

A KINETIC ANALYSIS OF ORGANIC RELEASE FROM THE AQUIFER SOIL IN RIVERBANK/BED FILTRATION

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INTRODUCTION

In riverbank/bed(RBF) filtration a significant amount of the organic matter may be released from the aquifer soil.⁵⁾ Unlike most European aquifers, the aquifers used for RBF in Korea are composed of the alluvial layers which contain high contents of fine grains and organic matter. In addition, the permeability of the aquifers in Korea is about a hundred times smaller than that of the European aquifers. These aquifer characteristics may increase the possibility of a significant release of organic matter from the aquifer soil resulting in the high content of manganese and iron in the filtrate. For example, manganese and iron were detected in the riverbank filtrate along the Nakdong river^{1,4,7)} in spite of the abundant electron accepting capacity of the river water,^{1,7)} which suggests that a significant amount of organic release takes place from the soil in the aquifer.

There are not many studies on the organic release from the aquifer soil in ground water and/or riverbank filtration. Kinzelbach⁸⁾ con-

firmed that the organic carbon in ground water could originate from the aquifer soil in addition to the introduction from outside sources and the release from dead bacteria. Doussan⁶⁾ reported that the organic matter attached on the soil surface should be first hydrolyzed and dissolved before it was used by microbes, and that the denitrification could be used to remove the nitrate in riverbank filtration without any adverse side effects if the soil organic content and the flow velocity were appropriate. Lensing⁹⁾ modeled the oxidation-reduction in ground water by microbes assuming the relationship between the dissolved organic carbon level and the organic content in the soil to be 1st order reactions. Gerlach and Gimble¹⁰⁾ reported that the adsorption of organic matter on the soil surface could be analyzed by the adsorption isotherm.

The retardation factor is most frequently employed in the analyses of contaminant transport in most ground waters.¹¹⁾ However, in the vicinity of high production wells such as riverbank/bed filtration sites the kinetic approach should be used because the flow velocity is relatively high compared to the reaction rates of adsorption and desorption resulting in the

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collapse of the equilibrium distribution of the contaminants between water and soil phases.¹²⁾

In this study, a kinetic approach through mathematical modeling and experiments was employed to investigate the release of organic matter from aquifer soil in hope of the quantification of organic release in aquifer and the estimation of detention time for manganese and iron not to be dissolved in the riverbank/bed filtrate.

MATERIALS AND METHODS

The experiments were divided into two categories. The first was a kinetic experiment to measure the organic release from soil and the second was to measure the equilibrium distribution of organic matter between water and soil phases. Some preliminary experiments were also carried out before the two experiments. The soil was obtained from a riverbed of the Nakdong river near Hyonpoong. The soil was washed in distilled water to remove colloidal particles, dried for 48 hours at 40°C, and kept in a desiccator before use. The soil contained 87.0% sand, 12.7% silt, and 0.3% clay by weight. About 20g and 1g of the soil samples were analyzed for Chemical Oxygen Demand(COD) and organic content of the soil, respectively. The organic content was regarded as the difference between the weights before and after the ignition in a furnace for 2 hours at 360°C.¹³⁾ About 1g of the soil, after the ignition, was also analyzed for COD. In order to investigate the biodegradability of the dissolved organic matter about 460g of the soil was put in 1L glass bottle along with 800mL of distilled water. Then the glass bottle was kept rolling at 6 rpm for agitation in a room controlled at a constant temperature of 4°C. After 5 hours of agitation the water sample from the bottle was taken and centrifuged for 5 minutes at 300 rpm to obtain clear water to be analyzed for COD and BOD₅.

In the kinetic experiment the soil sample of 280g was put in a 1.1L bottle together with 900mL of distilled water. The soil sample was

evenly divided into 7 parts, each of which was wrapped with #100 stainless steel mesh. The glass bottle was treated with 1N HCl solution and rinsed with distilled water before the use. In order to prohibit the microbial activity in the bottle during the experiment, HgCl₂ was added to reach 0.05% in its concentration.¹⁴⁾ The bottle was agitated by rolling for 3 minutes a day at 6 rpm and was kept calm for the rest of time. Eight mL of water samples were drawn every 3 days from the bottle for 30 days. The samples were centrifuged for 5 minutes at 300 rpm and were analyzed for COD. This experiment was performed in triplicate.

