Scientia Iranica, Vol. 12, No. 3, pp 300–305
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SCIENTIA IRANICA

Research Note

Estimating Volatile Organic Compound Emissions from Wastewater Circulating Aeration Tanks

S. Yaghmaei* and A. Rashidkhani[1]

The need for the control of Volatile Organic Compounds (VOCs) has led engineers to modify wastewater aeration tank systems. In this research, air recirculation has been investigated as a possible VOC control strategy for these systems. A steady-state mathematical model of VOC emission rates has been developed from the fundamentals of VOC convection, volatilization and biodegradation. This model has been used to study the effect of aeration recirculation in enhancing the biodegradation of VOCs in the system, using dichloromethane as a typical VOC. A feasibility study considering plants of various sizes is needed to compare the costs and benefits of air recirculation to other VOC control strategies.

INTRODUCTION

There have been dramatic changes in the treatment of chemical and petrochemical wastewater over the past several years. While, in the 1970's, primary emphasis was on BOD and suspended solids, recent legislation in industrialized nations now targets volatile organic carbon, aquatic toxicity and priority pollutants [1]. The net effect of these regulations is to place increased emphasis on waste minimization and source control.

Volatile Organic Compounds (VOCs) comprise 31 out of 129 priority pollutants designated by the U.S. Environmental Protection Agency (EPA) [2], exposure to all of which is harmful to humans.

Although adsorption and biodegradation can affect the fate and behavior of VOCs in wastewater treatment processes, volatilization has been considered to be one of the main mechanisms for removal of VOCs from wastewater [3,4]. VOCs entering wastewater treatment plants can be released to the atmosphere from wastewater during collection and treatment. There are also other studies on VOC modeling related to this work [5-8].

Among air emission sources within a wastewater treatment plant, aeration units are a major emission source, due to their large area open to the atmosphere and the intensive stripping effect of the aeration air supplied for biological reactions [9].

In many cases, modifications to the biological technology is required to control VOC emissions. Recent work [10,11] has shown that an air recirculation system around the aeration basin can reduce the volume of exhaust air. In this research, air recirculation has been selected as a VOC control strategy.

A portion of the aeration gas from covered aeration units can be recycled to reduce the net discharge to the atmosphere.

The overall feasibility of air recirculation needs to be examined with mathematical models incorporating various mechanisms to quantitatively evaluate the effects on the fate of VOCs.

MATHEMATICAL MODELING

To provide an accurate estimate of the actual VOC emission rate, a mathematical model for the activated sludge treatment process has been developed from the fundamentals of VOC convection, volatilization to air, adsorption to biological solids and biodegradation.

The mass balance of an individual compound in water found in a completely mixed aeration tank is:

$$\text{accumulation} = \text{influent} - \text{effluent} + r_{\text{bio}} + r_{\text{ads}} + r_{\text{vol}}. \qquad (1)$$

Since a steady state is assumed, the accumulation term equals zero. Moreover, all of the r terms are negative because they represent removal of the compound from

*. *Corresponding Author, Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. Iran.*
1. *Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. Iran.*

the water, so, all of the k and K constants in the formulas below are negative.

The following sections describe the calculation of volatilization, adsorption and biodegradation for r terms in the equation.

Biodegradation

When based on Monod kinetics, the biological reaction rate is expressed as:

$$r_{\text{bio}} = \frac{k_{\max} X_a C_w V}{K_s + C_w}. \tag{2}$$

Because most VOCs are present in the influent at low concentrations [12], a reasonable simplifying assumption is that $C_w < C_{\text{wi}} << K_s$, which reduces the Monod kinetics to a first-order relation in C_w:

$$r_{\text{bio}} = k_1 X_a C_w V. \tag{3}$$

Adsorption

Organic compounds are known to be adsorbed to organic solids, of which biological solids are a prime example. The adsorbed compound is removed from the system when biomass is wasted. The amount of compound removed via adsorption is expressed by [13]:

