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Modeling the formation of soluble microbial products (SMP) in drinking water biofiltration

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Abstract: Both a theoretical and an empirical model were developed for predicting the formation of soluble microbial products (SMP) during drinking water biofiltration. Four pilot-scale biofilters with ceramsite as the medium were fed with different acetate loadings for the determination of SMP formation. Using numerically simulated and measured parameters, the theoretical model was developed according to the substrate and biomass balance. The results of this model matched the measured data better for higher SMP formation but did not fit well when SMP formation was lower. In order to better simulate the reality and overcome the difficulties of measuring the kinetic parameters, a simpler empirical model was also developed. In this model, SMP formation was expressed as a function of fed organic loadings and the depth of the medium, and a much better fit was obtained.

Key words: *drinking water*; *biofiltration*; *soluble microbial products* (*SMP*); *mathematical modeling*

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1 Introduction

Nowadays biofiltration is widely used in drinking water treatment as a supplement or enhancement of the conventional treatment (Wang and Liu 1999; Urfer et al. 1997). Biofilters have dual functions: one is reducing the turbidity and pathogen particles like the conventional filters, and the other is removing the biodegradable organic matter (BOM) and other bioavailable materials through the microbial metabolism of the biofilm attached to the media. The latter function currently draws more attention because the micro-pollution of source water with BOM has become a common problem in many countries, especially in economically booming ones (Wang and Liu 1999).

The microbes do not only eliminate the substrate from the influent, they can also excrete or release some organic compounds, the so-called soluble microbial products (SMP), into the extracellular environment during substrate utilization and biomass decay (Barker and Stuckey 1999). In fact, SMP were first found and thoroughly investigated in wastewater biological treatment (Barker and Stuckey 1999). It was revealed that SMP sometimes consist of most of the effluent of the wastewater bioreactor. The composition of SMP is very complicated, and includes humic and fulvic acids, polysaccharides, proteins, nucleic acids, amino acids, organic

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acids, steroids, antibiotics, extracellular enzymes, and siderophores (Barker and Stuckey 1999; Manka and Rebhun 1982). SMP in wastewater are usually refractory or less biodegradable, except for some newly formed substrate-utilization-associated products (UAP). Their molecular weight is distributed around "dual peaks" (greater than 100 000 or lower than 1 000) (Kuo and Parkin 1996). SMP can also act as a chelating reagent and have a toxic effect on the activity of the biomass (Kuo and Parkin 1996; Huang et al. 2000).

In contrast to what is known about SMP formation in wastewater treatment, the research on SMP formation in drinking water treatment is very limited. Only a few related references can be found, of which the work by Carlson and Amy (2000) might be the most important. They investigated SMP with mathematical modeling and direct measurement and regarded SMP as an important factor in the underestimation of dissolved organic carbon (DOC) removal in biofiltration. However, many more characteristics of SMP in drinking water biotreatment remain unrevealed. Since drinking water is so important to human health, more work should be done on this theme. In this study, efforts were directed toward establishing models of SMP formation during drinking water biofiltration with acetate as the sole carbon source, based on pilot-scale reactors. Both a theoretical and an empirical model were developed, and the results were compared in order to approach the true SMP profiles.

2 Materials and methods

2.1 Pilot-scale biofilter system

The experimental system contained four parallel biofilters (Figure 1) with ceramsite as the medium. The influent to the reactors was tap water. First, the organic matter in the tap water was removed through granular activated carbon filtration. Then, a sodium acetate solution was fed into the influent as the carbon source. The final concentrations of acetate in the influent were 1.0, 0.5 and 0.2 mg/L, in biofilters A, B and C, respectively. These concentrations of acetate were converted into the concentrations of carbon. Biofilter D was used as the blank control and no acetate was added to it. The other parameters of the biofilters can be seen in Table 1. All four reactors were run for about two months before this study began to guarantee that they would be in a steady state while the study was being conducted.