A similar methodology to the kinetic experiment was applied in the equilibrium distribution experiment. Varying amounts of soil samples together with 250mL of distilled water were put in each of 15 BOD bottles of 300mL capacity. The same treatment methods were applied for the glass bottles, the solution and soil, and the agitation as those for the kinetic experiment. After 30 days the water samples were taken, centrifuged and analyzed for COD. The remaining CODs of the soil in the bottles were also measured. COD and BOD₅ were determined according to the Standard Method,¹⁵⁾ and the soil particles were directly used in the measurement of the soil COD. All the experiments were performed at a room temperature of 20±1°C.

RESULTS AND DISCUSSION

The organic content of the soil was 0.28% (number of sample, n = 9, standard deviation, s = 0.03%) by weight. The soil COD before the ignition was 2737(n = 12, s = 245)mg-COD/kg-Soil. The one after the ignition was 233(n = 12, s = 38)mg-COD/kg-Soil. Hence the COD caused only by the organic matter in the soil phase could be regarded as 2504mg-COD/kg-Soil, and the COD of the organic matter attached to the soil was calculated as 0.89mg-COD/mg-OM(Organic Matter). From this we can obtain 0.33mg-C/mg-OM for the organic carbon

content of the soil organic matter if the COD of the soil organic matter is caused only by the organic carbon, which is smaller than 0.58mg-C/mg-OM for the normal soil and 0.4mg-C/mg-OM reported for the deep soils.¹⁶⁾ The COD and BOD₅ of the dissolved organic matter were averaged as 4.3mg/L and 2.8mg/L, respectively, from 7 measurements for each, which results in 65% as the BOD₅/COD ratio. The COD and BOD₅ of the water samples obtained from the riverbed of the Kumho river were 4~7mg/L and 0.4~2.1mg/L, respectively, yielding 10~35% as the BOD₅/COD ratio.²⁾ The higher value in this study was presumably caused by the prohibition of the microbial activity in this study.

Adsorption and desorption of organic matter on the interface between water and soil phases in a closed system was schematically shown in Figure 1 to analyze the phenomenon kinetically. Adsorption reaction on the soil phase may be modeled as¹⁷⁾

$$r_1 = k_1 C \tag{1}$$

and the transfer of organic matter from soil to water phase can be modeled as

$$r_2 = k_2 S \tag{2}$$

assuming the reaction to be 1st order,¹⁸⁾ where r_1 is the adsorption reaction rate (mg-COD/L-sec), r_2 means the desorption reaction rate (mg-COD/Kg-sec), k_1 and k_2 represent, respectively, the adsorption and desorption reaction rate constants with the same unit of 1/sec, and C and S express the organic content in water (mg-COD/L) and soil phases (mg-COD/Kg-Soil), respectively. The 1st order reaction employed in equation (1) can be justified by the result of the linear equilibrium distribution of organic matter between the two phases as shown in Figure 2.¹⁹⁾ When soil comes in contact with clean water in a closed system organic matter starts to be dissolved into the water phase and also the

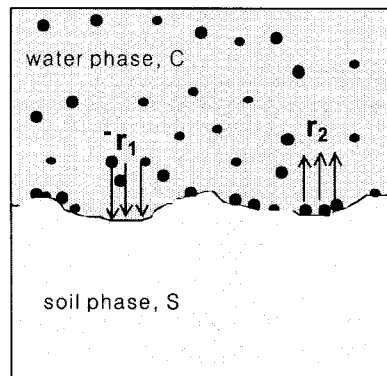


Figure 1. Schematization of mass transfer kinetics between water and soil phases in a closed system.

organic matter in the water phase starts to adsorb on the soil surface. Based on the mass balance the change in concentrations of organic matter in the water and soil phases can be, respectively, described along the contact time as²⁰⁾

$$\frac{dC}{dt} = -k_1 C + \frac{M_s}{V_w} k_2 S \tag{3}$$

and

$$\frac{dS}{dt} = -k_2 S + \frac{V_w}{M_s} k_1 C \tag{4}$$

where V_w is the volume of the water phase (L) and M_s denotes the mass of the soil phase (kg). If the contact time is enough the adsorption rate will approach to the desorption rate resulting in the equilibrium distribution of which the relationship between the two concentrations can be described as¹⁹⁾ $S = K_d C$ where $K_d = \frac{k_1 V_w}{k_2 M_s}$ means the ratio of the adsorption to desorption rates or the equilibrium distribution coefficient (L-water/Kg-soil).

The experimental results of the equilibrium distribution between the water and soil phases was shown in Figure 2, where the solid line denotes $S = K_d C$. The best matching K_d value with the experimental data was obtained as 890L-water/Kg-soil.