$$r_{\text{ads}} = Q_w X_a q. \tag{4}$$

The partitioning of a compound onto the organic solids usually follows a linear relationship with the solute concentration:

$$q = k_p C_w, \tag{5}$$

$$r_{\text{ads}} = Q_w X_a k_p C_w. \tag{6}$$

Volatilization

The transfer of a volatile compound between a liquid phase and a gas phase can normally be modeled as a quasi-equilibrium process [14]:

$$r_{\text{vol}} = K_L a (C_w - C^*) V. \tag{7}$$

When the gas exits the liquid, its partial pressure, P_p, is assumed to be in equilibrium with the solute concentration:

$$C^* = \frac{P_p M_W}{H}, \tag{8}$$

where H is the Henry's law constant.

Combining All Mechanisms Together

A mass balance on a VOC in the liquid phase can be made:

$$Q_w C_{\text{wo}} - Q_w C_w + K_L a V \left(\frac{P_p M_W}{H} - C_w \right) - k_p C_w X_a Q_w - k_1 X_a C_w V = 0. \tag{9}$$

Another mass balance on the VOC in the gas phase is also obtained.

Normally, the compound is present in negligible amounts in the inlet gas:

$$0 + Q_r C_a - (Q_a + Q_r) C_a + K_L a (C_w - C^*) V = 0. \tag{10}$$

Conventionally, VOCs in the air are expressed in concentration, C$_a$. It is related with partial pressure by:

$$C_a = \frac{P_p M_W}{RT}. \tag{11}$$

The two mass balance equations should be solved simultaneously to give the compound concentrations in both phases. The hydraulic residence time of wastewater and the aeration tank are defined as:

$$\theta_w = \frac{V}{Q_w}, \tag{12}$$

$$\theta_a = \frac{V}{Q_a + Q_r}, \tag{13}$$

and the aeration circulation ratio is defined as:

$$r = \frac{Q_r}{Q_a + Q_r}. \tag{14}$$

In this way, VOC concentration in off-gases and wastewater effluent can be determined, respectively, by Equations 15 and 16:

$$C_a = C_{\text{wo}} \left[(1 - r) \left(\frac{1 + k_p X_a + k_1 X_a \theta_w}{K_L a \theta_a} + \frac{\theta_w}{\theta_a} \right) + \frac{1 + k_p X_a + k_1 X_a \theta_w}{H_c} \right]^{-1}, \tag{15}$$

$$C_w = C_a \left(\frac{1 - r}{K_L a \theta_a} + \frac{1}{H_c} \right), \tag{16}$$

$$H_c = \frac{H}{\text{RT}}. \tag{17}$$

The VOC removals by biodegradation, adsorption, volatilization or stripping and discharge with effluent can be calculated using the following equations:

$$R_{\text{bio}} = \frac{\text{Bio degraded VOC}}{\text{Total influent VOC}} = \frac{k_1 X_a C_w \theta_w}{C_{W_i}}, \quad (18)$$

$$R_{\text{ads}} = \frac{\text{Adsorbed VOC}}{\text{Total influent VOC}} = \frac{k_p C_w X_a}{C_{Wi}}, \quad (19)$$

$$R_{\text{VOL}} = R_{\text{str}} = \frac{\text{Stripped VOC}}{\text{Total influent VOC}} = \frac{(1-r)C_a\theta_w}{C_{\text{Wi}}\theta_a}, \quad (20)$$

$$R_{\text{eff}} = \frac{\text{Effluented VOC}}{\text{Total influent VOC}} = \frac{C_w}{C_{\text{Wi}}}. \quad (21)$$

As the assumptions imply, these equations determine the pathways of VOCs in the aeration basin and the total of the four fractions is equal to 1, i.e., $R_{\text{strip}} + R_{\text{ads}} + R_{\text{bio}} + R_{\text{eff}} = 1$.

