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MODELING OF BIOLOGICALLY MEDIATED REDOX PROCESSES USING SAWDUST AS A MATRIX

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A model simulating reactive transport in natural filter using sawdust as materials to improve the efficiency of filter is developed. The transport part of the model computes the changed in concentration over time caused by the processes of advection and dispersion. The kinetic sub model describes the heterotrophic metabolisms of several groups of bacteria. To model a complete redox sequence (aerobic oxidation, denitrification, Mn (IV)-reduction, Fe (III)-reduction and sulfate reduction) four functional bacterial groups (X1, X2, X3 and X4) are defined. The growth and metabolisms are formulated using the Double Monod kinetic equation. The model takes into account the exchange between the different phases (mobile phase, bio phase and matrix phase). The results from a laboratory soil-sawdust columns experiments are used to verify the simulation results of the model. While the availability of organic carbon is one of the most important factors that affects bacterial activity in natural filter. This study demonstrates that using sawdust as a carbon source can improve the biologically mediated redox processes.

Key words: *redox processes, sawdust, organic carbon source, reactive transport model, bacteria growth.*

1. INTRODUCTION

The problem of removing pollutants from water and wastewater has grown enormously with rapid industrialization in recent decades. Heavy metals, dyes, oil and other substances, which are toxic to many organisms and raise increasing environmental concerns, are present in wastewater streams coming from many industries. Wastewater generated in large volumes with high pollutant load must be cleaned before it is released or reused. Many methods exist to remove unwanted materials from water and wastewater, such as membrane filtration, coagulation, adsorption, oxidation, ion exchange and precipitation. However, these methods may have its own limitations, in terms of, for example, cost, efficiency and appropriateness for certain pollutants.

Biological removal of pollutants is widely used in the treatment of domestic and complex industrial wastewaters[1),2),3),4)]. Biological treatment, among the various available treatment methods, is very attractive because of its economical and environmental advantages.

Redox reactions play an important role in biological processes. Reductants and oxidants are defined as electron donors and electron acceptors[1)]. The redox state of the filter is mainly influenced by microbial mediated redox reaction. In the filter flow path, the following sequence of processes can be observed: aerobic reaction, denitrification, Mn (IV)-reduction, Fe (III)-reduction and sulfate reduction. However, carbon source feeding is required to maintain biological activity inside the filter.

Many agricultural byproducts have little or no economic value. However, some byproducts available in large quantities, such as sawdust in lumber mills, even represent a disposal problem. On the other hand, use of sawdust for removing pollutants would benefit both the environment and the wood agriculture. For example, contaminated waters would be cleaned, and a new market would be opened for the sawdust. Sawdust, a relatively abundant and inexpensive material is being used as a porous treatment media to enhance removal of contaminants from water.

Sawdust can be used for the removal of nitrate from water; for example, denitrification walls amended with sawdust are effective in nitrate removal[4)]. The denitrification wall was constructed by digging a trench that intercepts groundwater. The excavated soil was mixed with sawdust 30% as a carbon source and then returned to the trench. Nitrogen levels in the wall and in the surrounding groundwater were monitored for one year. The denitrification wall successfully removed nitrates from water but did not provide long-term removal. Effectiveness of the wall depended on nitrate concentration not only depended on the amount of carbon in the sawdust. Throughout the year, the wall proved to be very efficient even with the decrease in sawdust availability. This technique proved to be very useful in nitrate removal from groundwater.

Sawdust material has proven to be a promising material for removal of contaminants from wastewater. Sawdust is not only abundant but also it is really an efficient and economic adsorbent that is effective to many types of pollutants, such as dyes, oil, salts and heavy metals[5)].

The overall objectives of this study are to: (i) investigate the biologically mediated redox processes for secondary wastewater by using soil-sawdust filter; (ii) develop a mathematical solute-transport model to predict the biologically mediated processes through the natural filter enhanced by sawdust; and (iii) evaluate and calibrate the mathematical model using the laboratory soil-sawdust column experiments.