Table 1 Parameters of biofilters A-D

Item	Value	Item	Value
Empty bed contact time (EBCT)	10 min	Depth of water	1 100 mm
Diameter	60 mm	Interval of adjacent sampling ports	150 mm
Height of the medium (ceramsite)	750 mm	Flow rate	20 L/h
Diameter of ceramsite	2-3 mm	Backwash cycle	24 h

2.2 Analytical method

COD_{Mn} and NH_4^+-N were measured using standard Chinese methods (SEPA 2002).

Biomass was determined with the phospholipids analysis method (Yu et al. 2002). The concentration of acetate was measured with an ion chromatography analyzer (DX-100, Dionex, U.S.A.). DOC was measured using a TOC (total organic carbon) analyzer (TOC-5000, SHIMADZU, Japan).

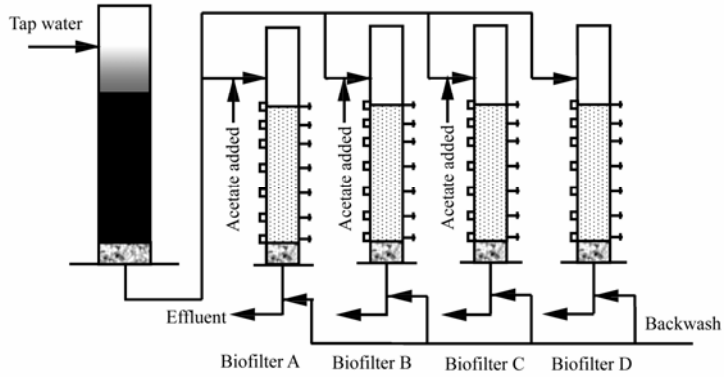

Figure 1 Schematic of the experimental system

2.3 SMP calculation

The concentration of SMP is expressed as the concentration of DOC in this study. After pretreatment of granular carbon and addition of acetate, the DOC in the influent to each of the biofilters consisted of the following components:

$$\rho(\mathrm{DOC_{inf}})=\rho(\mathrm{NBDOC})+\rho(\mathrm{BOM_{inf}}) \tag{1}$$

where $\rho(\mathrm{DOC_{inf}})$ is the concentration of dissolved organic carbon in the influent (μg/L), $\rho(\mathrm{NBDOC})$ is the concentration of non-biodegradable dissolved organic carbon in the influent (μg/L), and $\rho(\mathrm{BOM_{inf}})$ is the concentration of biodegradable organic matter in the influent (μg/L).

The DOC from the No. *n* sampling port was

$$\rho(\mathrm{DOC}_n)=\rho(\mathrm{NBDOC})+\rho(\mathrm{BOM}_n)+\rho(\mathrm{SMP}_n) \tag{2}$$

where $\rho(\mathrm{DOC}_n)$ is the concentration of dissolved organic carbon of the No. *n* sampling port (or effluent) (μg/L), $\rho(\mathrm{BOM}_n)$ is the concentration of biodegradable organic matter of the No. *n* sampling port (μg/L), and $\rho(\mathrm{SMP}_n)$ is the concentration of soluble microbial products of the No. *n* sampling port, the biodegradable fraction included (μg/L).

Combining Eqs. (1) and (2), the SMP were calculated with Eq. (3):

$$\rho(\mathrm{SMP}_n)=\left[\rho(\mathrm{BOM_{inf}})-\rho(\mathrm{BOM}_n)\right]-\left[\rho(\mathrm{DOC_{inf}})-\rho(\mathrm{DOC}_n)\right] \tag{3}$$

The completely formed SMP (SMP_{n0}) might have been somewhat greater than SMP_n because a portion of the SMP were biodegraded during filtration. SMP_{n0} can be expressed as the sum of the following items (Eq. (4)):

$$\rho(\mathrm{SMP}_{n0})=\left[\rho(\mathrm{BOM_{inf}})-\rho(\mathrm{BOM}_n)\right]-\left[\rho(\mathrm{DOC_{inf}})-\rho(\mathrm{DOC_n})\right]+r_{\mathrm{BAP}}+r_{\mathrm{UAP}} \tag{4}$$

where $\rho(\mathrm{SMP}_{n0})$ is the concentration of the total formation of SMP in the No. *n* sampling port, the biodegradable fraction included (μg/L), and r_{BAP} and r_{UAP} are biomass-associated products (BAP) and UAP formation (μg/L), respectively.

