Study of the impact of natural organic matter on the variation of the overall reaction coefficient in a simulated water distribution network

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Abstract- The main objective of this research was to study the factors that influenced the variation of the overall reaction coefficient (k_{OR}) in a water distribution network. Experiments were carried out in a simulated water distribution network constructed with four sets of independent polyvinyl chloride (PVC), galvanized steel (GS), polypropylene (PP) and high-density polyethylene (HDPE) loop pipes of 50 mm in diameter and 12 m in length each, and located at the Hydraulic Laboratory of the Engineering Institute at the National Autonomous University of Mexico. A sampling campaign was conducted at 2-hour intervals over an 8-hour period. Water samples were taken to the laboratory for analysis of pH, turbidity and COD, while chlorine concentration and temperature were measured during the experiments. Results of this research showed that initial chlorine concentration, the presence of high levels of natural organic matter (NOM) and the characteristic of pipe material should be considered as the main factors which modified the wall decay constant.

Index Terms- wall chlorine decay, natural organic matter, pipe material, initial chlorine concentration, simulated water distribution systems.

I. INTRODUCTION

W ater is vital, water is life and water saves. There are many reasons why water is important to our daily life. It is indispensable for normal function of the body. The human anatomy and physiology cannot function without an adequate supply of water per day. It is essential for life, and without it people can survive for only few days. Massive waterborne diseases, however, are associated with the presence of contaminants in water.

Surface and groundwater are susceptible to pollution from both natural and man-made sources. Naturally occurring substances such as iron, manganese, barium, selenium, total nitrogen, urea nitrogen, K_2O water-soluble potassium, total humic carbon, humic acid carbon and fulvic acid carbon hydrogen sulfide, and salt may be present in undesirable levels. Bacteria and nitrate-nitrogen from sewage, septic tanks, animal waste, and fertilizers are a common problem.

Chlorine is a strong oxidant commonly used in water during the oxidation and disinfection process. It is also used to control biological growth and to inhabit microbial activity in the network system (EPA 2014). While flowing through pipes, however, the chlorine concentration decreases.

The simplest model for chlorine decay is the first decay model, and the equation used to describe this phenomenon is as follows:

$$C(t) = C_0 \exp(-kt) \qquad [1]$$

where C is the final chlorine concentration [mg/L] at time t, C_0 is the initial chlorine concentration [mg/L], t is the residence time in the pipe (h) and k is the first order decay constant [h^{-1}](Chambers et al. 1995, Powell et al. 2000).

Therefore, the overall decay constant is often expressed as the sum of the bulk decay (k_b) (Biswas and Clark 1993; Clark et al. 1994, Hua et al. 1999) and the wall decay . For the purpose of this study, the wall decay rate (k_w) is substitute by the overall reaction coefficient (k_{OR}). Eq.1 becomes:

$$C = C_0 \exp(-k_{OR}t) \qquad [2]$$

in which C: final chlorine concentration (mg/L); C_0 : initial chlorine concentration (mg/L);
k_{OR} : overall reaction coefficient (h^{-1}) and t: time (h)

Bulk chlorine decay depends on the physicochemical characteristic of the source, while wall decay depends on the pipe material and its conditions (Nejjaria et al. 2014). Thus, it is crucial to model them separately to provide a fair approximation.

The determination of this coefficient (k_{OR}) can be obtained by performing either field or laboratory study. Few field studies, however, have been performed because of the complexity of the water distribution systems. Currently, during the expansion of an existing network, water supply authorities are using high-density polyethylene, polypropylene and PVC pipelines because of their flexibility during an earthquake and their low cost compared to metal pipes. Because of the special interest of using large amounts of polyethylene, polypropylene and PVC pipelines by the water utilities, the aim of this work presented in this paper is to estimate the overall reaction coefficient in four different pipe materials mounted in a laboratory-scale distribution system.