2. THEORETICAL DEVELOPMENT

(1) Model processes

The model used in this study is based on the reactive solute transport and biological processes. It describes the interactions between O_2, NO_3^-, CH_2O, Mn^{2+}, Fe^{2+} and SO_4^{2-} concentrations and bacteria growth. The model takes into account three different phases: mobile pore water phase, immobile bio phase and matrix phase; the bio phase is assumed to include all bacteria growth and biological processes. Matrix phase is organic matter in soil, it assumed to include sawdust material.

Fig. 1 shows the chemical species considered in the model and mass transfer processes.

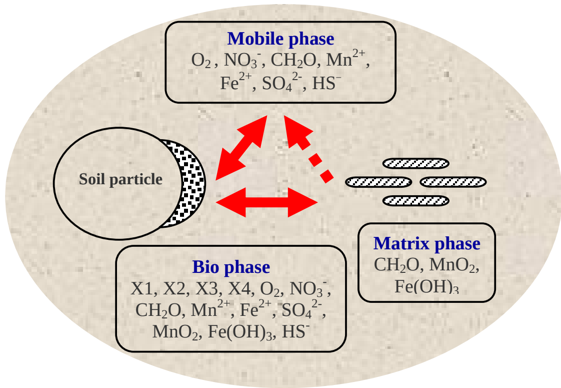

Fig. 1 Chemical species considered in the model and mass transfer processes between different phases.

The reaction term takes into consideration of the mass transfer processes (i) mass transfer between the mobile phase and the bio phase; (ii) mass transfer between the mobile phase and the matrix phase; and (iii) mass transfer between the bio phase and the matrix phase.

(2) Reactive-solute transport

The fundamental one-dimensional partial differential equation governing the advective-dispersive solute transport of contaminants can be written as[3),6),7)]:

$$\frac{\partial C_{mob}}{\partial t}=\frac{\partial}{\partial y}\left(D_L\frac{\partial C_{mob}}{\partial y}\right)-v'\frac{\partial C_{mob}}{\partial y}+S_i \qquad (1)$$

where C_{mob} is the concentration of solute in the mobile phase, D_L is the longitudinal dispersion coefficient, v' is the average pore velocity, t is the time, y is the distance, and S_i is the chemical source-sink term representing the exchange processes formulated as:

$$S_1=\frac{\alpha(1-n)}{a}\cdot\frac{\theta_{bio}\sqrt{D_L}}{\theta_{bio}+\theta_w}(C_{bio}-C_{mob}) \qquad (2)$$

$$S_2=\frac{\beta(1-n)}{a}\cdot\frac{\theta_{mat}\sqrt{D_L}}{\theta_{mat}+\theta_w}(C_{mat}-C_{mob}) \qquad (3)$$

$$S_3=\frac{\gamma(1-n)}{a}\cdot\frac{\theta_{mat}\sqrt{D_L}}{\theta_{bio}+\theta_{mat}}(C_{bio}-C_{mat}) \qquad (4)$$

However, to simplified the exchange equations 2, 3 and 4 it can be written as following:

$$S_1=\alpha'(C_{bio}-C_{mob}) \qquad (5)$$

$$S_2=\beta'(C_{mat}-C_{mob}) \qquad (6)$$

$$S_3 = \gamma'(C_{bio} - C_{mat}) \tag{7}$$

where S_1, S_2 and S_3 are the exchange rate between the mobile, bio and matrix phases, C_{bio} and C_{mat} are the concentration of solute in the bio phase and matrix phase, α, β and γ are the exchange coefficient between the different phases, n is the porosity, a is the diameter of soil particles (uniform particle size) and $\theta_{bio}, \theta_{mat}$ and θ_w is the specific volume for different phases.

The longitudinal dispersion coefficient D_L is given by:

$$D_L = \alpha_L |v'| + D_M \tag{8}$$

where α_L is the longitudinal dispersivity and D_M is the molecular diffusion coefficient.

(3) Bacterial growth

Bacteria can utilize several substrates simultaneously. Bacteria growth is often controlled by availability of substrates. The specific growth rate is assumed to be a function of the concentration of the substrates.

