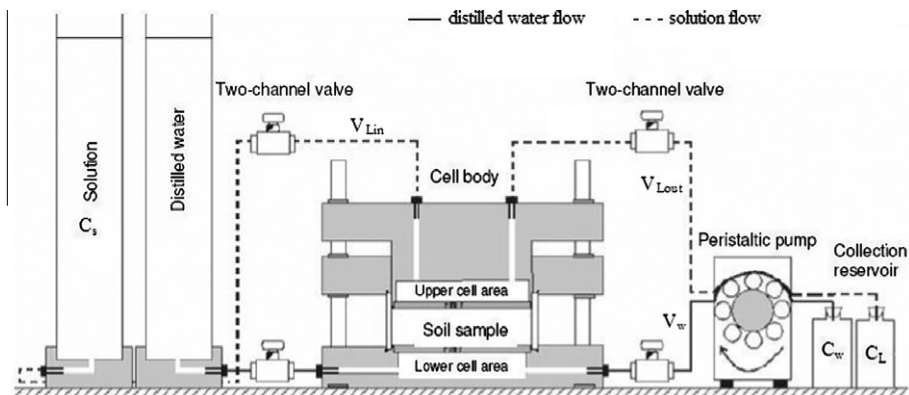


Fig. 1. Schematic diagram of diffusion-cell test apparatus.

### 3.1. Batch adsorption experiments

#### 3.1.1. Kinetic study

The adsorption kinetics of nitrate in three German soils is shown in Fig. 2. The adsorption kinetics exhibited an immediate rapid adsorption in all the soils and pseudo-adsorption equilibrium was obtained after 7 h in soil-2 and soil-3, whereas it was observed within 4 h in soil-1. After reaching the pseudo-equilibrium, less than 1% variation in the residual nitrate concentration was observed even after 24 h. The time taken to reach the pseudo-equilibrium was increased with increase in OM content of the soils. A short equilibrium time of 20–30 min for the sorption of nitrate in protonated cross-linked chitosan gel beads was reported (Jaafari et al., 2004). The rapid initial adsorption of nitrate is a surface phenomenon and it depends on the availability of number of adsorption sites along many other parameters such as pH, solute concentration, temperature, etc. Several studies have shown that the sorption of nitrate on several acidic soils was in the broken bonds of the soil molecules created by the acidification of the medium (Li, 2003; McLay et al., 2001). A control experiment was also conducted to estimate the loss of nitrate by volatilization and reaction with soil mixture. The variation of nitrate concentration in the blank experiment with respect to time was insignificant (<0.5%).

A variety of kinetic models including Lagergreen pseudo first-order model and Ho's pseudo second-order model have been used to find out the mechanism involved in the nitrate sorption on various sorbents (Ozturk and Bektas, 2004; Wang et al., 2007). The applicability of pseudo first-order and pseudo second-order models has been tested for the sorption of nitrate on different soil specimens and the outcomes are shown in Table 2. Both these models have well fitted the kinetics data; however, the pseudo second-order-model was superior for all soils with ( $R^2 > 0.99$ ). It can be noticed in Table 2 that the maximum quantity of nitrate sorption ( $q_e$ ) was in the order of soil-3 (0.280 mg g<sup>-1</sup>) followed by soil-2 (0.230 mg g<sup>-1</sup>) and soil-1 (0.120 mg g<sup>-1</sup>). This indicates that the increase in soil OM content could increase the quantity of nitrate sorption in the soil specimens. This observation is in good agreement with the experimental outcomes of Ndala et al. (2006), where they reported that the increase in soil OM content increased the sorption of nitrate in the forested catchments of the eastern escarpment of South Africa.

