Modeling sulfide production in full flow concrete sewers based on the HRT variation of sewerage

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ABSTRACT

The corrosion and odor in concrete sewers are mainly related to the sulfide production, which is, under certain circumstances, directly proportional to the hydraulic retention time (HRT) of the sewer. To reduce the corrosion and control the odor in concrete sewers, it is necessary to model the production of sulfide in the concrete sewers with different HRTs. However, previous researches were mostly carried out in simulated Perspex-made sewers, and the obtained theoretical formulas based on the Monod equation were impractical because of the complexity. An actual concrete pipe with domestic sewage was employed in this study to obtain a simple but practical model, which can be applied to quantitively describe the sulfide production according to the HRT of the sewer and the chemical oxygen demand (COD) of the sewage. The empirical equation obtained was \( r_s = (0.045 \times \ln \text{HRT} + 0.071) \times \left(\frac{[\text{COD}]}{C_0}\right)^{0.6} \), the coefficient is a logarithmic function of the HRT, and the sulfide production rate and COD have a power relationship. Based on the data of COD and HRT obtained in the realistic sewer, the production of sulfide in the sewer can be predicted for better maintaining sewers through sulfide control.

Key words | COD, concrete sewer, HRT, modeling, sulfide

HIGHLIGHTS

- An actual concrete pipe was used to evaluate the effect of HRT on the variation of pollutants.
- Few degradations of nitrogen and phosphorus in an actual concrete pipe were found with HRT.
- The degradation of COD in an actual concrete pipe accorded with the first-order reaction law.
- Sulfide production rate was the power function of solute COD, and the coefficient is the logarithmic function of the HRT.
INTRODUCTION

The municipal drainage system is an important infrastructure including septic tanks, sewer networks, pumping stations, sewage treatment plants, and other facilities; among them, the sewer network has played a key role in collecting and transporting sewage and stormwater. In China, the total length of sewer was 577,000 km by the end of 2016 (NBSC 2016), and the sewage treatment rate had reached 94.5% in 2018. However, the quality of the water environment in China has not improved significantly; it can be implied that many pollutants have not been effectively collected and discharged directly into the environment. Compared with developed countries such as Japan and Germany, China has a rather lower intact sewer rate (Huang et al. 2018), which is mainly caused by the insufficient construction, irregular inspection, and maintenance of the sewers in China, especially the lack of the control of sewer corrosion. The long-distance transportation of sewage and the nearly closed state of urban sewers has resulted in the accumulation of harmful gas, including that most concerned, H₂S (Talaiekhozani et al. 2016). It is reported that the concentration of H₂S in actual sewers can reach 12 mg/L (Eijo-Río et al. 2015), which accordingly corrodes the sewer structure and leads to sewage leakage and groundwater infiltration (Pikaar et al. 2014). Moreover, it endangers the quality of the water environment and possibly results in urban waterlogging. Simultaneously, the degradation of organic pollutants by microorganisms in sewers may result in chemical oxygen demand (COD) concentrations in the influent and thus affect the biological nitrogen removal of downstream sewage treatment plants.