As described by the ecological redox sequence, microbially mediated redox processes are described by the following reactions[1]:

Aerobic respiration
$CH_2O + O_2 \rightarrow CO_2 + H_2O$

Denitrification
$CH_2O + 4/5NO_3^- + 4/5H^+ \rightarrow CO_2 + 2/5N_2 + 7/5H_2O$

Manganese dioxide-reduction
$CH_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 3H_2O + CO_2$

Iron hydroxide-reduction
$CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow 4Fe^{2+} + 11H_2O + CO_2$

Sulfate (SO_4^{2-})-reduction
$CH_2O + 1/2SO_4^{2-} + 1/2H^+ \rightarrow CO_2 + 1/2HS^- + H_2O$

The growth of bacteria is described by the Double Monod kinetic equation can be written as:

$$\frac{\partial X}{\partial t} = v_{\max} \frac{C_1}{K_{s1} + C_1} \cdot \frac{C_2}{K_{s2} + C_2} X \tag{9}$$

where v_{max} is the maximum growth rate, C_1 is the primary substrate concentration in bio phases, C_2 is the secondary substrate concentration in bio phases, K_{s1} is the primary substrate half-saturation constant, K_{s2} is the secondary substrate half-saturation constant, and X is the bacteria concentration.

The equation of bacteria decay is given by:

$$\frac{\partial X}{\partial t} = -v_{dec} X \tag{10}$$

where v_{dec} is the bacteria decay rate.

The concentration of the microbial population can increase on one or more respirative pathways. For example, many aerobic bacteria are facultatively anaerobic and can also grow under denitrifying conditions[7]. The model extended to include the switching between aerobic and denitrifying growth conditions is based on the assumption that the same microorganisms are capable of either aerobic or denitrifying growth, depending on the oxygen concentration in their nearby environment, and can be written as[7]:

$$F([O_2]_{bio}) = 0.5 - \frac{1}{\pi} \tan^{-1}\{([O_2]_{bio} - [O_2]_{thres}) \times f_{s1}\} \tag{11}$$

where $F([O_2]_{bio})$ is the switching function, $[O_2]_{bio}$ is the concentration of oxygen O_2 in the bio phase, $[O_2]_{thres}$ is the threshold concentration of oxygen O_2, and f_{s1} is the slope of the switch function.

(4) Carbon sources

The organic carbon is one of the most important factors that affects bacterial activity.

The bacteria that mediates the redox processes requires an organic carbon source to continue the reduction activity. The possible sources of this organic carbon are dissolved organic carbon supplied from the wastewater and solid organic carbon supplied to the system in the form of sawdust. Literature[4] shows that the carbon supplied from sawdust was a sufficient source of carbon to enhance microbially mediated processes.

The model assumes that the solid organic carbon (released from sawdust) is located in a matrix phase as shown in **Fig. 1.**

The organic carbon as the matrix phase provided from sawdust is initially given by following equation:

$$[CH_2O]_{mat} = R \frac{M_{CH_2O}}{n} \tag{12}$$

where $[CH_2O]_{mat}$ is the initial concentration of organic carbon in matrix phase, R is the available organic carbon coefficient, M_{CH_2O} is the mass of carbon and n is the porosity

3. METHOD

(1) Column experiment

The column experiment was carried out using glass columns of 45 cm height and 10 cm internal diameter. The wire mesh and the filter paper were placed at the bottom of each column as shown in **Fig. 2**. The top and the bottom of the column were closed using glass transparent resin plates with tubes for the influent and effluent collection, respectively. Sampling points were placed at depths of 0, 5, 10, 20, and 30 cm.

The columns were packed to a height of 30 cm with different mixtures of soil, sawdust and bamboo chip as shown in **Table 1**. The secondary wastewater is constantly supplied at the top of the four columns by keeping the level of influent tank constant for the duration of 56 days and the average temperature was measured at 22^0C

(2) Numerical simulation

In this study, the finite difference method and the method of characteristics were used as numerical solution techniques to solve the model equations[9]. The model for the biologically mediated redox processes is highly complex, as it needs to involve a large number of parameters. Monod kinetic, stoichiometric and switching function parameters were taken from several studies related to wastewater treatment modeling and simulation of redox processes[1),2),3),4)]. The parameters were adjusted to obtain the best fit of the model to the experimental data. The values of the kinetic, stoichiometric and switching function parameters are listed in **Table 2.** The initial and boundary conditions were selected depending on the experimental set-up, injection wastewater analysis and chemical components of raw materials.

