BEHAVIOR OF CHEMICAL SPECIES UNDER REDOX ENVIRONMENT USING MULTICOMPONENT SOLUTE TRANSPORT MODEL

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In order to understand the physical, chemical and biological processes of the chemical species in a subsurface environment, it is important to include the biochemical and cation exchange reactions in the solute transport model. In this study, a two-soil column experiment was carried out to examine the behavior of chemical species in sub-aqueous soils similar to paddy field. A solute transport model that predicts the behavior and transport of multicomponent chemical species in the subsurface environment was developed and applied. The biochemical reactions and cation exchange reactions are modeled in the transport equation as the sink/source terms. This model simulates solute transport and computes changes in concentration over time caused by the biochemical and cation exchange processes. The results of numerical simulation correlated fairly well with the measured concentration.

Keywords: *multicomponent solute transport, oxidation and reduction, cation exchange process, biochemical process*

1. Introduction

Due to increasing demand on water resources, the reuse of treated sewage water has become indispensable. However, the potential health and ecological effects of the chemical contaminants in treated sewage water are not well understood. It is necessary to identify the chemical contaminants likely to be present in treated sewage water and develop approaches for minimizing their release. Land application of treated sewage water in the paddy field has gradually become the popular way of reuse. In a paddy field situation, successive chemical transformations occur like denitrification, oxidation and reduction (redox) reactions and cation exchange reactions. Oxidation and reduction processes play an important role on the distribution of chemical species like O_2, NO_3^-, Mn^{2+} and Fe^{2+} etc. under natural condition in groundwater. In order to assess and predict groundwater flow and solute transport numerical simulation models have been developed.

Recently, different approaches have been developed for the simulation of transport processes involving in chemical reaction. Kinzelbach et al.[1)] developed a model of microbial denitrification processes that describes the interaction of oxygen, nitrate, organic carbon and bacteria. Three phases (mobile pore water, biophase, and aquifer material) are taken into account. Lensing et al.[2)] used a multicomponent transport reaction model to bacterially catalyzed redox processes. The exchange between the three different phases is also considered. The sub-models are coupled with the equations of the microbially mediated redox reactions.

Schäfer et al.[3)] developed the transport, biochemistry and chemistry (TBC) model that numerically solves the equations for reactive transport in three-dimensional saturated groundwater flow. Solute transport is coupled

with microbially mediated organic carbon degradation. Microbial growth is assumed to follow Monod type kinetics. Schäfer et al.[4] in their model application to a column study on organic carbon degradation considered five microbial groups in the model. The model provides a temporally and spatially resolved quantification of microbial degradation activity.

The purpose of this study is to determine the behavior and transport of the chemical species in the soil column applied with secondary treated sewage water. In order to predict the biochemical changes, the multicomponent solute transport model that considers both the biochemical and cation exchange reactions was developed. Treated sewage water was used as injection water because of its complex mixture and may still contain nitrate that is of potential concern for human health. From the simulation result of the solute transport model, the vertical distribution of the nitrate concentration can be determined. A two-soil column experiment was conducted to determine the thickness of plow layer that is safe for nitrate leaching.

2. Experimental Apparatus and Procedure

The soil column experiment was conducted using soils collected from actual paddy field and were packed in two 10 cm diameter PVC cylinder columns of different thickness of plow layers 10 cm and 20 cm respectively (Fig.1). Treated sewage water was constantly supplied up to 5 cm at the top of the two soil columns in order to reproduce the redox condition similar to paddy field. Table 1 showed the concentration of the injection water. Glass beads were used as oxidized layer at 15 cm for both soil columns. Soil solution samples collected by porous cups and column outflow were analyzed for Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, NH_4^+-N and NO_3^- -N concentrations. EC (Electrical Conductivity), pH and ORP (Oxidation Reduction Potential) were also measured.