II.   MATERIALS AND METHODS

II. Experimental setup and preparation

In order to estimate the overall reaction coefficient, a series of experiments were performed using an experimental setup consisting of three parts:
1) A water reservoir of 2.12 m^3 of capacity,
2) A storage tank (450 L of capacity) at elevated position for gravity flow, and
3) A simulated water distribution network consisting of four sets of independent polyvinyl chloride (PVC), galvanized steel (GS), polypropylene (PP) and high-density polyethylene loop pipes of 50 mm in diameter and 12 m in length each.

The system also included
   a) nine flow control valves,
   b) an on-line CL763 (B&C Electronics, Italy) chlorine analyzer installed in each loop, which can monitor and control operating continuously and detect chlorine concentration in the range from 0.1 to 20 mg/L,
   c) a data logger (El-USB-4, Lascar Electronics, USA) (connected in each chlorine analyzer that records data over time for their analysis,
   d) a manual mixer installed at the storage tank to obtain a homogeneous mixture of tap water, natural organic matter and chlorine,
   e) a 4HME200 centrifugal pump,
   f) a 350 mercury thermometer (Lauka, USA), and
   g) a M530P (Pinnacle Series, USA) unit was used for pH measurement.

A schematic diagram of the lab-scale water distribution network (2D, 3D) and a schematic drawing of a manual mixer are shown in Fig. 1 and Figs. 2 and Fig. 3, respectively.
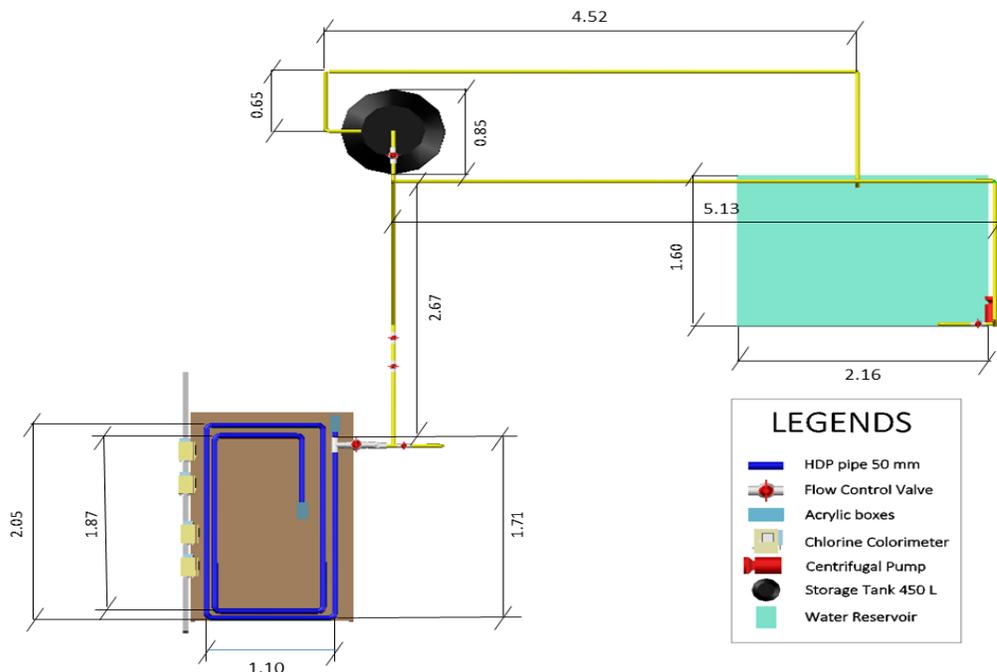