However, the majority of SMP were usually regarded as refractory organic matter, and r_{BAP} and r_{UAP} were neglected in many cases. Furthermore, the biodegraded SMP could not be determined, since they were removed and did not exist in the effluent. Therefore, in this study, SMP refers to the fraction determined from Eq. (3).

Since sodium acetate was the only carbon source added to the biofilters, its concentration is represented in the BOM level from Eq. (2).

3 Model development

3.1 Kinetics of substrate degradation

The BOM degradation along the depth of the biofilter can be expressed based on Monod kinetics by Eq. (5):

$$v\frac{\mathrm{d}\rho(\mathrm{BOM})}{\mathrm{d}z}=-q_{\mathrm{m}}\frac{\rho(\mathrm{BOM})}{K+\rho(\mathrm{BOM})}X \tag{5}$$

where v is the hydraulic loading rate (cm/min), z is the depth of the filter (cm), q_{m} is the maximum rate of BOM degradation by cells (μg/(μg·min)), X is carbon biomass (μg/L), and K is the half-maximum rate concentration for BOM degradation (μg/L).

3.2 Kinetics of SMP generation and degradation

Generally, SMP can be divided into two subcategories: UAP and BAP (Rittmann and McCarty 2001). UAP are produced during substrate metabolism and biomass growth, at a rate proportional to substrate utilization, while BAP are formed from biomass decay and endogenous respiration at a rate proportional to the concentration of biomass. According to this definition, the UAP and BAP formation rate expression is

$$r_{\mathrm{UAP}}=-k_{\mathrm{UAP}}r_{\mathrm{ut}}=k_{\mathrm{UAP}}q_{\mathrm{m}}\frac{\rho(\mathrm{BOM})}{K+\rho(\mathrm{BOM})}X \tag{6}$$

$$r_{\mathrm{BAP}}=k_{\mathrm{BAP}}X \tag{7}$$

where r_{ut} is the substrate degradation rate (μg/(min·L)), k_{BAP} is the BAP formation rate constant (μg/(μg·min)), and k_{UAP} is the UAP formation rate constant (μg/μg).

Most research on their degradation (Rittmann and McCarty 2001; Namkung and Rittmann 1986) suggests that the degradation kinetics of UAP and BAP are so distinct that they can be described with separate Monod-degradation expressions:

$$r_{\mathrm{deg\text{-}UAP}}=-\frac{q_{\mathrm{UAP}}\rho(\mathrm{UAP})}{K_{\mathrm{UAP}}+\rho(\mathrm{UAP})}X \tag{8}$$

$$r_{\text{deg-BAP}} = -\frac{q_{\text{BAP}}\rho(\text{BAP})}{K_{\text{BAP}} + \rho(\text{BAP})}X \tag{9}$$

where $r_{\text{deg-BAP}}$ and $r_{\text{deg-UAP}}$ are the BAP and UAP degradation rate (μg/(min·L)), respectively; q_{UAP} and q_{BAP} are the maximum rates of UAP and BAP degradation by cells (μg/(μg·min)), respectively; and K_{UAP} and K_{BAP} are the half-maximum rate concentrations for UAP and BAP degradation (μg/L), respectively.