#### 3.1.2. Equilibrium study

Adsorption isotherms provide useful information about the retention capacity and a macroscopic view of the retention phenomena (Puebla et al., 2004). In order to understand the short-term behavior of nitrate sorption in the soils, adsorption isotherm

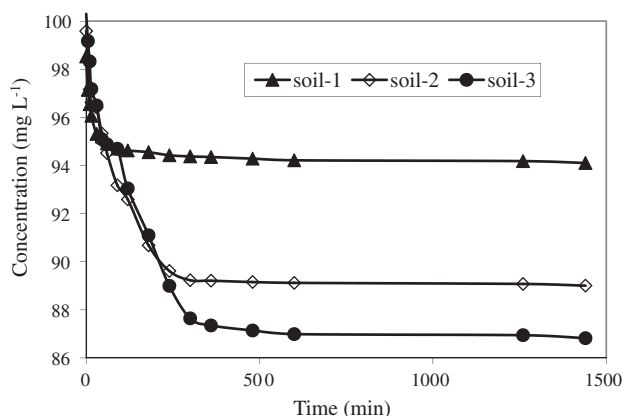


Fig. 2. Nitrate adsorption kinetics in soil samples.

studies were conducted and the MSNAC of the soils was calculated by Langmuir and Freundlich isotherms. The isotherm constants and the maximum sorption capacity of the soil were determined separately for lower, i.e. 0.5, 1, 5, 10 and 15 mg L<sup>-1</sup>, and higher, i.e. 20, 25, 50 and 100 mg L<sup>-1</sup>, nitrate concentrations. All the data were fitted well to both the isotherms with very high correlation coefficients for both ranges of nitrate concentrations (Table 3a). Although both the isotherms were fitted well with the experimental data, Langmuir's isotherm was found to be better with high correlation coefficients in both the ranges studied. In the lower nitrate concentration range studied, both Langmuir and Freundlich equilibrium models have shown an increase in the MSNAC with increase in soil OM content. In the higher nitrate concentration range, the MSNAC was found to be increasing with increase in OM content as per Langmuir's isotherm (Table 3b). In contrast, decreasing MSNAC was found with increasing soil OM content in case of Freundlich isotherm. The reason for such contrasting adsorption pattern was unclear at this particular moment.

The MSNAC of the soils estimated by Langmuir isotherm were varied from 0.080–0.091 and 0.335–1.403 mg g<sup>-1</sup> in the lower and higher nitrate concentration ranges, respectively. The difference in adsorption capacity between lower and higher nitrate concentration range is attributed to the equilibrium concentration of nitrate. Kumar and Philip (2006) reported similar trends while conducting soil-adsorption studies with endosulfan. Highest MSNAC was observed in the soil with highest OM content, i.e. soil-3. This can be attributed to the greatest number of binding sites provided by chemically active OM and its extremely large surface area. Sanchez-Martin et al. (2003) reported similar data while studying the adsorption of linuron in different soils.

### 3.2. Diffusion-cell experiments

Samples collected from the upper and lower cell areas of the diffusion-cell at various time intervals were analyzed for nitrate concentration. The mass flux curves of the three soil samples are congruent throughout the experiment duration (Fig. 3). The mass flux has decreased very rapidly in the initial stages of the diffusion-cell tests (0–20 d); subsequently, the rate of decrease in mass flux has reduced considerably (20–60 d) and reached pseudo-equilibrium after 80 d. Similar trends was observed under the entire nitrate concentrations studied, i.e. 20, 30 and 80 mg L<sup>-1</sup>. The effective diffusion-coefficient, apparent diffusion-coefficient, retardation factor and impedance factor (i.e. apparent tortuosity) were calculated from the outcomes of diffusion-cell experiments (Table 4). The time-lag required for the calculation of apparent diffusion-coefficient was obtained from the plot of cumulative mass flux versus time (data not shown). The effective diffusion-coefficient was found to be decreasing with increase in OM content. The value of apparent diffusion-coefficient was significantly lower than the effective diffusion-coefficient, which demonstrates the influence of nitrate sorption in soil. The retardation factor and apparent tortuosity of the soil samples were in the range of 95–149 and 1.21–1.37, respectively. The maximum value of retardation factor was obtained in the soil with the highest OM content; whereas, the maximum value of apparent tortuosity was observed in the soil with the lowest OM content. This reveals that the apparent tortuosity and retardation factor have good correlation with the soil OM content.

### 3.3. Comparison of batch and diffusion-cell experiments

The MSNAC of soils-1–3 obtained from batch and diffusion-cell test under various initial nitrate concentrations are compared in Fig. 4A–C, respectively. It can be noticed in Fig. 4 that the batch test over-estimates the MSNAC of the soils compared to the



**Table 2**  
Nitrate sorption kinetics in various soils.

Name of soil	Pseudo-first-order model		Pseudo-second-order model		
	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$R^2$
Soil-1	0.0051	0.753	0.120	0.83	0.990
Soil-2	0.0094	0.975	0.230	0.11	0.998
Soil-3	0.0100	0.960	0.280	0.05	0.993

**Table 3a**Adsorption isotherm constants at lower nitrate concentrations in different soils (0.5–15  $\text{mg L}^{-1}$ ).