Most of China’s sewer pipes are made of concrete, which has a rough surface and large specific surface area, which is favorable for the growth of heterotrophic bacteria. In pressure mains, which are completely anaerobic, complex organic matters of macromolecules can be hydrolyzed into fermentable and rapid biodegradable substrate, and further fermented into volatile fatty acids (VFAs). In the sewage drainage system, H₂S is mainly from the anaerobic reduction of sulfate by sulfate-reducing bacteria (SRB). Due to a low velocity of sewage and a long hydraulic retention time (HRT), organic or inorganic suspended solids in the sewage will deposit at the bottom of the pipe and form an anaerobic sludge layer. Moreover, SRB, which accounted for 20% of the total bacteria on the biofilm (Sun et al. 2014), can convert sulfate in the raw sewage into sulfide with the help of electron donors such as hydrogen, acetic acid, and short-chain fatty acids. As the HRT of the sewage in the drainage pipe increases, more organic matter is degraded and more suspended solids are deposited, which accelerates the formation of the anaerobic sludge layer at the bottom of the pipe and the production of sulfide converted by the SRB in the sewer. Thus, it can be implied that HRT has a positive relationship with the sulfide (especially H₂S) released in the pipe. The amount of sulfide produced in
sewers can be simplified as the product of sulfide production rate and HRT. HRT is defined as the time a certain sample spends in the sewer, which is usually calculated by the ratio of pipe length and average velocity. For a given pipe (the diameter and length are determined), the HRT of the pressure mains is determined by the pumping rate and pumping frequency. Generally, when there is no significant change in the composition and number of microorganisms on the biofilm, the rate of sulfide production remains unchanged. However, as the concentration of substrate varies under different HRT, the microorganisms on the biofilm may change, which leads to different sulfide production rates. Moreover, the sulfide production is inhibited by oxygen, nitrate/nitrite, alkali, and metal salts, etc. (Zhang et al. 2008), and HRT has an impact on the inhibitor concentration and contact time with inhibitors. Therefore, HRT is an important kinetic parameter highly related to the degradation of pollutants and the production of sulfide.

Researchers have established models between HRT and sulfide production in sewers (Sharma et al. 2008); however, with parameters difficult to measure, some of the existing models are not suitable for practical applications. To better guide sewer maintenance work, it is necessary to build a simple and practical model based on parameters obtained easily in the actual maintenance work. Besides, most laboratory-scale experiments were conducted in reactors made of Perspex, which is different from concrete pipes in roughness and pH, providing a distinct environment for microorganisms. However, there is limited research on the effect of concrete sewers on the degradation of pollutants and the production of sulfide. To better simulate the municipal sewer network, an actual concrete pipe section was applied in this study, and the effect of HRT on COD consumption and sulfide production rates was quantitatively evaluated. This study provides a convenient and accurate way to evaluate the rate of sulfide production and COD consumption, and helps to further formulate pertinent maintenance measures.

MATERIALS AND METHODS

Experimental sewer reactor setup and operation

Sections of concrete sewers were used to study the law of the pollutant degradation and sulfide production in the actual sewer network. The schematic and practical images of the experimental setup are shown in Figure 1. The sewer reactor used in this study was made of a reinforced concrete pipe section that had been used in the actual municipal sewer network for several years. With a length of 0.23 m and a cross-sectional diameter of 0.28 m, the reactor was wheel-shaped, and two Perspex flanges (Φ 0.50 m) were installed at both ends. Four holes were opened on the top of the reactor to insert inlet and outlet pipes, stirrers, and DO probes. During each HRT, 14.7 L of domestic sewage was pumped into the reactor by a peristaltic pump (LONGER BT300-2 J), which was collected from the main well of a campus (Renmin University of China) and heated to 20°C before being pumped in. DO in the reactor was maintained at 0 mg/L except for the gap of sewage exchange. The stirring simulated the shear force of the
sewage flow on the biofilm and the actual sewer can be seen as a series of these reactors.

Wastewater characteristics

The sewer reactor was fed with wastewater collected from the main well of a campus (Renmin University of China). Wastewater withdrawn from the main well was immediately transported to the laboratory and stored in a cold box to minimize the biological activity, thus the composition of wastewater remained stable. The influent wastewater contained 77.43 ± 6.82 mg/L NH₄⁺-N, 86.74 ± 3.97 mg/L TN, 7.90 ± 0.77 mg/L TP, 315.31 ± 39.96 mg/L COD, and 51.86 ± 5.89 mg/L SO₄²⁻, with slight fluctuations among experimental groups.

Experimental procedures

The choice of HRT takes actual urban sewers into account. Ganigue et al. surveyed 165 chemical dosing sites of sewers in Australia and found that nearly half of the sewers had HRT of 3–12 h (Ganigue et al. 2011). Moreover, the acid-producing bacteria under short HRT are not able to hydrolyze enough macromolecular organic matter into VFAs, resulting in insufficient substrate concentration for SRB. Studies have shown that the anaerobic residence time before the formation of sulfate generally exceeds 2 h (Hvitved-Jacobsen et al. 2002). Therefore, in our study, the HRT was adjusted to 12 h, 10 h, 8 h, 6 h, and 3 h, and the HRT of 10 h was used to examine the model developed.