3. Multicomponent Solute Transport

(1) Conceptual Model

The biochemical and chemical model (Fig.2) describe the interaction of O_2, NO_3^-, CH_2O, bacteria, MnO_2, $Fe(OH)_3$, Na^+, K^+, Mg^{2+} and Ca^{2+}. This model takes into account the microbially mediated redox reaction and the cation exchange reaction. It also takes into consideration the four different model phases. The bacteria are assumed to reside in an immobile biophase. Exchange processes are considered between the different model phases. The organic contaminant present in the immobile phase can dissolve into the mobile pore water. The organic compounds can be adsorbed from the pore water onto the solid phase and vice versa. They can also exchange

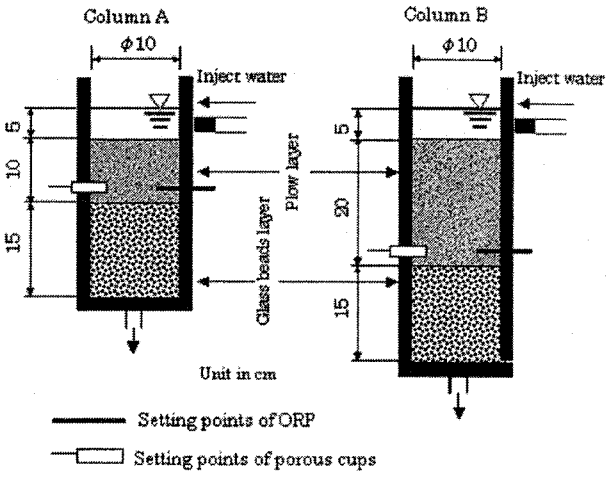

Fig. 1. Experimental column equipment

Table 1. Concentration of injection water

Na^+	10.146 meq/L	NH_4^+	0.432 meq/L
K^+	0.775 meq/L	NO_3^-	0.378 meq/L
Ca^{2+}	4.164 meq/L	TOC	18.7 mg/L
Mg^{2+}	2.085 meq/L	EC	1.55 mS/cm
Fe^{2+}	0.066 meq/L	pH	7.2
Mn	0.024 meq/L		

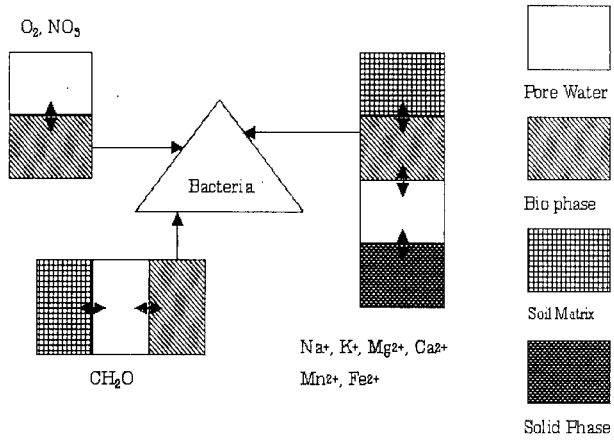

Fig. 2. Scheme of biochemical model

with the biophase where they are modified by microbially mediated redox reactions.

(2) Theoretical Model Development - Reactive Solute Transport Model

The one-dimensional partial differential equation governing the convective-dispersive solute transport of chemical species i considering biochemical and chemical reactions in a sub-aqueous soil can be written as[5]:

$$\frac{\partial C_i}{\partial t} + v\frac{\partial C_i}{\partial z} - \frac{\partial}{\partial z}\left(D\frac{\partial C_i}{\partial z}\right) = S_{(i)} \qquad (1)$$

where $i=1,2,...,N$, C_i is the concentration of chemical species i in the pore water (mmol l^{-1}), v is pore water velocity (cm s^{-1}), t is time (s), z is distance, D is the hydrodynamic dispersion coefficient (cm^2 s^{-1}), $S_{(i)}$ is the chemical sink/source term representing the exchange with other phases and chemical or biochemical reactions (mmol $l^{-1}s^{-1}$). N is 9 and the chemical species given by i= 1,2,3,4,5,6,7,8, and 9 correspond to Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, O_2, NO_3^- and CH_2O, respectively. The biochemical reactions and the cation exchange reactions were modeled in the convective-dispersive equation as the sink/source terms. The chemical species considered are summarized in Table 2.