Name of soil	Langmuir constants			Freundlich constants		
	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	$b$	$R^2$	$K_f$	$1/n$	$R^2$
Soil-1	0.080	1.75	0.989	0.036	0.333	0.933
Soil-2	0.090	4.48	0.988	0.052	0.303	0.903
Soil-3	0.091	5.76	0.999	0.057	0.321	0.956

**Table 3b**Adsorption isotherm constants at higher nitrate concentrations in different soils (20–100  $\text{mg L}^{-1}$ ).

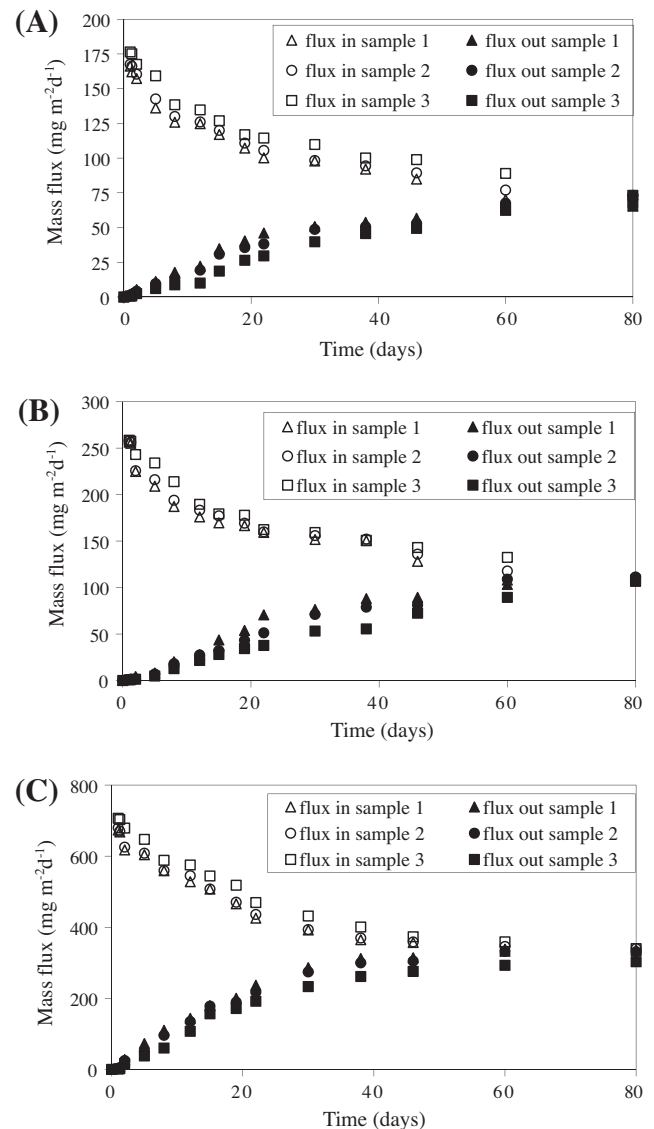
Name of soil	Langmuir constants			Freundlich constants		
	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	$b$	$R^2$	$K_f$ ( $\text{mg g}^{-1}$ )	$1/n$	$R^2$
Soil-1	0.335	0.019	0.985	0.018	0.550	0.970
Soil-2	1.141	0.007	0.939	0.012	0.811	0.967
Soil-3	1.403	0.006	0.921	0.017	0.767	0.958

diffusion-cell test. The MSNACs observed in the diffusion-cell test following the integration and mass balance methods were similar in all the soil samples irrespective of the nitrate concentration studied. The deviation between the MSNACs observed in the batch and diffusion-cell tests is also increasing considerably with the increase in initial nitrate concentration and soil OM content. At an initial nitrate concentration of 20  $\text{mg L}^{-1}$ , the MSNAC of soils-2 and -3 were 91% (Fig. 4B) and 102% (Fig. 4C) more in the batch test compared to diffusion-cell test, respectively. However, these values were reduced to 51% and 60% in soils-2 and -3, respectively at an initial nitrate concentration of 80  $\text{mg L}^{-1}$ . In both the cases, the percentage difference in the MSNAC was higher in soil-3 compared to soil-2.