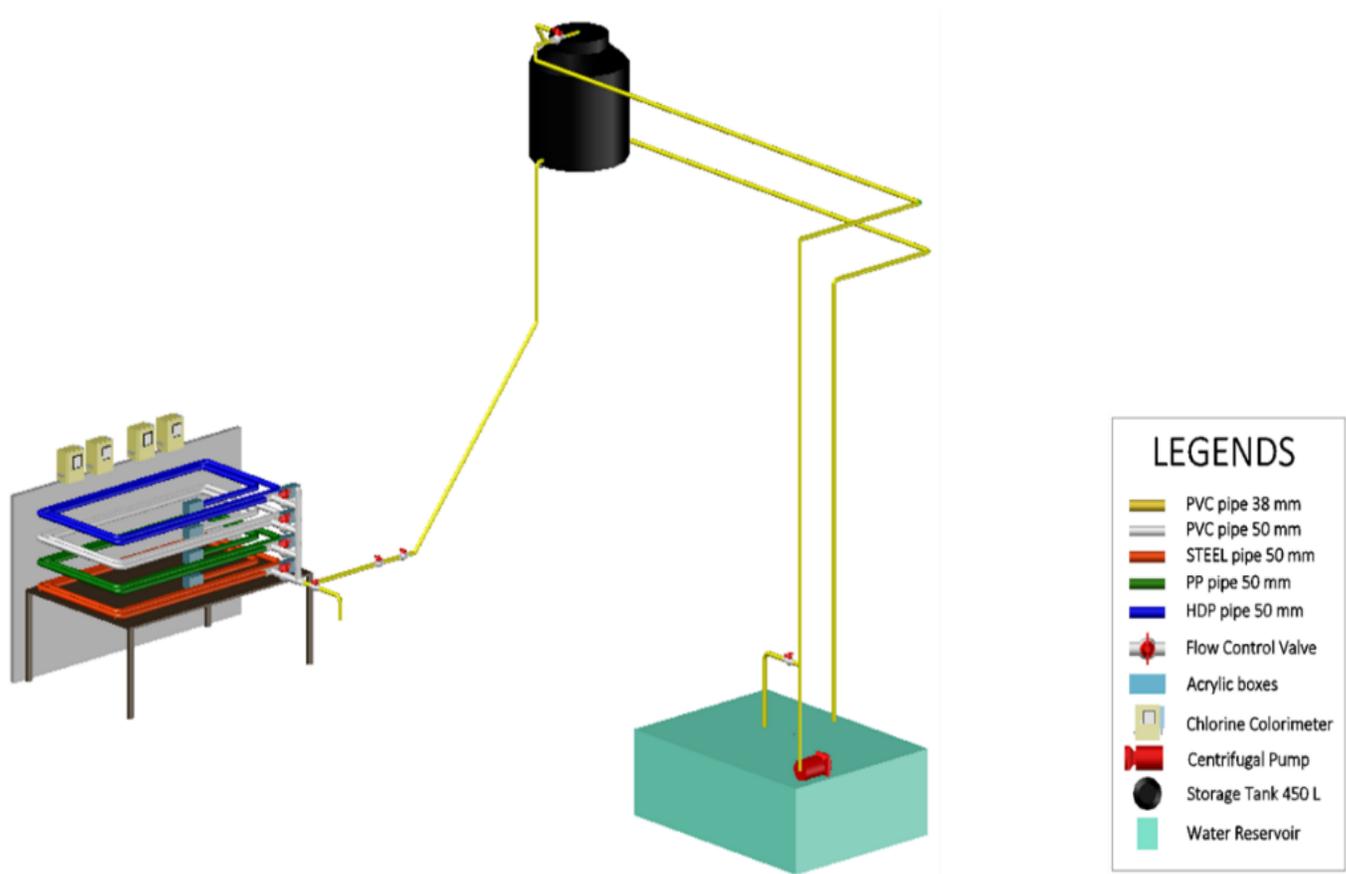**Fig. 1** Schematic diagram of the lab-scale water distribution network.

Fig. 2. 3D view of the schematic diagram of the lab-scale water distribution network.