Therefore, the kinetics of SMP (UAP and BAP) generation and degradation along the depth of the biofilters can be described as follows:

$$v\frac{\mathrm{d}\rho(\text{UAP})}{\mathrm{d}z} = k_{\text{UAP}}q_{\text{m}}\frac{\rho(\text{BOM})}{K + \rho(\text{BOM})}X - q_{\text{UAP}}\frac{\rho(\text{UAP})}{K_{\text{UAP}} + \rho(\text{UAP})}X \tag{10}$$

$$v\frac{\mathrm{d}\rho(\text{BAP})}{\mathrm{d}z} = k_{\text{BAP}}X - q_{\text{BAP}}\frac{\rho(\text{BAP})}{K_{\text{BAP}} + \rho(\text{BAP})}X \tag{11}$$

3.3 Biomass balance equations

The generation of biomass in the reactors can be divided into two processes:

(1) the synthesis of biomass due to substrate utilization:

$$B_{\text{gen1}} = Yq_{\text{m}}\frac{\rho(\text{BOM})}{K + \rho(\text{BOM})}X \tag{12}$$

where Y is the growth yield of cells associated with BOM (μg/μg); and

(2) the synthesis of biomass due to UAP and BAP utilization:

$$B_{\text{gen2}} = Y_{\text{smp}}\left[q_{\text{UAP}}\frac{\rho(\text{UAP})}{K_{\text{UAP}} + \rho(\text{UAP})} + q_{\text{BAP}}\frac{\rho(\text{BAP})}{K_{\text{BAP}} + \rho(\text{BAP})}\right]X \tag{13}$$

where Y_{smp} is the growth yield of cells associated with SMP (μg/μg).

The degradation of biomass in the reactors can be divided into three parts:

(1) the endogenous decay of biomass: $B_{\text{deg1}} = bX$ (14)

where b is the biomass endogenous decay coefficient (min^{-1});

(2) the biomass that is converted into SMP: $B_{\text{deg2}} = k_{\text{BAP}}X$ (15)

(3) the biomass taken away by the backwash current: $B_{\text{deg3}} = a_{\text{cells}}X$ (16)

where a_{cells} is the rate of removal of biomass from media during backwash (min^{-1}).

Because the biofilters were run in a steady state, the biomass followed the balance equations:

$$B_{\text{gen1}} + B_{\text{gen2}} = B_{\text{deg1}} + B_{\text{deg2}} + B_{\text{deg3}} \tag{17}$$

and,

$$Yq_{\text{m}}\frac{\rho(\text{BOM})}{K + \rho(\text{BOM})}X + Y_{\text{smp}}\left[q_{\text{UAP}}\frac{\rho(\text{UAP})}{K_{\text{UAP}} + \rho(\text{UAP})} + q_{\text{BAP}}\frac{\rho(\text{BAP})}{K_{\text{BAP}} + \rho(\text{BAP})}\right]X = bX + k_{\text{BAP}}X + a_{\text{cells}}X \tag{18}$$

Eqs. (5), (10), (11) and (18) comprise the SMP kinetics set, which has also been used in

similar studies (Carlson and Amy 2000).

4 Results and discussion

Table 2 shows the units and values of the parameters necessary for the model quantification. Some of the parameter values were determined directly in this study, while others were adopted from published references (Rittmann and McCarty 2001; Namkung and Rittmann 1986). It was shown that parameter values would change with the water quality and the components of biomass. In this study, we found that the model results were significantly impacted by the value of k_{UAP}. Therefore, its value was adjusted through the following methods to make the simulation match the determined results: the reported value of k_{UAP} was input into the model and SMP were computed. Then, the model output value was compared with the measured value. According to the comparison results, the k_{UAP} was adjusted by a step of 0.01 and then input into the model, and the same process was repeated until a satisfactory result was obtained.