3) Bacteria Growth

The growth of different groups of microbial populations in the biophase is described by Monod kinetics. Its general expression is shown for one arbitrary bacteria group:

$$\left[\frac{\partial X}{\partial t}\right]_{growth} = \sum_r v_{\max} \cdot X \cdot \prod_m MT_m \cdot \prod_i IT_i \cdot IT_{TotX} \qquad (2)$$

where v_{max} is the maximum growth rate of bacteria, X is the bacterial population, MT_m is the Monod terms for species m, IT_i is the inhibition term of the inhibiting species i and IT_{TotX} is the inhibition term to control maximum microbial activity.

The modelling of complex redox sequence requires the consideration of different metabolisms. Bacteria X1, X2 and X3 that reside in the immobile biophase are considered in the model. Under aerobic conditions bacteria X1 uses O_2 as electron acceptor while under anaerobic conditions

Table 2 Chemical species considered in the model

Bio phase	$O_{2\,bio}$ $NO_3^-{}_{bio}$ $Mn^{2+}{}_{bio}$ $Fe^{2+}{}_{bio}$ $MnO_{2\,bio}$ $Fe(OH)_{3\,bio}$ CH_2O_{bio}
Pore water	$Na^+{}_{mob}$ $Ca^{2+}{}_{mob}$ $K^+{}_{mob}$ $Mg^{2+}{}_{mob}$ $Mn^{2+}{}_{mob}$ $CH_2O_{\,mob}$ $Fe^{2+}{}_{mob}$ $O_{2\,mob}$ $NO_3^-{}_{mob}$
Solid Phase	$Na^+{}_{im}$ $Ca^{2+}{}_{im}$ $K^+{}_{im}$ $Mg^{2+}{}_{im}$ $Mn^{2+}{}_{im}$ $Fe^{2+}{}_{im}$
Soil matrix	CH_2O_{mat} MnO_{2mat} $Fe(OH)_{3mat}$
Bacteria	X1 X2 X3

NO_3^- is used as electron acceptor. Bacteria X2 uses MnO_2 while bacteria X3 uses $Fe(OH)_3$ as electron acceptor. These bacteria use dissolved organic carbon (CH_2O) as carbon source and oxidize this substrate to CO_2 in the model.

For the chemical species Fe^{2+} the following equations are formulated:

Biophase:

$$Fe^{2+}: \frac{\partial}{\partial t}(\theta_{bio}[Fe^{2+}]_{bio}) = \frac{\theta_{bio}}{P_{Fe^{2+}}}\left[\frac{\partial X3}{\partial t}\right]_{Iron} - \frac{\lambda\,\theta_{bio}\theta_w}{\theta_{bio}+\theta_w}([Fe^{2+}]_{bio} - [Fe^{2+}]_{mob}) \qquad (3)$$

$$Fe(OH)_3: \frac{\partial}{\partial t}(\theta_{bio}[Fe(OH)_3]_{bio}) = -\frac{\theta_{bio}}{U_{Fe(OH)_3}}\left[\frac{\partial X3}{\partial t}\right]_{grow} - \frac{\gamma\,\theta_{bio}\theta_{mat}}{\theta_{bio}+\theta_{mat}}([Fe(OH)_3]_{bio} - [Fe(OH)_3]_{mat}) \qquad (4)$$

Pore water phase:

$$Fe^{2+}: \frac{\partial}{\partial t}(\theta_w[Fe^{2+}]_{mob}) + \frac{\partial}{\partial x}(\theta_w v'[Fe^{2+}]_{mob}) = \frac{\partial}{\partial x}(\theta_w D\frac{\partial[Fe^{2+}]_{mob}}{\partial x}) + \frac{\lambda\,\theta_{bio}\theta_w}{\theta_{bio}+\theta_w}([Fe^{2+}]_{bio} - [Fe^{2+}]_{mob}) + \theta_w S3_{Fe} \qquad (5)$$

Solid Phase:

$$Fe^{2+}: \frac{\partial}{\partial t}(\theta_w[Fe^{2+}]_{im}) = -\theta_w S3_{Fe} \qquad (6)$$