Analytical methods

Wastewater samples were collected and detected twice a week. Samples were immediately filtered through 0.22 μm filter membranes and stored at 4°C in an icebox until analysis was done. The concentration of COD, total nitrogen (TN), ammonia nitrogen (NH₄⁺-N), and total phosphorus (TP) were respectively analyzed according to standard methods (APHA 2012). The concentration of sulfate and sulfide were monitored using the ion chromatography method by Keller-Lehmann et al. (2006) and Gutierrez et al. (2008). Average values extracted from three parallel experiments were used for data analysis.

RESULTS AND DISCUSSION

The start-up phase of the laboratory-scale sewer system

As shown in Figure 2, during the start-up phase, the removal rate of various pollutants in five experimental groups’ effluent showed an obvious trend. After 25 d of cultivation, the removal rate of COD, TN, and TP had already become stable. The removal rate of sulfate and the effluent concentration of sulfide increased significantly after 15 d of cultivation but stabilized until another 20 d. The growth of most SRB requires VFA as a substrate, and only a few SRB can directly utilize complex organics (Muyzer & Stams 2008). The concrete pipe used in the experiment has been used in the actual urban sewer network for several years, where a small amount of biofilm has already been attached to the inner wall, better simulating the internal environment of actual sewer pipes. Therefore, sulfide can be detected immediately after the injection of wastewater. However, it was only after the acid-producing bacteria were colonized that the amount of SRB would then increase significantly, causing a rapid reduction of sulfate. Auguet’s colonization experiment used actual pipeline biofilm and found that the H₂S production rate increased significantly after 2 weeks (Auguet et al. 2013), which is similar to the results of this experiment.

It can be seen from Table 1 that the removal rate of nitrogen and phosphorus in each experimental group was within 6.0%, and no obvious relationship was found with HRT. The removal of nitrogen and phosphorus pollutants requires a certain aerobic reaction time, while the DO of the experimental group was zero through the experiment, and only a small amount of oxygen entered in the gap of automatic sewage exchange. Therefore, it can be considered that there was little degradation of nitrogen and phosphorus under the conditions of full pipe flow. However, the removal rate of COD and sulfate, and the production of sulfide, were found to positively correlate with HRT. The longer the biological reaction time, the more COD and sulfate were degraded, and the more sulfide was produced. But for the reaction rate, the quantitative relationship needed further investigation.

In full pipe flow, the amount of sulfate consumed should strictly correspond to the amount of sulfide formed following the stoichiometric ratio. Results showed that the average difference between the sulfate formed and the sulfide produced was 0.19 mg S/L in all groups, which could be explained by part of the sulfide being dissipated.
or oxidized by a small amount of sulfur-oxidizing bacteria (SOB) that existed in the biofilm (Liu et al. 2015).

The pollutant removal rate after stabilization in each experimental group is shown in Table 1.

Since SRB can utilize a variety of organic matters as substrates, the stoichiometric relationship between the sulfide formed and the COD consumed was not clear. Based on the most commonly used substrate, acetic acid, the COD consumption per gram of sulfide was assumed to be 2 g COD/g H₂S-S. The proportion of COD consumed by sulfide production during the start-up phase is shown in Figure 3.

As the cultivation time prolonged, the proportion of COD consumed by the production of sulfides gradually increased, and eventually reached about 25%. The previous study

<table>
<thead>
<tr>
<th>Removal rate of major pollutants for each HRT</th>
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<tbody>
<tr>
<td>NH₄-N</td>
</tr>
<tr>
<td>2.28%</td>
</tr>
<tr>
<td>TN</td>
</tr>
<tr>
<td>TP</td>
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<tr>
<td>COD</td>
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<td>SO₄²⁻</td>
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Figure 2 | Removal rate of major pollutants and the effluent concentration of sulfide during the start-up phase of the laboratory-scale sewer system.