RESULTS AND DISCUSSION

The parameter values applied to the models are within the range conditions commonly found in conventional secondary treatment plants: $K_La = 6\text{hr}^{-1}$; $\theta_a = 0.4$ hr, $\theta_w = 4$ hr, $X_a = 2100$ mg/l.

The influent concentration of the VOC, C_{wi}, is assumed to be 127.5 mg/l [13].

Figures 1 through 6 give results of how the biodegradation rate constant will affect the fate of VOCs with $H_c = 0.15$ and $k_p = 0.073$ (Dichloromethane) [13].

Figure 1 shows the off-gas concentration contour. At any circulation ratio, values of the smaller degradation rate constant result in higher off-gas concentrations. This trend becomes more significant as the circulation ratio increases. Similarly, the least degradable VOC has the most significant accumulation in the off-gas with the increase of circulation. The volumetric flow of the net discharged off-gas is proportionally reduced with the increase of aeration circulation.

Although the off-gas concentration is higher at higher recirculation ratios, the total amount of stripped VOCs in the net off-gas is reduced when circulation is increased, as illustrated in Figure 2. More degradable compounds have fewer emissions by stripping. Figure 3 gives the VOC removals by biodegradation. For degradable compounds, degradation can be enhanced by aeration recirculation and the largest enhancement is found for the most degradable compounds at the highest possible recirculation ratio. Discharge with the

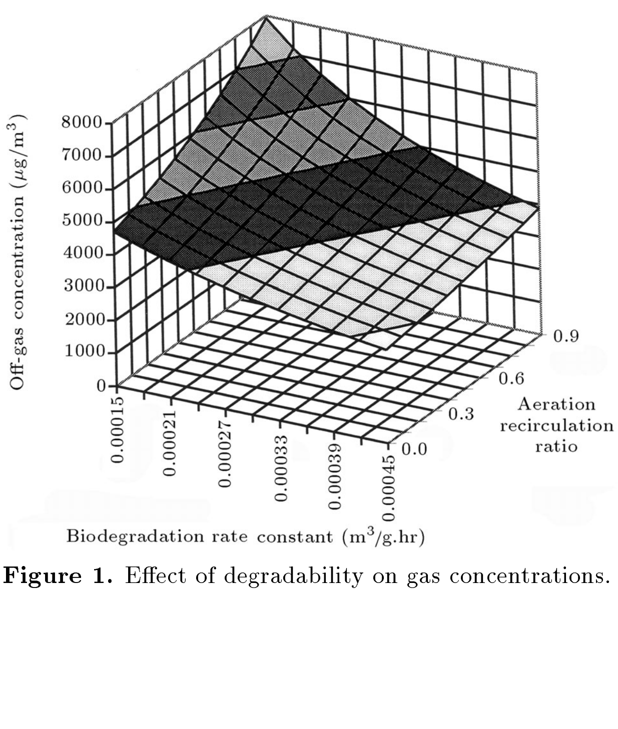

Figure 1. Effect of degradability on gas concentrations.

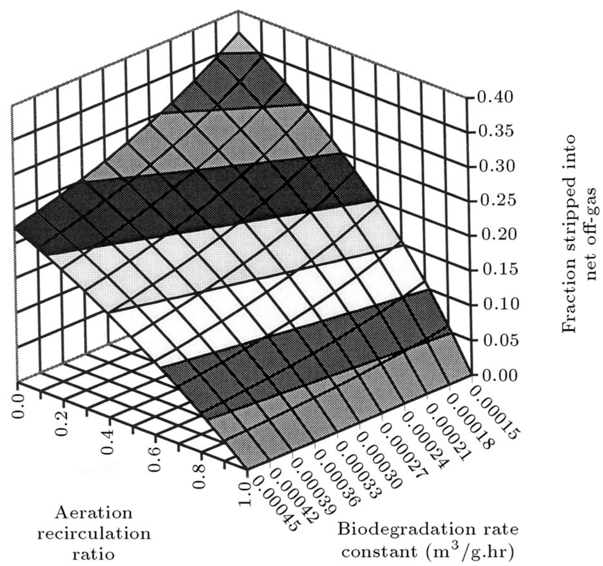

Figure 2. Effect of degradability on air stripping.