The highly exposed surface area and lower soil-solution ratio may be the causes for the higher sorption in case of batch experiments. Moreover, it can be envisaged that the disintegration of soil samples in batch experiments due to rigorous shaking might have increased the MSNAC. The lower nitrate sorption of soil-1 in batch test might be due to the lower binding strength of the solute caused by fewer soil OM content. These observations reveal that batch test could not accurately determine the quantity of retarded pollutant in the field condition. On the other hand, the nitrate retention data and the permeation rate in and out of soils can be precisely determined by the diffusion-cell test.

#### 3.4. Effect of soil OM content in nitrate sorption

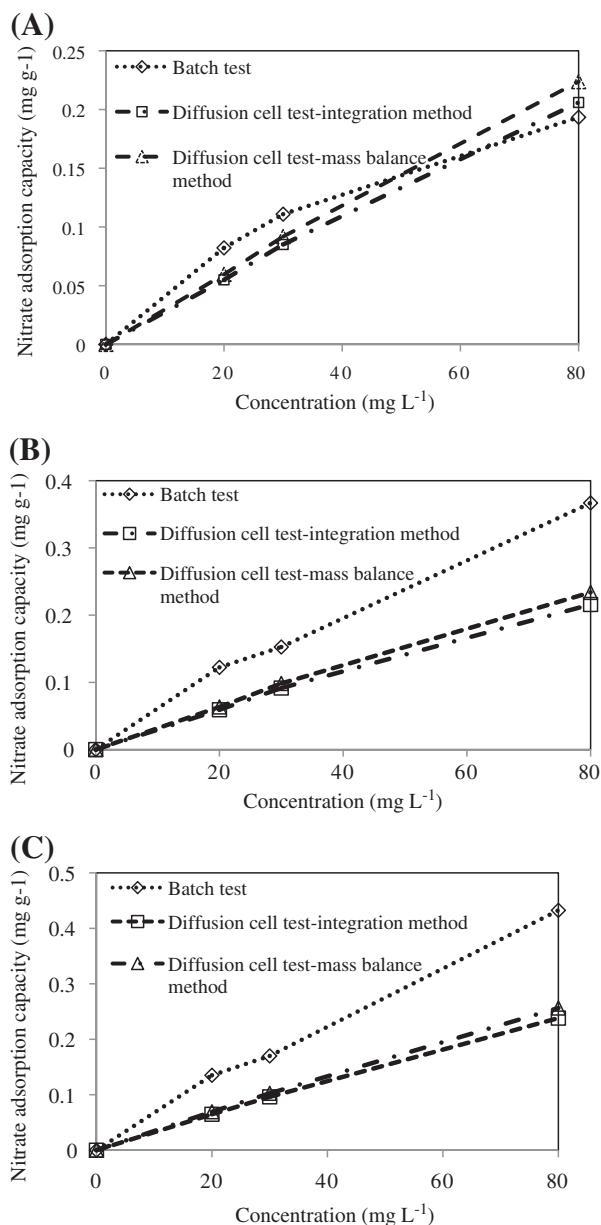
The soil OM has a polyelectrolytic character with various chemically reactive functional groups, hydrophilic and hydrophobic sites, which influences the soil-solute interaction. Moreover, it was reported that the mobility of pesticides and nitrate often related to the active components of organic fraction (when OM content greater than 5%) and clay-sized fractions (Ndala et al., 2006; Rama Krishna and Philip, 2008). The properties of three soil samples used for the present study were similar except the OM content (Table 1). Therefore, the difference in MSNAC of the soils can solely

**Fig. 3.** Mass flux curve for initial nitrate concentration of (A) 20  $\text{mg L}^{-1}$ , (B) 30  $\text{mg L}^{-1}$  and (C) 80  $\text{mg L}^{-1}$ .

depend on the OM content of the soils. At low initial nitrate concentrations, not much variation in the nitrate adsorption capacity was observed with increase in soil OM content. On the other hand, the nitrate adsorption capacity was increased greatly with increase in soil OM content under higher initial nitrate concentrations, i.e. 50 and 100  $\text{mg L}^{-1}$ . When the soil OM content increased from 3.43% to 9.42%, the nitrate adsorption capacities were increased from 0.212 to 0.519  $\text{mg g}^{-1}$  (increase of 145%) and 0.166 to 0.303  $\text{mg g}^{-1}$  (increase of 83%) at initial nitrate concentrations of 50 and 100  $\text{mg L}^{-1}$ , respectively. These observations infer that OM content plays a major role in the nitrate sorption capacity of the soils.