Figure 3 | The proportion of COD consumed by sulfide production during the start-up phase.
showed that the soluble COD (sCOD) utilization of sulfide production accounted for 28% of the total sCOD consumed (Guisasola et al. 2008). Since the complex organic matter of total COD was degraded by acid-producing bacteria, the calculated proportion in the present study was slightly smaller than the value reported by the literature (Guisasola et al. 2008). The production of sulfide in sewers is closely related to the degradation of COD. To improve the quality and efficiency of the subsequent sewage treatment plant and reduce the consumption of organic matter in sewers, both the law of COD degradation and sulfide formation should be studied.

The development and verification of the COD degradation model

The development of the COD degradation model

After the continuous cultivation for 60 d, batch tests were carried out to analyze the changes of COD, sulfate, and sulfide. As shown in Figure 4, COD consumption gradually increases as the HRT increases. The COD consumption was 48.2 mg/L when HRT was 3 h, which was increased to 85.7 mg/L at HRT of 12 h. The previous report showed that the degradation process of dissolved carbohydrates followed the first-order reaction, and the reaction constant was related to specific experimental conditions (mainly temperature) (Raunkjær et al. 1995). The same rule can be applied to the present study, where the results of each group were fitted to the following first-order reaction equation

\[ c = c_0 e^{-at} \]  

where \( c_0 \) is the initial COD concentration, \( a \) is the reaction rate constant, which reflected the effect of HRT on COD degradation, and \( t \) is the reaction time.

As can be seen from Figure 4, COD consumption was fitted with the first-order reaction in batch tests. The results showed that reaction rate constant \( a \) were 0.040 h\(^{-1}\), 0.037 h\(^{-1}\), 0.036 h\(^{-1}\), and 0.029 h\(^{-1}\) at the HRT of 3 h, 6 h, 8 h, and 12 h, respectively. The normalized COD

![Figure 4](http://iwaponline.com/wst/article-pdf/83/9/2063/888746/wst083092063.pdf)

**Figure 4** | Changes of COD in batch tests and fitting COD consumption with the first-order reaction in batch tests.
degradation rate decreased with higher HRT, which is probably because the COD concentration of sewage in the shorter HRT group was always at a high level during the whole experimental period, causing more microbial biomass, resulting in a higher rate constant. In a long sewer, nutrients in sewage would be consumed continuously, causing decreased biofilm thickness (Jin et al. 2014; Sharma et al. 2014), which could also explain this phenomenon. Besides, the reaction rate constant obtained was between 0.029–0.04 h\(^{-1}\) (0.72–0.96 d\(^{-1}\)), which is higher than the literature value (Zheng 2012), 0.2 d\(^{-1}\) for concrete sewage pipes regarded as a micro river under poor re-oxygenation conditions. The actual sewage pipe usually has a large diameter and a small wet circumference, causing a smaller area of biofilm per unit volume of sewage, which is often described as \(A/V\) (surface area of the biofilm/volume of pipe) (Hvitved-Jacobsen et al. 1988).

According to Figure 4, the linear function and exponential function were respectively used to fit the relationship between HRT and the COD degradation rate constant \(a\). The fitting effect of the linear function was better, so Equation (2) was obtained. And thus, the degradation model of COD was adjusted to Equation (3).

\[
a = -0.0012 \times \text{HRT} + 0.044 \quad (2)
\]

\[
c = c_0 e^{-(-0.0012 \times \text{HRT} + 0.044)t} \quad (3)
\]

where \(a\) is the reaction rate constant, \(c_0\) is the initial COD concentration, and \(t\) is the reaction time.