4. RESULTS AND DISCUSSION

(1) Experimental results

Columns 1, 2, 3 and 4 were initially run at flow velocities of 2.55×10^{-4} cm/sec, 2.55×10^{-4} cm/sec, 3.18×10^{-4} cm/sec and 2.17×10^{-4} cm/sec, respectively. After four days, the flow velocities of these columns were reduced to 8.85×10^{-5} cm/sec, 6.37×10^{-5} cm/sec, 1.06×10^{-4} cm/sec and 8.85×10^{-5} cm/sec, respectively. **Fig. 3** shows that the columns flow decreased during the running time. Calculation of the average velocity and permeability was based on Darcy's Law. **Fig. 4** shows that the permeability in the columns decreased during the running time. Such decreases in the permeability are due to clogging of the soil pores as a result of bacteria growth.

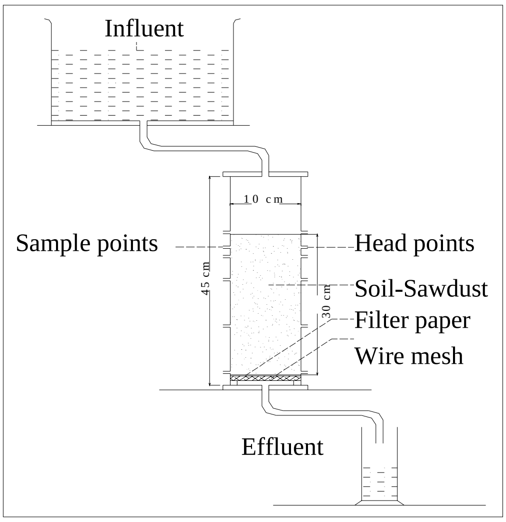

Fig. 2 Schematic of laboratory column experimental.

Table 1 Percentage of materials used in columns.

Material	Col. 1	Col. 2	Col. 3	Col. 4
Soil	100%	70%	30%	50%
Sawdust	0%	0%	0%	50%
Bamboo	0%	30%	70%	0%

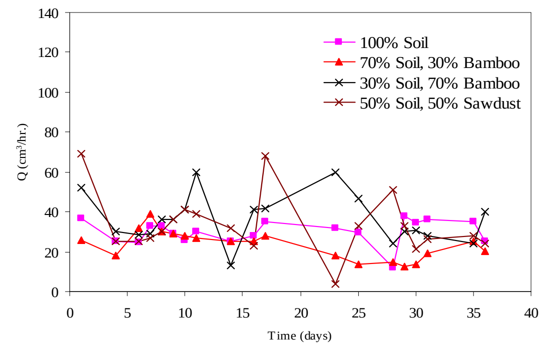

Fig. 3 Flow rate changes during the experiment.

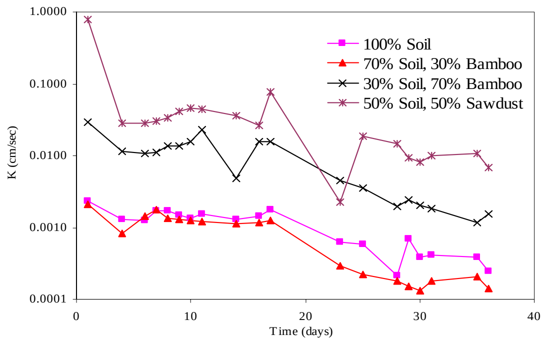

Fig. 4 Permeability changes during the experiment.

The experimental results of flow rate and permeability showed high permeability was obtained with sawdust mixed soil.