III. EXPERIMENTAL PROCEDURE

Experiments were performed with the final objective of estimating the overall reaction coefficient in four different new pipe materials as a function of initial chlorine concentration and natural organic matter. Before each set of experiments, unchlorinated water from the 2.13 m^3 reservoir was pumped to the elevated storage tanks by using the 4HME200 centrifugal pump. In each test, 2.5 mL of K-Tonic solution (1.15 g/mL), which is a mix of six compounds such as total nitrogen, urea nitrogen, K$_2$O water-soluble potassium, extract of total humic carbon, humic acid carbon and fulvic acid carbon were used (as contaminant agent) to provide 1.50 mg/L of NOM. The chlorination process was conducted for a given chlorine dosage of 1.20 mg/L in scenario 1 and 1.60 mg/L and 0.71 mg/L in scenarios 2 and 3, respectively. In order to get a homogeneous mixture of tap water and chemicals (NOM and chlorine), a manual mixer was installed at the storage tank; see Fig. 3.
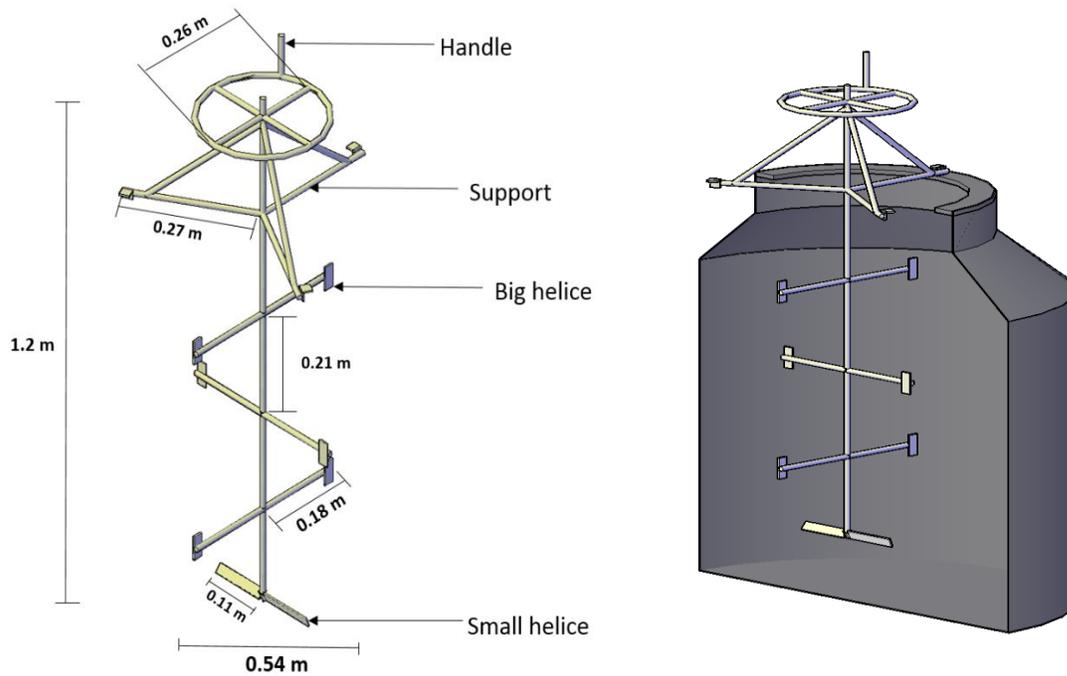
Fig. 3. Schematic drawing of a manual mixer.   NOTA: helix