Soil Matrix:

$$Fe(OH)_3: \frac{\partial}{\partial t}(\theta_{mat}[Fe(OH)_3]_{mat}) = \frac{\gamma\,\theta_{bio}\theta_{mat}}{\theta_{bio}+\theta_{mat}}([Fe(OH)_3]_{bio} - [Fe(OH)_3]_{mat}) \qquad (7)$$

Bacteria:

$$X3: \left[\frac{\partial X3}{\partial t}\right]_{Total\_Growth} = \left[\frac{\partial X3}{\partial t}\right]_{grow} + \left[\frac{\partial X3}{\partial t}\right]_{decay} \qquad (8)$$

$$X3: \left[\frac{\partial X3}{\partial t}\right]_{grow} = v_{\max}^{Fe(OH)_3} \cdot \frac{IC_{NO_3^-}}{IC_{NO_3^-} + [NO_3^-]_{bio}} \cdot \frac{[CH_2O]_{bio}}{K_{CH_2O} + [CH_2O]_{bio}} \cdot \frac{[Fe(OH)_3]_{bio}}{K_{Fe(OH)_3} + [Fe(OH)_3]_{bio}} \cdot X3 \qquad (9)$$

$$\left[\frac{\partial X3}{\partial t}\right]_{decay} = -v_{X3dec} \cdot X3 \qquad (10)$$

Notations:

λ, γ = exchange coefficients

θ_{bio}, θ_w, θ_{mat} =water content for bio, mobile and matrix phase

P_{Fe2+} = Production factor for Fe^{2+}

$U_{Fe(OH)3}$ = Growth yield factor for $Fe(OH)_3$

$S3_{Fe}$ = Pore water and solid phase exchange reaction term of Fe

IC_{NO3-} = Inhibition concentration of NO_3^- against O_2

K_{CH2O} = Half velocity concentration for CH_2O

$v_{max}^{Fe(OH)3}$ = maximum growth rate of Bacteria X3

v_{X3dec} = constant decay rate of Bacteria X3

Table 3 Parameters used for the simulation model [3),6)]

Biochemical Parameters	
Specific volume of biophase (n_{bio})[3)]	0.02
Specific volume of mobile phase (n_{mob})[3)]	0.48
Specific volume of matrix phase (n_{mat})[3)]	0.50
Exchange coefficient (α)[3)]	50 day^{-1}
Exchange coefficient (β)[3)]	$5x10^{-3}$ day^{-1}
Exchange coefficient (γ)[3)]	$8x10^{-5}$ day^{-1}
Maximum microbial capacity	---
Monod constant	
Organic carbon (MC_{OC})[3)]	0.1 mmol/l
Oxygen (MC_{OXY})[3)]	$1x10^{-5}$ mmol/l
Switching function parameter	
Threshold value of O_2 (O_t)[3)]	$1.5x10^{-2}$ mmol/l
Slope of switch function (f_{sl})[3)]	40
Inhibition Concentration	
Denitrifiers against O_2	---
Fe(III), Mn(IV) reducers against O_2	---
Aerobic Bacteria	
Yielding Coefficient Y^{O2}_{CH2O}[3)]	0.1 mmol cell-C/mol OC
Maximum growth rate v_{max}^{O2}[3)]	5.0 day^{-1}
Constant decay rate v_{x1dec}[3)]	0.75 day^{-1}
Nitrate Reducers	
Yielding Coefficient YNO^{NO3}_{CH2O}[3)]	0.081 mmol cell-C/mol OC
Maximum growth rate v_{max}^{NO3}[3)]	4.05 day^{-1}
Constant decay rate v_{x1dec}[3)]	0.75 day^{-1}
Manganese Reducers	
Yielding Coefficient Y^{MnO2}_{CH2O}[3)]	0.015 mmol cell-C/mol OC
Maximum growth rate v_{max}^{MnO2}[3)]	0.75 day^{-1}
Constant decay rate v_{x1dec}[3)]	0.113 day^{-1}
Iron Reducers	
Yielding Coefficient $Y^{Fe(OH)3}_{CH2O}$[3)]	0.01 mmol cell-C/mol OC
Maximum growth rate $v_{max}^{Fe(OH)3}$[3)]	0.50 day^{-1}
Constant decay rate v_{x1dec}[3)]	0.075 day^{-1}
Soil properties	
Porosity[6)]	0.480
Dispersivity α_L[6)]	0.01cm
CEC[6)]	0.1352 meq/100g