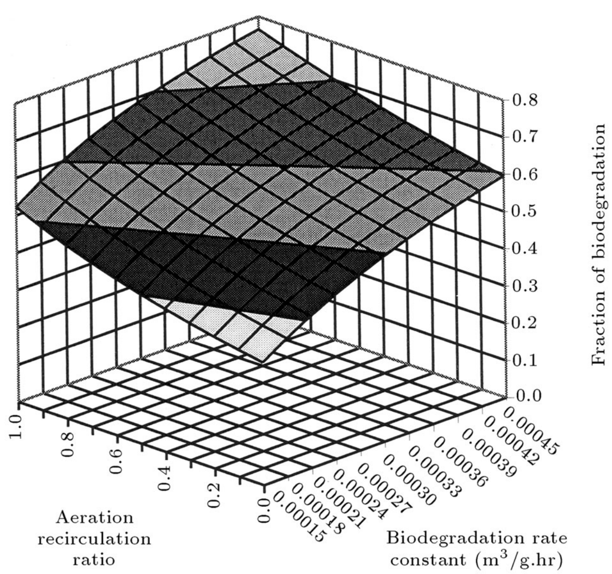

Figure 3. Effect of degradability on VOC removals by biodegradation.

wastewater effluent is also increased with the increase of aeration recirculation (see Figure 4) and it has a contour similar to the off-gas concentration. Most of the least degradable compounds will remain in the wastewater at high recirculation ratios.

Figure 5 gives the VOC removals by adsorption on solids. As this figure shows, the maximum fraction removal by this mechanism is 0.065 and is not significant when compared to other removal mechanisms. Previous studies [15,16] indicate that most VOCs do not have a high affinity for wastewater solids and do not concentrate in the sludge.

Figures 6 shows the off-gas concentration change with the recirculation ratio for a fixed biodegradation

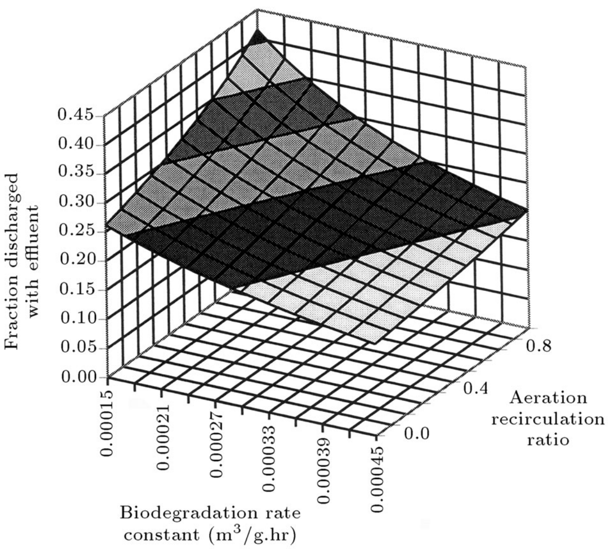

Figure 4. Effect of degradability on VOC removals with wastewater effluent.