Once completed the initial data measurement in the storage tank was completed, the flow control valves (A- F) were kept open. In addition, each pipe loop was first flushed with clean water (free of chlorine) for approximately 10 minutes to ensure that no chlorine demand was present; it was then filled with the chlorinated water from the storage tank. At the extremity of each loop is located a 0.18 m × 0.09 m acrylic box. The first box (1) is equipped with a mini (4203, Aquakril) submersible water pump which takes the sample to the chlorine analyzer (overflow cell) through a 1/4" connection. The cell's manufacturing characteristics allow the sample to run through the (sensor) potentiostatic electrode site with a constant velocity then exit through a 10 × 14 mm tubing to the second acrylic box (located in the other extremity of the loop). Thus, water was continuously recirculated in the simulated distribution system. The experiments were performed at a constant recirculation velocity of 0.0061 m/s. The chlorine decay was determined continuously since the sample was run through the sensor. Upon activation, data loggers were deployed to record chlorine concentration at two-hour intervals for the duration of the monitoring period (8 h). Once the experiments were completed, software was used to download and analyze the collected data. Experiments were performed three times to ensure that the results are reliable and to carry out statistical analysis. A schematic diagram of the experimental procedure is shown in Figure 4.
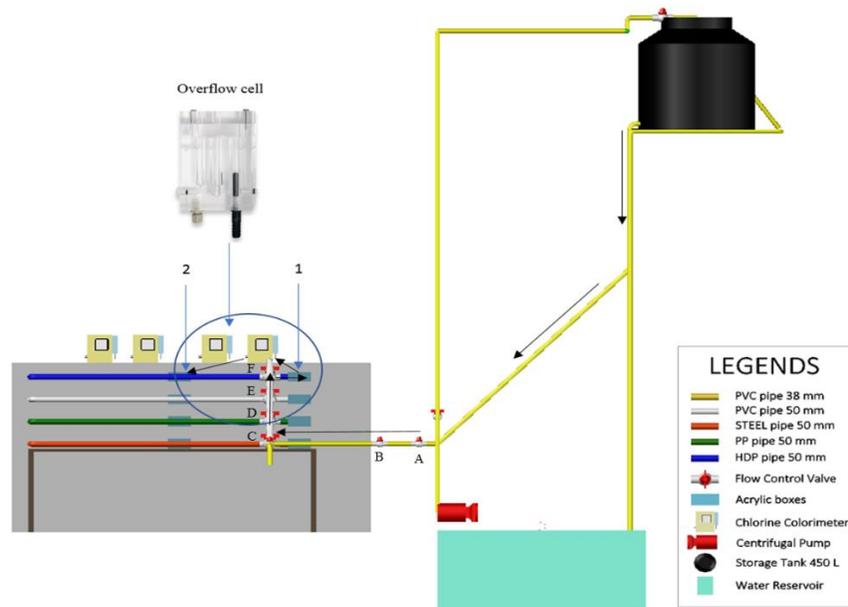
Fig. 4. Schematic diagram of the experimental procedure.

IV.   EXPERIMENTAL RESULTS

1.   Scenario 1

The experiment's results are summarized from Table 1 to Table 7. Table 1 summarizes chlorine decay observed in samples collected in each pipe loop for the first experimental run. Results showed how chlorine reacted differently with pipe material. The ranking of the chlorine decay rate observed in the pipe loop system after 8 hours was as follows: steel pipe (with the highest percentage of decay, 100%) > high-density polyethylene (88.42%) > PVC (82.62%) > polypropylene (79.33%). The decrease in chlorine concentration with reduced hydraulic residence time (8 h) appears to be associated directly with the effect of NOM.

Table 1. Chlorine decay observed in samples collected in four pipe loops [mg/L]

Time (h)	Cl_2 [mg/L] Steel Pipe	Cl_2 [mg/L] Polypropylene pipe	Cl_2 [mg/L] PVC pipe	Cl_2 [mg/L] HDPE pipe
0	1.21	1.21	1.21	1.21
2	0.50	0.78	0.74	0.57
4	0.28	0.53	0.46	0.39
6	0.07	0.35	0.32	0.21
8	0.00	0.25	0.21	0.14

In most of the cases, the chlorine decay is represented by the first-order decay equation. In this study, a kinetic model was suggested in which two separated decay formulae can be used: the second-order decay equation (Eq.2) for the first phase and the first-order decay equation for the second phase.

$$C = \frac{C_0}{1 + C_0 k_{OR} t} \qquad [3]$$

where C is the final chlorine concentration [mg/L] at time t, C_0 is the initial chlorine concentration [mg/L], t is the residence time in the pipe [hour] and k_{OR} is the overall reaction coefficient [h^{-1}].