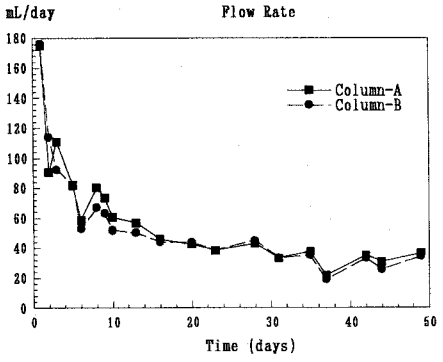

Fig. 3 Flow rate in Columns A and B

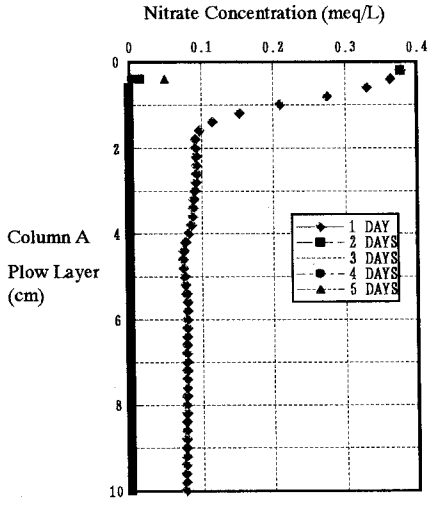

Fig. 4 Simulation result of nitrate concentration

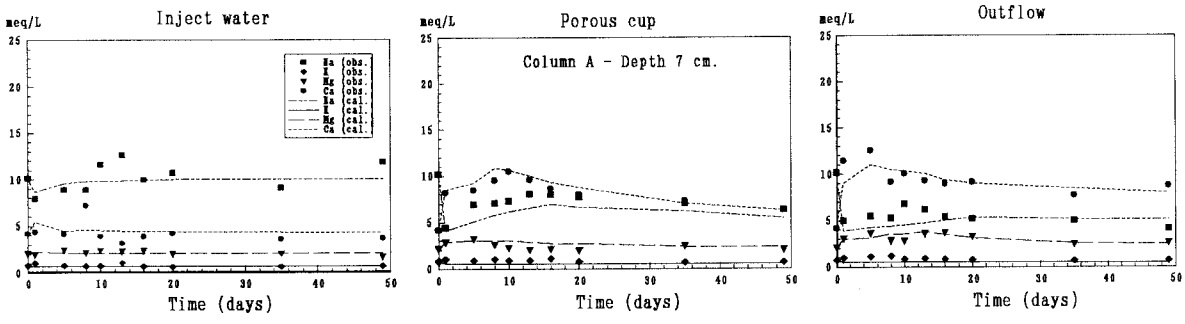

Fig. 5 Comparison of observed and calculated cation concentration

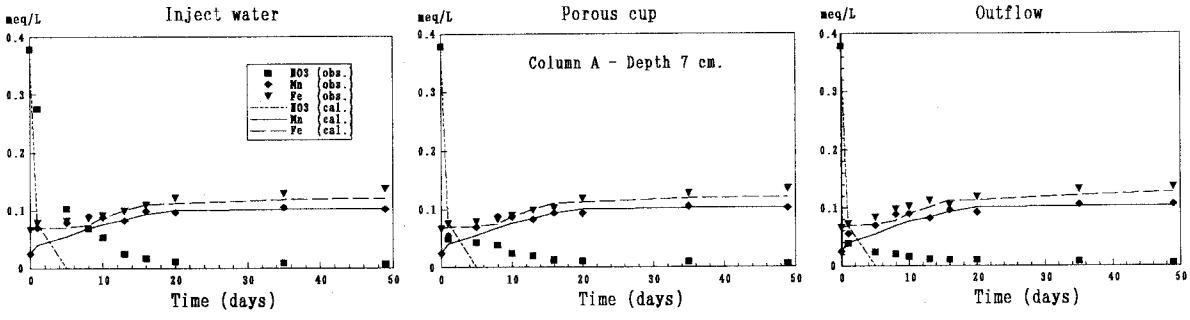

Fig. 6 Comparison of observed and calculated NO_3^-, Mn^{2+} and Fe^{2+} concentration