### The verification of the COD degradation model

As shown in Figure 5, an HRT of 10 h was used to examine the linear function. When HRT = 10 h, the results of the degradation of COD were fitted to the first-order reaction equation, and the degradation model of COD in sewers was the following equation:

\[
c = 250.76e^{-0.032t} \quad (4)
\]

Thus, \(a = 0.032\). Moreover, according to Equation (2), it can be calculated that \(a = 0.03\) at the HRT of 10 h. And the deviation from the theoretical value of 0.032 was 6.7\%. Also, the Pearson correlation coefficient of actual value and simulated value at each time point is 0.95, indicating a good simulation effect. Therefore, the degradation model of COD in full flow sewers can be described as Equation (5):

\[
c = c_0 e^{-(-0.0012t + 0.044)} \quad (5)
\]

Hvitved-Jacobsen et al. proposed a model to decompose the sCOD and connected the rate of sulfide production with a certain part of COD (Equation (6)) (Hvitved-Jacobsen et al. 1988; Nielsen et al. 1998).

\[
r_t = a \times ([\text{sCOD}] - 50)^{0.5}1.05^{(T - 20)} \quad (6)
\]
Figure 6 | (a) Changes of sulfate and sulfide in batch tests; (b) fitting results of sulfide production model when $k$, $b$, $c$ were not fixed; (c) fitting results of sulfide production model when $c = 0.6$. 
where parameter $a$ can be $1.5 \times 10^{-3}$, $3 \times 10^{-3}$ or $6 \times 10^{-3}$ for sewage from different sources. Term $(sCOD - 50)$ represents biologically active COD components, deducting the typical inert part from sCOD.

Both Equations (5) and (6) are trying to better relate $r_s$ to the COD component used by SRB. Therefore, as the temperature was around 20 °C in the experiment, to purpose a simple and practical model, we supposed that Equation (7) is valid:

$$r_s = k([COD] - b)^c$$

(7)

where the parameter $b$ represents slowly biodegradable COD, which is often estimated through the oxygen uptake rate (OUR) (Melcer et al. 2004). The parameter $c$ reflects the relationship between the rate of sulfide production and COD concentration, which should be a fixed value. The parameter $k$, however, is the rate constant of sulfide production, which is affected by various experimental conditions such as temperature.

In this study, we calculated the corresponding $b$ value of each experimental group by model fitting. Since the experimental data was a series of discrete values, it was impossible to accurately determine the rate of sulfide production at a certain time, so the slope between the two-time points before and after the measuring time point was calculated instead. Fitting results are shown in Figure 6(b). Raw sewage used in each experimental group was actual domestic sewage, and the water quality fluctuated greatly, so correspondingly, the parameter $b$ differed greatly. Additionally, the parameter $c$ was not fixed, which were 0.63, 0.58, 0.59, and 0.56 at the HRT of 3 h, 6 h, 8 h, and 12 h, respectively. According to the results of section 3.1, the parameter $k$ should have a positive correlation with HRT. Therefore, parameter $c$ was taken as the mean value of each batch test ($c = 0.6$), and the fitting was performed again to obtain a certain relationship between different HRT and parameter $k$. Figure 6(c) showed that the fitting results of the sulfide production model when $c = 0.6$. The R-squares of fitting curves in every experimental group exceeded 0.9, which achieved acceptable fitting effects.

As parameter $k$ should have a positive correlation with HRT, the fitting of the relationship between HRT and $k$ was carried out. As can be seen from Figure 7, there is a logarithmic relationship between HRT and $k$, and the fitted result was Equation (8). Therefore, the following empirical Equation (9) can be used to describe the effect of HRT on the rate of sulfide production.

$$k = 0.045 \times \ln\text{HRT} + 0.071$$

(8)

$$r_s = (0.045 \times \ln\text{HRT} + 0.071) \times ([\text{COD}] - b)^{0.6}$$

(9)

Parameter $b$ should be based on the actual proportion of slowly biodegradable COD in the raw sewage. In this study, the ratio of parameter $b$ to the initial COD is 72.20%.