In the present study, since the hydraulic residence time was very short (8 hours) determining only a coefficient (k_{OR}) was suggested. Figure 5 shows free chlorine decay profiles of water measured at temperatures ranging from 20-25°C.
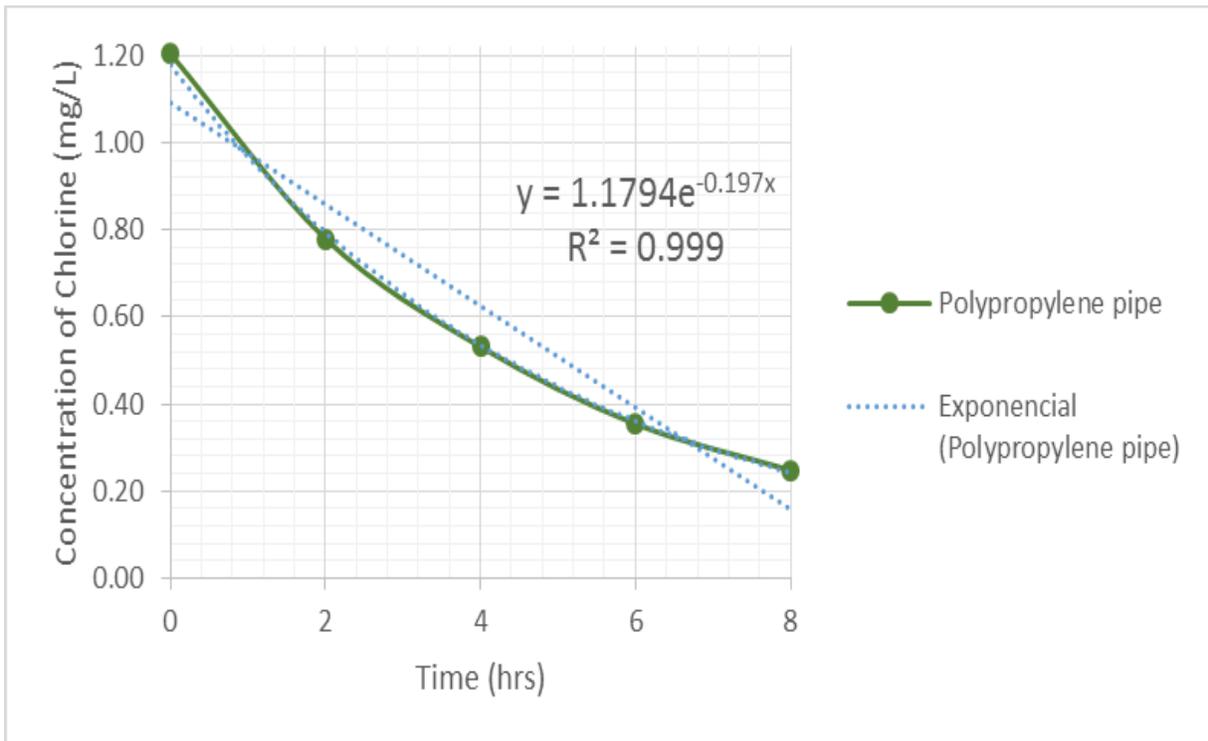

Fig. 5. Chlorine decay observed in simple collected in polypropylene pipe.   NOTA: Exponential

Table 2 shows the regression equation for the relationships between initial chlorine concentrations. In most of the cases (except in the steel pipe), the coefficients of determination R^2 were better than 0.91. The overall reaction coefficient (k_{OR}) was found to be greater in the steel pipe (0.807 h^{-1}) followed by high-density polyethylene (0.263 h^{-1}), PVC pipe (0.216 h^{-1}) and polypropylene (0.197 h^{-1}).