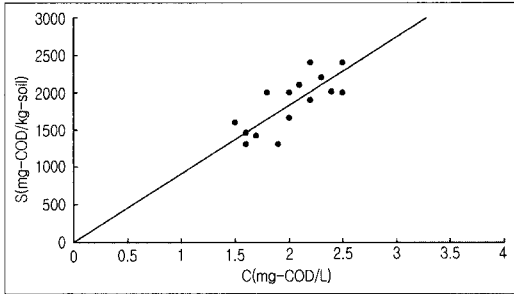


Figure 2. Equilibrium distribution of organic matter between water and soil phases.

Results of the kinetic experiments are shown in Figure 3 along with the solution to equation (3). From the curve fitting with experimental data, the best k_1 and k_2 values were obtained as $1.5 \times 10^{-6}/\text{sec}$ and $5.4 \times 10^{-9}/\text{sec}$, respectively. Preliminary experiments showed that the agitation strength had a great influence on the dissolution of the organic matter, which suggests that the organic release in the aquifer may be greatly influenced by the filtration velocity and that there could be a significant error involved in this study unless the agitation strength matches well with the real flow in the riverbank/bed filtration. The Runge-Kutta method was used in the analysis of each of the equations (3) and (4)²¹⁾ and the sequential solution technique was employed in the simultaneous analysis of the two equations.²²⁾ From Figure 3, it was seen that 30 days was required for the distribution of the organic matter to equilibrate between the two phases.

If a long detention time is applied to the

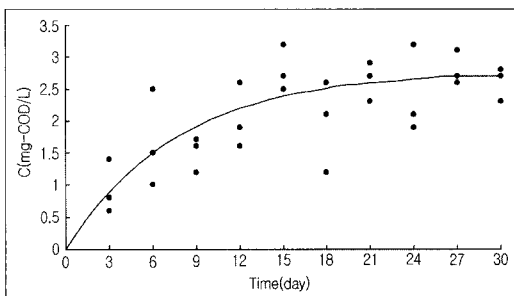


Figure 3. Comparison of model prediction with experimental data of water phase concentration of organic matter released from soil phase.

RBF in Korea, high concentration of organic matter can be released from soil phase during the passage. The release rate can be estimated by equation (3). Assuming the organic content of the filtrate to be 5mg-COD/L ²⁾ and the soil organic content to be 0.3%, which are typical of the situation in Korea, the organic release rate in the aquifer is estimated as 4.7mg-COD/L-day or $3.1\text{mg-BOD}_5/\text{L-day}$ based on the results of this study.

Riverbank filtration exploits the biodegradation of organic matter during the migration in the aquifer using the oxygen supplied through the permeable soil from the atmosphere.³⁾ In Korea, the conditions are not favorable in terms of the oxygen supply due to several factors including the low permeability of the soil, the concentrated precipitation during monsoon, and the deep water table. These unfavorable conditions can readily cause the dissolution of manganese and iron in the riverbank filtrate due to the deficiency of the electron acceptors if the production wells are located away from the river.

The riverbed filtration was developed in Korea in order to overcome the problems occurring in the riverbank filtration.^{2,23)} Contrary to the riverbank filtration there is no chance of the oxygen supply from the atmosphere in the riverbed filtration. In other words, manganese and iron start to dissolve as the electron acceptors infiltrating together with the river water such as the dissolved oxygen and nitrate are depleted. Since the required soil depth for about 10mg/L of BOD to be decomposed is less than 2m ,²³⁾ the organic release from the soil is expected to take a major role in the electron donor supply in deeper soil. In the case of the Nakdong river, the average total amount of the electron acceptors is larger than that of the donor in the river water by about $13\text{mg-O}_2/\text{L}$.⁶⁾ If the organic release rate, about 3.1mg/L , obtained in this study is applied to the case, the appropriate detention time for the excessive electron acceptors (mostly nitrate) to be depleted and for the filtrate not to contain manganese and

iron is 4~5 days. However, this estimation should be used with caution as the conditions in the riverbank/bed filtration sites may differ from the ones in this study.

CONCLUSION

The organic release rate coefficient from the aquifer soil used in this study was 5.4×10^{-9} /sec, and using this value the organic release rate in the riverbank filtration in the Nakdong river was estimated as 4.7mg-COD/L-day or 3.1mg-BOD₅/L-day. From this estimation, it can be seen that manganese and iron start to be dissolved in the filtrate in about 5 days of detention time in the aquifer. It was also seen that the COD and the BOD₅/COD ratio of the soil organic matter were 0.89mg-COD/mg-OM and 65%, respectively. When the result of this study is applied to a riverbank/bed filtration the different conditions should be first taken into consideration.

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