Table 2 Parameters used for the simulation.

parameter		value
Exchange coefficient	α`	10 day^{-1}
	β`	0.005 day^{-1}
	γ`	0.00005 day^{-1}
Longitudinal dispersivity	α_L	0.01cm
soil diameter	a	0.01mm
O C coefficient	R	0.4
Half-saturation constant	K_{CH2O}	0.10 mmol/L
	K_{O2}, K_{NO3}, K_{MnO2}, $K_{Fe(OH)3}$, K_{SO4}	1.0 x 10^{-3} mmol/L
Aerobic bacteria X1	Yield Coefficient Y^{O2}	0.10 mol cell-C/mol OC
	Max. growth v_{max}	5.0 day^{-1}
	Decay rate v_{X1dec}	0.15 day^{-1}
Denitrification bacteria X1	Yield Coefficient Y^{NO3}	0.09 mol cell-C/mol OC
	Max. growth v_{max}	1.4 day^{-1}
	Decay rate v_{X1dec}	0.15 day^{-1}
Mn(II)-reduction bacteria X2	Yield Coefficient Y^{MnO2}	0.004 mol cell-C/molOC
	Max. growth v_{max}	0.25 day^{-1}
	Decay rate v_{X2dec}	0.15 day^{-1}
Fe(III)-Reduction bacteria X3	Yield Coefficient $Y^{Fe(OH)3}$	0.025 mol cell-C/molOC
	Max. growth v_{max}	0.42 day^{-1}
	Decay rate v_{X3dec}	0.15 day^{-1}
Sulfate Reduction bacteria X4	Yield Coefficient Y^{SO4}	0.002 mol cell-C/molOC
	Max. growth v_{max}	0.06 day^{-1}
	Decay rate v_{X4dec}	0.15 day^{-1}
Switching parameter	Threshold Concentration $[O_2]_{thres}$	1.5 x 10^{-2} mmol/L
	Slope of switch f_{s1}	40.0

(2) Comparison between measured and simulated data

The simulated concentrations of the electron acceptors (nitrate, manganese, iron, and sulfate) and the electron donor (carbon) agreed well with the measured concentrations as shown in **Figs. 5** to **9**.

Fig. 5 shows that the column packed with 100 % soil of low permeability (1.45 x 10^{-3} cm/sec) yielded significant nitrate reductions, while the column, packed with a mixture of 50% soil and 50% sawdust of high permeability (7.39 x 10^{-2} cm/sec) showed significant nitrate reductions either. Additional advantage of using the sawdust is that the permeability of the column material can be increased.

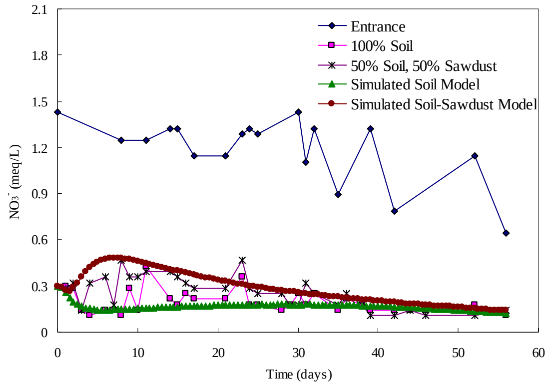

Fig. 5 Comparison between measured and simulated NO_3^-.

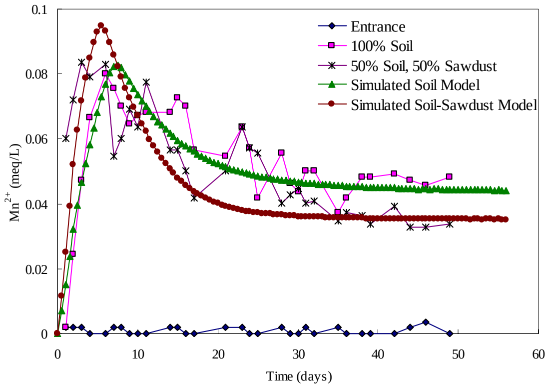

Fig. 6 Comparison between measured and simulated Mn^{2+}.