The verification of the sulfide production model

The model was verified by the experiment group cultivated with an HRT of 10 h. The raw sewage used in this batch test was consistent with other experimental groups, so the proportion of slowly biodegradable COD was also considered to be 72.20%; that is, $b = 198.53$. When HRT = 10, the formula of sulfide production was estimated as follows:

$$r_s = 0.17 \times ([\text{COD}] - 198.53)^{0.6}$$

(10)

Sulfide production model calibration with the experiment HRT = 10 h is shown in Figure 8, the results indicating that the measured data were close to the simulated curve equation. Besides, the Pearson correlation coefficient between the measured value and simulated value was 0.98, which represented a good fitting effect. Nevertheless, for an actual urban drainage system, the COD concentration of sewage before injecting into a septic tank will be relatively higher. But whether the model equation is applicable to higher COD concentrations seems to need further verification. However, in the drainage system in China, the use of septic tanks is still ubiquitous,
causing a certain degree of degradation in the organic pollutants. Besides, the infiltration of groundwater or the inflow of surface water caused by the breakage of pipes also decreased the COD concentration in the pipe network. Therefore, this model is expected to have certain guidance on the degradation of COD in actual pipe networks with septic tanks at the front.

Comparison between our model and state-of-the-art model

Equation (6) was established in a full-scale experiment with an HRT of 1.67 h, and the unit of sulfide production rate was g S/(m²·h), which should multiply the A/V of the sewer to become mg S/(L-h). Because this experiment simulates the full pipe flow state of the sewer, the surface area of microbial adhesion can be regarded as the inner wall area of the pipe. The sewer of this study has an A/V of 14.3 by calculation, so when HRT = 1.67 h, the model of this study was adjusted to $r_s = 0.0066([\text{COD}] - b)^{0.6}$. For typical Danish domestic sewage, Equation (6) was $r_s = 0.0015([\text{sCOD}] - 50)^{0.5}$. Both the coefficient and the power are different from our study, which is mainly because Hvitved-Jacobsen used solute COD rather than total COD, and the specific experimental conditions also have a certain influence on the model parameters. Moreover, the COD concentration of the raw sewage will fluctuate with the changes in seasons, regions, and other external conditions. Therefore, the concentration of slowly biodegradable COD and the typical inert part from sCOD in different raw sewage have certain differences. However, Hvitved-Jacobsen et al. described the typical inert part from sCOD as a fixed value. In this way, the calculation result may deviate greatly from the actual value. Different from Equation (6), in our study, it is not necessary to determine the solute COD, and after only a simple determination of the characteristic of specific raw sewage, the sulfide production rate can be calculated according to COD and HRT, which is simpler in actual operation and the calculation result is closer to the true value. Besides, due to the actual operation of sewage pipes, the difference in sewage flow rate and the length of the pipe leads to a general difference in the HRT of sewage, and HRT is precisely the key factor in the amount of sulfide. The model established in this study introduces the important parameter HRT, which has more practical significance for the prediction of the amount of sulfide under different HRT conditions in actual operation.

CONCLUSIONS

Using the domestic sewage of a university campus as raw sewage, the laboratory-scale experiment was carried out in a concrete pipe section with a diameter of 280 mm. The main research conclusions are as follows:

1. Under the condition of full pipe flow, the nitrogen and phosphorus pollutants in the sewage were not reduced, while COD and sulfate were consumed and simultaneously dissolved sulfides were produced. The removal rate of COD, sulfate and the concentration of effluent sulfides increased with the increase of HRT.

2. The degradation of COD accorded with the first-order reaction law. Considering the effect of HRT, the degradation model of COD in sewers is $c = C_0 e^{-(0.0012-HRT^{0.044})}$. The longer the HRT, the smaller the COD degradation rate constant.

3. The rate of sulfide production is related to COD and HRT. It can be expressed by the empirical equation, $r_s = (0.045 \times \ln\text{HRT} + 0.071) \times ([\text{COD}] - b)^{0.6}$, where parameter $b$ represented slowly biodegradable COD in the raw sewage.

A simple but practical model was obtained from this study employing an actual concrete pipe with domestic sewage, which can quantitatively describe sulfide production based on the HRT of the sewer and the COD of the sewage. However, the effect of other significant factors such as temperature and velocity itself should be further investigated and considered in the model to improve the accuracy and applicability.
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DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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