**Table 4**  
Results of diffusion-cell test.

Parameters	Soil-1	Soil-2	Soil-3
Effective diffusion-coefficient, $D_e$ ( $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ )	2.6	2.4	2.3
Apparent diffusion-coefficient, $D_{app}$ ( $1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ )	2.8	1.9	1.7
Retardation factor, $R_d$	94.5	123.2	148.5
Apparent tortuosity, $\gamma$ ( $\tau_a$ )	1.37	1.25	1.21



**Fig. 4.** Comparison of batch and diffusion-cell tests for (A) soil-1, (B) soil-2 and (C) soil-3.

The results of this study indicate that increase in soil OM content can reduce the nitrate leaching from the soils. Therefore, *in situ* addition of the organic amendments could be helpful to control leaching of nutrients. Compost, an organic amendment, provides organics and nutrients for plant growth and has the property of adsorbing/immobilizing wide range of heavy metals and

nutrients (Xu et al., 2010; Tapia et al., 2010). Therefore, the application of natural-compost (as nutrient and soil conditioner) has to be motivated in order to prevent the nutrient leaching and to acquire green-agriculture. On the other hand, humic substances and the other divalent or trivalent cations such as iron and manganese present in the soil can increase the nitrate adsorption capacity of the soils. Moreover, the MSNAC can fluctuate largely based on the pH of the soil. Practically, nitrate leaching to groundwater is mainly controlled by immobilization using chemicals without altering the pH of the soil. The change in pH of soil can control the nitrate leaching (Ndala et al., 2006) but the fertility of the soil could be highly affected. Therefore, in this investigation no attempt was made to study the nitrate adsorption at various pH values of soil. Moreover, desorption experiments can visualize the extent of nitrate adsorption, bond strength and the mobility of nitrate in the soil systems. Further studies are in progress to achieve these goals.

#### 4. Conclusions

The nitrate adsorption kinetics in three surface soils under the batch and diffusion-cell tests was investigated. The MSNAC was observed in the soil with the highest soil OM content. Batch adsorption test has shown higher nitrate adsorption capacity than that predicted in the diffusion-cell test. However, the diffusion-cell test was appropriate in the estimation of nitrate sorption in soils. A positive correlation was observed between the soil OM content and nitrate sorption in both batch and diffusion-cell tests. Further studies on the effects of ionic strength, clay and silt content, humic substances and other geo-matrix are useful in nitrate control.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.biortech.2010.12.044](https://doi.org/10.1016/j.biortech.2010.12.044).