Fig. 6 shows the simulated and measured results of soil and soil-sawdust columns for the concentration of manganese. There is a small difference between the results of soil and soil-sawdust columns.

Fig. 7 shows that the column packed with soil-sawdust yielded significant iron hydroxide reduction more than that yielded by the column packed with soil only.

Fig. 8 also shows that the column packed with soil-sawdust yielded significant sulfate reductions more than that of the column packed with soil only.

Fig. 9 shows that the average carbon concentration of soil-sawdust column increased about 50% more than the average carbon concentration of soil column. It shows that the sawdust materials have proven to be promising materials for supplying a sufficient carbon to enhance microbially mediated processes when the carbon concentration of treated water is low.

The carbon concentration was also measured once for verification. The value obtained was in good agreement with the simulated one for that time. The simulated value was obtained by calculated the concentration of carbon in the matrix phase depending on equation 12.

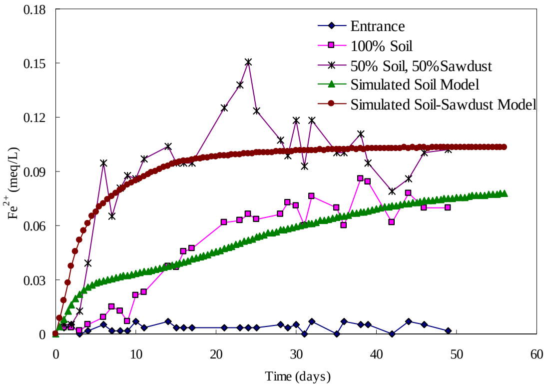

Fig. 7 Comparison between measured and simulated Fe^{2+}.

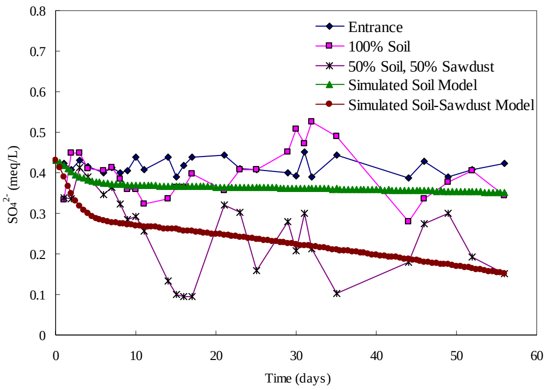

Fig. 8 Comparison between measured and simulated SO_4^{2-}.

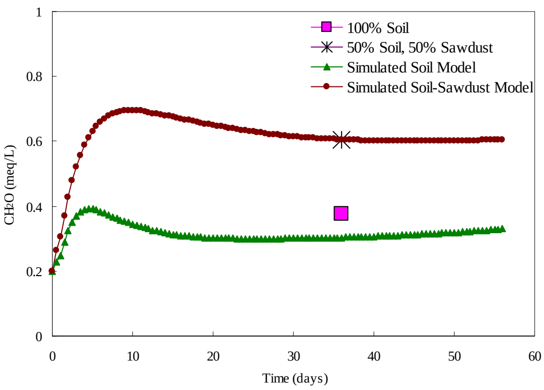

Fig. 9 Comparison between measured and simulated CH_2O.

5. CONCLUSION

The results from this study showed that it was generally possible to simulate the laboratory experimental results with a mathematical numerical model. A detailed comparison between the experimental and the simulation results showed that good agreement was obtained.

Experimental results showed that bacteria growth and microbial biomass build-up had the ability to reduce the permeability of the columns, producing more resistance to flow through the columns. This is due to rapid increases in microbial population when food and energy are available in excess.

The carbon source utilized in the microbial degradation comes from two different sources, dissolved organic carbon from secondary wastewater and solid organic carbon from the sawdust and soil.

Sawdust materials have proven to be promising materials for controlling and increasing the permeability and removal of pollutants from wastewater. The results from the laboratory column experiments showed significant reduction in pollutant concentration and increase the permeability when sawdust was used as a carbon source to enhance microbial activity.

The usefulness of pollutants concentration reduction of secondary wastewater using sawdust is dependent on their relative cost to environmental benefit.

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