Table 2 Parameter values for the model

Parameter	Value	Parameter	Value
q_{UAP}	0.9×10^{-3} μg/(μg·min)	Y	0.6 μg/μg
q_{BAP}	1.39×10^{-3} μg/(μg·min)	Y_{smp}	0.6 μg/μg
K_{UAP}	2.1×10^{4} μg/L	z	Determined
K_{BAP}	1.4×10^{4} μg/L	v	Determined
k_{UAP}	0.04 μg/μg	$\rho(\mathrm{DOC})$	Determined
k_{BAP}	4.89×10^{-5} μg/(μg·min)	X^{*}	Determined

*The units of determined biomass were nmol/cm^3 of phosphrus. Before the model reached a solution, the units were converted, according to the empirical bacterial molecular formula ($C_{55}H_{77}O_{22}N_{11}P$) (Rittmann and McCarty 2001), into μg/L of carbon, as used in the model.

Figure 2 shows the trends of measured and simulated SMP accumulation along the filter depths for the three different reactors, biofilters A, B and C. It can be seen that the concentration of SMP increased with the increase of the biofilter depth. SMP concentrations also increased with the substrate concentrations in the influent. Biofilter A, with the most acetate added to the influent (1.0 mg/L), had the highest SMP level, up to 38.0 μg/L. Biofilter B, with the moderate acetate addition of 0.5 mg/L, had an SMP accumulation of 28.8 μg/L. Biofilter C, with the lowest addition of 0.2 mg/L, had the lowest SMP accumulation in the effluent of 18.8 μg/L. When the acetate addition and SMP formation was higher, the simulated SMP fit the measured SMP better. The error became more significant with lower organic loading and SMP formation. For Biofilter A, the relative error of the simulation increased to 7.63% at the deepest sampling port. However, the corresponding values for biofilters B and C were 19.10% and 43.62%, respectively. Because some of the important kinetic parameters, such as r_{BAP} and r_{UAP}, could not be determined in this study, the only way to obtain them was from references. The relative errors originating from these parameters were magnified when the input organic loading decreased. This might be the reason for the error trends.

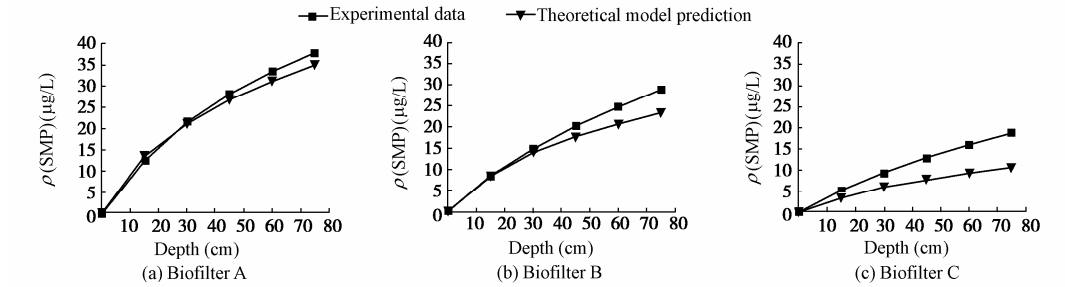

Figure 2 Model prediction and measured SMP of the biofilters

The theoretical model of SMP formation and degradation had sufficient microbiological rationale. However, as mentioned above, the parameters in the model were difficult to determine, especially in the drinking water biological treatment system, because of the low levels of substrate and microbial biomass.

From analysis of the SMP data, it can be concluded that more SMP accumulated with greater depth of the medium, and SMP accumulation was higher when there was more substrate in the influent. The depth of the medium and the initial organic load (BOM_0) were evidently the two key factors influencing SMP accumulation. The biomass level might be another candidate, but it was also influenced by the depth of the medium and the organic loading. Therefore, SMP is a function of the depth of the medium and BOM_0, i.e., $\rho(\mathrm{SMP}) = f\left[\rho(\mathrm{BOM}_0), z\right]$.