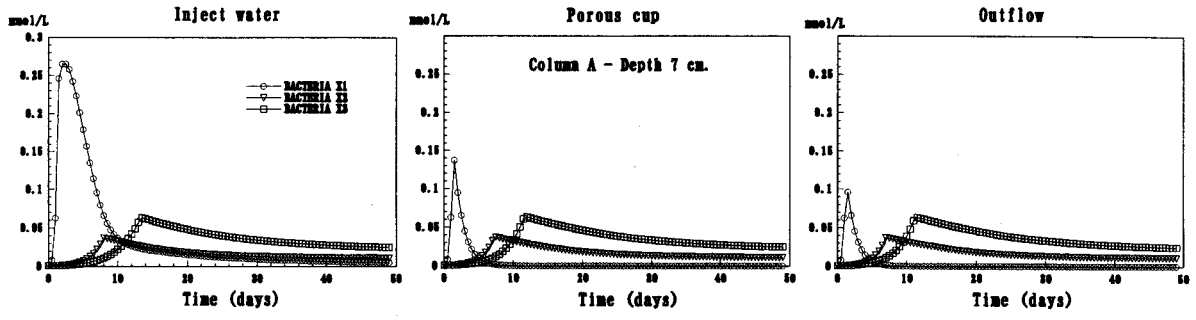

Fig.7 Temporal variation of bacteria concentration at different depths

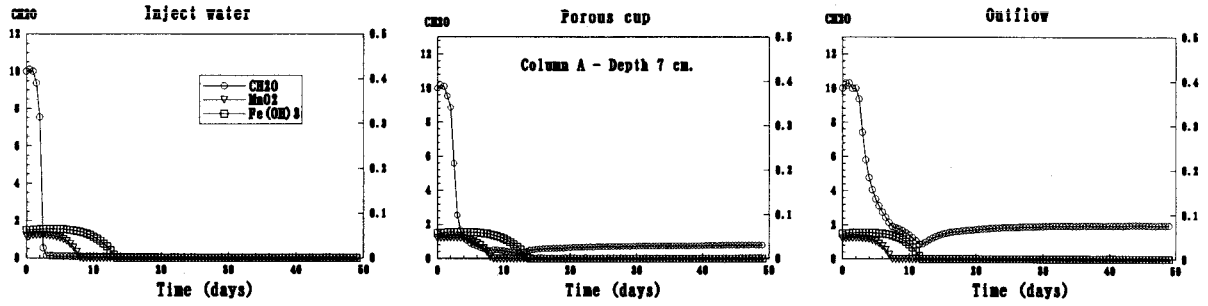

Fig. 8 Temporal variation of CH_2O, MnO_2 and $Fe(OH)_3$ in biophase

4. Results and Discussions

The concentration of inject water in the simulation model are identical to those in the soil column experiment (Table 1). Boundary concentration values were based on values suggested by Hiroshiro et al.[6]. In the simulation model the pore water velocity was assumed constant due to the steady state conditions in the saturated zone. The model simulated solute transport and changes in concentration due to advection, dispersion, biochemical and cation exchange reactions.

The modelling of multicomponent solute transport with biochemical reaction processes is complex because it involves specification of many biochemical parameters. Table 3 showed some of the biochemical parameters applied in the simulation model. The values of parameters were based on values suggested by Schäfer et al.[3] and Hiroshiro et al.[6].