Table 2. Regression equation for the relationships between initial chlorine concentration and the overall reaction coefficient for different pipe materials (scenario 1, Cl_2 initial = 1.21 mg/L)

PIPE MATERIAL	REGRESSION EQUATION	R^2
GS pipe	y = 2.6151e-0.807x	0.835
PP Pipe	y = 1.1794e-0.197x	0.999
PVC Pipe	y = 1.1602e-0.216x	0.997
HDPE Pipe	y = 1.0915e-0.263x	0.989

Once k_{OR} values for each pipe loop were obtained, the second-order decay equation was used for the first phase (0-2) since the percentage of decay was approximately 53% and the first-order decay equation for the second phase (2-8 hours). Table 3 shows the results for polypropylene pipe.

Table 3. Comparison of measured and estimated chlorine concentration for scenario 1

POLYPROPYLENE PIPE								
Time [hrs]	Cl_2 [mg/L]	K_{OR} [h^{-1}]	Cl_2 measured [mg/L]	Cl_2 estimated [mg/L]	D = Cl$_{2measured}$ − Cl$_{2estimated}$ [mg/L]	D^2 [mg/L]	Absolute error	Relative error
SECOND-ORDER EQUATION								
0	1.21	0.197	1.21	1.21	0.00	0.0000	0.0000	0%
2	1.21	0.197	0.78	0.82	0.04	0.0016	0.0506	5%
FIRST-ORDER EQUATION								
4	1.21	0.197	0.53	0.55	0.02	0.0003	0.0348	3%
6	1.21	0.197	0.35	0.37	0.02	0.0003	0.0467	5%
8	1.21	0.197	0.25	0.25	0.00	0.0000	0.0084	0%

Clearly the combined second- and first-order model provides good results. The predicted concentrations fit well together the measured concentrations. A relative error ranging from 3-5% was observed. From the present study, using sample water containing NOM, it was found that the highest value of k_{OR} was obtained in GS pipes followed by HDPE, PVC and PP pipes, respectively.

2.   Scenarios 2 and 3

Water quality analysis was performed in scenarios 2 and 3. Free chlorine concentration was measured at approximately 2-hour intervals over an 8-hour period. Results are summed up in Tables 4 to 7, respectively.

Table 4. Regression equation for the relationships between initial chlorine concentration and the overall reaction coefficient for different pipe materials (scenario 2, Cl$_2$ initial = 1.60 mg/L]

PIPE MATERIAL	REGRESSION EQUATION	R^2
GS pipe	y = 1.5823e-0.366x	0.978
PP pipe	y = 1.3757e-0.135x	0.925
PVC Pipe	y = 1.3655e-0.148x	0.927
HDPE pipe	y = 1.3763e-0.207x	0.969

From the present scenario with water containing 1.50 mg/L of NOM and 1.60 mg/L of chlorine, it was found that k_{OR} was in a range: 0.135 h^{-1} < k_{OR} < 0.366 h^{-1}.
Contrary to scenario 1, the second-order decay equation was used for the first phase (0-6 hours) instead of (0-2 hours) and the first-order decay equation for the second phase (6-8 hours) instead of (2-8 hours). Table 5 shows the results for polypropylene pipe. Once again it can be seen that the combined second- and first-order model provided good results with a relative error ranging from 9 to 21%.