After various attempts, an obvious linear relationship (R^2>0.99) between the reciprocal of SMP concentration and the depth of the medium was found. It can be expressed as follows:

$$\frac{1}{\rho(\mathrm{SMP})} = a\frac{1}{z} + b \tag{19}$$

and,

$$\rho(\mathrm{SMP}) = A\frac{z}{B+z} \tag{20}$$

where A, B, a, and b are parameters relevant to BOM_0, and z is the numerical value of the biofilter depth.

Linear and logarithmic data-fitting methods were applied to deal with the experimental data to describe the relationships between A, B, and BOM_0:

$$A = 25.90\ln\rho(\mathrm{BOM}_0) - 100.85 \tag{21}$$

$$B = 173.19 - 0.09\rho(\mathrm{BOM}_0) \tag{22}$$

Eqs. (20), (21) and (22) can be combined:

$$\rho(\mathrm{SMP}) = \frac{25.90z\ln\rho(\mathrm{BOM}_0) - 100.85z}{173.19 + z - 0.09\rho(\mathrm{BOM}_0)} \tag{23}$$

The fit between the empirical model simulation and the experimental data was satisfactory (Figure 3).

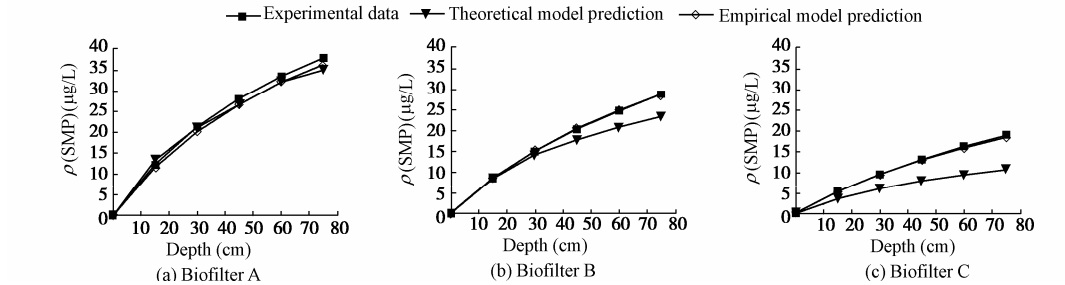

Figure 3 Empirical model prediction, theoretical prediction and measured SMP of the biofilters

These results indicate that the data generated by the empirical model matched the measured data better than the theoretical model data. But attention should be paid to the fact that the constants in the empirical model were obtained completely through numerical calculation, which could not reveal the microbiological rationale. In fact, *A* and *B* in Eqs. (19) through (22) comprise several microbial kinetic parameters dependent on community structures, so if the empirical model is applied in other cases, the constants should be adjusted, due to possible changes of the microbial consortium and different kinetics.

SMP are important in both drinking water and wastewater biological processes. As mentioned in the introduction, the characteristics of SMP in wastewater systems are much better understood than those in drinking water systems, but the available knowledge about wastewater cannot be directly applied to drinking water in many cases due to the huge differences in the composition of the pollutant reservoir and in the pollutant concentrations, and hence in the microbial communities. It is not redundant to develop the model of SMP in drinking water systems through the existing counterpart in wastewater systems. The authors have also tried to investigate the organic composition of SMP and found several short-chain fatty acids and many other peaks in the GC-MS profile that cannot be identified, which may introduce potential acute and genetic risks into drinking water. The model developed in this study should be helpful in controlling SMP formation during drinking water biological processes.

5 Conclusions

A theoretical model for predicting the formation of SMP in drinking water biofiltration was developed based on the substrate and biomass balance. Through numerical simulation and experimental determination, the appropriate parameter values were obtained. The results matched the measured data better when the measured SMP accumulation was higher, and the error became more significant with lower measured SMP formation.

A much simpler empirical model that did not measure the kinetic parameters was also developed, in which SMP were expressed as a function of the fed organic loading and the depth of the medium. The empirical model can better simulate the SMP formation, but constants in the model applied in other cases should be recalculated due to the possible

microbial and water quality changes.

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