#### References

- APHA, 2005. Standard Methods for the Examination of Water and Wastewater. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC.
- Azzam, R., Lambarki, M., 2004. Evaluation concept and testing method for heavy metal contaminant transport in the underground. Proceedings of 1st EurEnGeo IAEG Conference, 316–318.
- Bradl, H.B., 2004. Adsorption of heavy metal ions on soil and soil constituents. *J. Colloid. Interf. Sci.* 277, 1–18.
- Chabani, M., Amrane, A., Bensmaili, A., 2006. Kinetic modelling of liquid-phase adsorption of nitrates on ionized adsorbent. *Desalination* 197, 117–123.
- Davidson, E.A., Stark, J.M., Firestone, M.K., 1990. Microbial production and consumption of nitrate in an annual grassland. *Ecology* 71, 1968–1975.
- Ghosh, B.C., Bhat, R., 1998. Environmental hazards of nitrogen loading in wetland rice fields. *Environ. Pollut.* 102, 123–126.
- Golden, P.J., Weinstein, R., 1998. Treatment of high-risk refractory acquired with automated red blood cell exchange. *J. Clin. Apheresis* 13, 28–31.
- Hassett, J.J., Banwart, W.L., 1989. The sorption of nonpolar organics by soils and sediments. *Soil Sci. Soc. Am. J.* 22, 31–44.
- Jaafari, K., Ruiz, T., Elmaleh, S., Coma, J., Benkhoulja, K., 2004. Simulation of a fixed bed adsorber packed with protonated cross-linked chitosan gel beads to remove nitrate from contaminated water. *Chem. Eng. J.* 99, 153–160.
- Kezdi, A., 1980. Handbook of Soil Mechanics, Vol. 2. Elsevier Scientific Publishing Company, New York, USA.
- Kinjo, T., Pratt, P.F., 1971. Nitrate adsorption. I. In some acid soils of Mexico and South America. *Soil Sci. Soc. Am. J.* 35, 722–725.
- Kumar, M., Philip, L., 2006. Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. *Chemosphere* 62, 1064–1077.
- Li, Z., 2003. Use of surfactant modified zeolite as fertilizer carriers to control nitrate release. *Microporous Mesoporous Materials* 61, 181–188.
- Martinez-Villegas, N., Flores-Velez, L.M., Dominguez, O., 2004. Sorption of lead in soil as a function of pH: a study case in Mexico. *Chemosphere* 57, 1537–1542.
- McLay, C.D.A., Dragten, R., Sparling, G., Selvarajah, N., 2001. Predicting groundwater nitrate concentration in a region of mixed agricultural land use: a comparison of three approaches. *Environ. Pollut.* 115, 191–204.

- Ndala, S.M., Scholes, M.C., Fey, M.V., 2006. Soil properties and processes driving the leaching of nitrate in the forested catchments of the eastern escarpment of South Africa. *Forest Ecol. Manag.* 236, 142–152.
- Novakowski, K.S., van der Kamp, G., 1996. The radial diffusion method:2. A semi analytical model for the determination of effective diffusion coefficients, porosity and adsorption. *Water Resour. Res.* 32, 1823–1830.
- Ozturk, N., Bektas, T.E., 2004. Nitrate removal from aqueous solution by adsorption onto various materials. *J. Hazard. Mater.* 112, 155–162.
- Puebla, R.A.A., Calahorra, C.V., Garrido, J.J., 2004. Cu (II) retention on a humic substance. *J. Colloid Interf. Sci.* 270, 47–55.
- Rama Krishna, K., Philip, L., 2008. Adsorption and desorption characteristics of lindane, carbofuran and methyl parathion on various Indian soils. *J. Hazard. Mater.* 160, 559–567.
- Sanchez-Martin, M.J., Rodriguez-Cruz, M.S., Sanchez-Camazano, M., 2003. Study of the desorption of linuron from soils to water enhanced by the addition of an anionic surfactant to soil-water system. *Water Res.* 37, 3110–3117.
- Shackelford, C.D., Daniel, D.E., Liljestand, M., 1989. Diffusion of inorganic chemical species in compacted clay soil. *J. Contam. Hydrol.* 4, 241–273.
- Shackelford, C.D., 1991. Laboratory diffusion testing for waste disposal - a review. *J. Contam. Hydrol.* 7, 177–217.
- Shukla, B.D., Misra, A.K., Gupta, R.K., 1998. Application of nitrogen in production and post-production systems of agriculture and its effect on environment in India. *Environ Pollut.* 102, 115–122.
- Singh, B., Sekhon, G.S., 1978. Leaching of nitrate in calcareous soils as influenced by its adsorption on calcium carbonate. *Geoderma* 20, 271–279.
- Tapia, Y., Cala, V., Eymer, E., Frutos, I., Garate, A., Masaguer, A., 2010. Chemical characterization and evaluation of composts as organic amendments for immobilizing cadmium. *Bioresour. Technol.* 101, 5437–5443.
- US Environmental Protection Agency, 2000. Drinking Water Standards and Health Advisories. U.S. Environmental Protection Agency, Office of Water, 822-B-00-001, 12.
- Wang, Y., Gao, B.Y., Yue, W.W., Yue, Q.Y., 2007. Preparation and utilization of wheat straw anionic sorbent for the removal of nitrate from aqueous solution. *J. Environ. Sci.* 19, 1305–1310.
- Xu, X., Gao, B.Y., Yue, Q.Y., Zhong, Q.Q., 2010. Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal. *Bioresour. Technol.* 101, 8558–8564.