Parameter sensitivity analysis is important to determine the degree of influence of the various input parameters have on model results. Sensitivity analyses were performed by varying the values of the input parameters, it was found out that the value of the maximum growth v_{max} for the aerobic bacteria was important to fit the observed and calculated concentration of bacteria X1. The exchange coefficient γ and the initial concentrations of MnO_2 and $Fe(OH)_3$ in the biophase influenced the variation of growth of bacteria X2 and X3. The comparison of measured and calculated cation concentration demonstrated that the value of dispersivity α_L has a strong effect on the mobile liquid phase to fit the measured and calculated cation concentration.

(1) Fig. 3 showed the flow rate in Column A and Column B are rapidly decreasing during the first ten days and then after ten days the flow rate in Column A is almost the same with the flow rate in Column B. The average velocity was obtained by dividing the flow rate by the surface area of the column. It was assumed that the steady state was attained at the flow rate of 40 ml/day. Then the pore water velocity was determined by dividing the average velocity by porosity. In the simulation model the pore water velocity was assumed constant since the model considered only the reduced layer that is saturated. From the experimental results of flow rate, there is no big difference between Column A and Column B. Similar results can be expected with the two soil columns.

(2) In the soil column experiment, the reduction of NO_3^- started immediately after flooding of treated sewage water. In order to design the thickness of plow layer that is safe

for nitrate leaching, it is necessary to determine the depth where denitrification will occur. The multicomponent solute transport model simulated the vertical distribution of the NO_3^- concentration. Fig. 4 showed the simulation result of nitrate concentration in the mobile phase. Denitrification occurred immediately at the top 2 cm of the column where NO_3^- concentration decreased to zero after two days.

(3) Fig. 5 showed the observed cation concentration correlated fairly well with the calculated cation concentrations. K^+ concentration showed almost constant values. $Ca^{2+}$and Mg^{2+} concentrations increased at the porous cup and outflow of the columns due to desorption of Ca^{2+} and Mg^{2+} by Mn^{2+} and Fe^{2+} while Na^+ concentration decreased. These indicated that chemical reactions had occurred in all parts of the column.

(4) Fig. 6 showed the comparison of observed and calculated concentrations of NO_3^-, Mn^{2+} and Fe^{2+}. NO_3^- concentration rapidly decreased at the inject water layer due to denitrification and consumption of bacteria while Mn^{2+} and Fe^{2+} concentration increased due to dissolution of Mn^{2+} and Fe^{2+} from Mn- and Fe-hydroxides during infiltration through the plow layer (reduced layer).

(5) Fig. 7 showed the simulation results of the temporal variation of X1, X2 and X3 bacteria concentration at different depths. Bacteria X1 grew rapidly during the first 10 days and then rapidly decreased. Bacteria X2 and X3 grew after 10 days and then decreased gradually with time in all parts of the columns. The maximum growth of bacteria X1 occurred at the inject water layer, where high concentrations of O_2, NO_3^- and CH_2O are present.

(6) Fig. 8 showed the simulation results of the temporal variation of CH_2O, MnO_2 and $Fe(OH)_3$ in biophase. CH_2O concentration decreased during the first 10 days while MnO_2 and $Fe(OH)_3$ decreased after 10 days due to consumption of bacteria. As shown in Fig.7 and Fig 8, the increase in concentration of bacteria X1, X2 and X3 corresponded to the decrease in concentration of CH_2O, MnO_2 and $Fe(OH)_3$.

The result of the soil column experiment and the solute transport model had produced interesting observations on the behavior of chemical species present in the secondary treated sewage water. The result of the numerical simulation approximately agreed with the experimental results.

5. Conclusions

The multicomponent solute transport model was able to predict the behavior of chemical species present in secondary treated sewage water under redox environment.

The reduction of NO_3^- started immediately at the inject water layer of the column therefore, the thickness of plow layer in Column A which is 10 cm thinner than Column B is still safe for nitrate leaching.

More detailed parameter sensitivity analysis must be performed to quantify the effects of uncertainty in the estimates of model parameters on model results.

For future expansion of the model, the extension of the model into the unsaturated zone should be considered. The multicomponent solute transport model should also be upgraded into a two-dimensional heterogeneous solute transport model for more realistic application to practical problems.

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