Table 5. Comparison of measured and estimated chlorine concentration for scenario 2

POLYPROPYLENE PIPE								
Time [hrs]	Cl_2 [mg/L]	k_{OR} [h^{-1}]	Cl_2 measured [mg/L]	Cl_2 estimated [mg/L]	D = Cl$_{2measured}$ − Cl$_{2estimated}$ [mg/L]	D^2 [mg/L]	Absolute Error	Relative error
SECOND-ORDER EQUATION								
0	1.60	0.135	1.60	1.60	0.00	0.0000	0.0030	0%
2	1.60	0.135	0.92	1.12	0.20	0.0383	0.2122	21%
4	1.60	0.135	0.71	0.86	0.15	0.0223	0.2107	21%
6	1.60	0.135	0.64	0.70	0.06	0.0035	0.0921	9%
FIRST-ORDER EQUATION								
8	1.60	0.135	0.50	0.54	0.05	0.0022	0.0948	9%

Results for scenario 3 are presented in Tables 6 and 7.

Table 6. Regression equation for the relationships between initial chlorine concentration and the overall reaction coefficient for different pipe materials (scenario 3, Cl_2 initial = 0.71 mg/L]

PIPE MATERIAL	REGRESSION EQUATION	R^2
GS pipe	y = 1.3337e-1.641x	0.90
PP pipe	y = 0.9271e-0.749x	0.91
PVC pipe	y = 0.7388e-0.52x	0.99
HDPE pipe	y = 1.492e-1.641x	0.87

From the present scenario with water containing 1.50 NOM and 0.71 mg/L of chlorine, it was found that k_{OR} was in a range: 0.52 h^{-1} < k_{OR} < 1.64 h^{-1}. Table 7 shows the results for polypropylene pipe.

Table 7. Comparison of measured and estimated chlorine concentration for scenario 3

POLYPROPYLENE PIPE								
Time [hrs]	Cl_2 [mg/L]	k_{OR} [h^{-1}]	Cl_2 measured [mg/L]	Cl_2 estimated [mg/L]	D = $Cl_{2measured}$ − $Cl_{2estimated}$ [mg/L]	D² [mg/L]	Absolute error	Relative error
SECOND-ORDER EQUATION								
0	0.71	0.749	0.71	0.71	0.00	0.0000	0.0014	0%
2	0.71	0.749	0.35	0.34	0.01	0.0001	0.0294	3%
FIRST-ORDER EQUATION								
4	0.71	0.749	0.04	0.04	0.00	0.0000	0.0000	0%
6	0.71	0.749	0.00	0.01	0.01	0.0001	0.0000	0%
8	0.71	0.749	0.00	0.00	0.00	0.0000	0.0000	0%

The second-order decay equation was used for the first phase (0-6 h) instead of (0-2 h) and the first-order decay equation for the second phase (6-8 h) instead of (2-8 h). Again it can be seen that the combined second- and first-order model provided good results with a relative error of 3%.

V. CONCLUSION

Results of the experimental work performed on four pipe sections of different materials (steel, PVC, polypropylene and high-density polyethylene), different initial chlorine concentration and amount of natural organic matter (NOM) led to three conclusions.

1) The overall reaction coefficient (k_{OR}) was observed to vary with the initial chlorine concentration. For the range of 1.21 mg/L of initial chlorine concentration used in the first scenario of this study, k_{OR} ranged from 0. 197 h^{-1} to 0.807 h^{-1}. In the second scenario with the range of 0.71 mg/L of chlorine and 1.50 mg/L of NOM, k_{OR} ranged from 0.52 h^{-1} to 1.64 h^{-1}. Finally, in the third scenario with the highest initial chlorine concentration (1.60 mg/L), k_{OR} ranged from 0.135 h^{-1} to 0.366 h^{-1}.

2) The overall reaction coefficient was observed to show significant variation with pipe material. It has been observed increasing with steel pipe. It was found that the highest value of k_{OR} was obtained in steel pipes followed by HDPE, PVC and PP pipes, respectively.

3) A combined second- and first-order model provided good results with a relative error ranging from 3 to 5% in scenario 1, 9 to 21% in scenario 2 and 3% in scenario 3.

VI. ACKNOWLEDGMENT

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