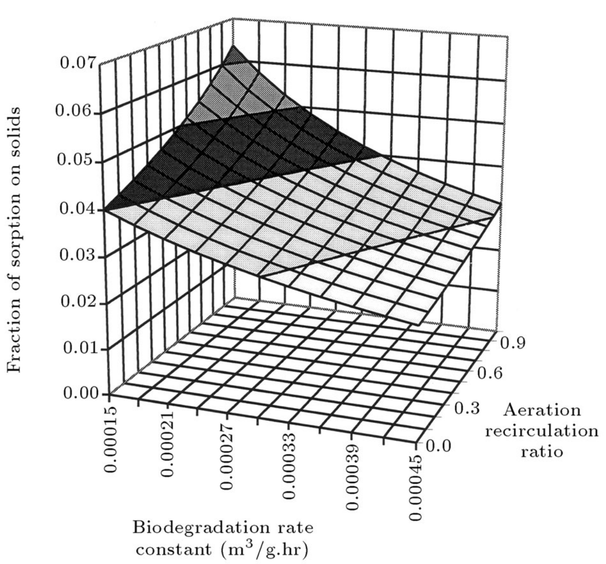

Figure 5. Effect of degradability on VOC removals by adsorption.

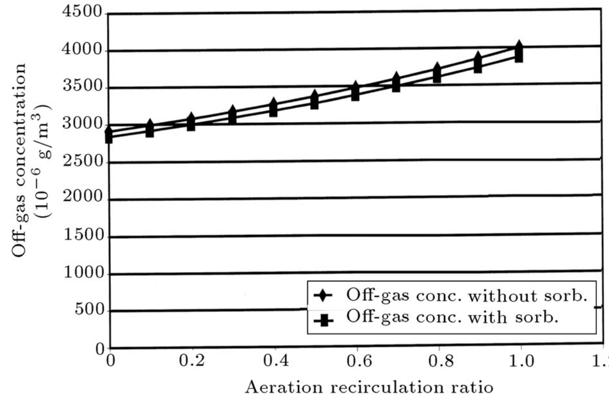

Figure 6. Off-gas concentration with and without adsorption vs aeration recirculation ($k_1 = 0.00045$ m^3/g.hr).

rate for two conditions: With and without considering adsorption mechanisms. Evidently, adsorption does not have a significant effect on off-gas concentration, as implied by Figure 5.

Accurate predictions on the fate of the VOCs under aeration recirculation are quite dependent on the accuracy of the parameters, such as Henry's law constants and the biodegradation rate constant. A better understanding of the biodegradation mechanisms of each compound will enable more accurate modeling of this process, especially for compounds that might be produced during wastewater treatment. If the microorganisms are acclimated to degrade the VOCs more efficiently, recirculation will improve the efficiency rate even more.

PRACTICAL CONSIDERATIONS

It seems worth noting that wastewater treatment plants that use the high-purity oxygen secondary treatment technology already capture VOCs that are stripped by the aeration that occurs in the enclosed chambers of this type of system. Also, the typical gas flow path through a large number of chambers inevitably results in some degree of return of VOCs to the water in the downstream chambers, promoting biodegration of a greater fraction of the incoming VOC load than that which occurs in the open aeration tanks that prompted the study reported here. Although VOC degradation has not, to the authors knowledge, been considered in the choice or design of these systems, this study may provide a starting point for investigating the VOC removal that occurs in them.

It is also evident that a substantial expense is likely to be required to install covers and new air ducts and blowers to recirculate the off-gas from any open-tank system designed for aeration with natural air. This is an obvious barrier to implementing the recirculation strategy. On the other hand, other methods for removing VOCs also have significant drawbacks. In air waste emissions, chemical scrubbers impose substantial operating costs and produce large amounts of waste, the same being true of charcoal filtration systems, while biofilters and biotrickling filters have shown little effectiveness on the removal of chlorinated VOCs [17,18]. It seems clear that it would be desirable to implement a more thorough feasibility study using the model developed here to evaluate removal factors for realistic combinations of VOCs using recirculation while also comparing the costs and benefits with those of other methods.

CONCLUSION

A mathematical model was developed to investigate the effect of air recirculation on VOC fates in a wastewater aeration tank.

The model predicts that air recirculation reduces VOC emissions by enhancing the fraction that is biodegraded, greatest enhancement being, as would be expected, when the biodegradation rate constant and the recirculation ratio are both high. As informal consideration suggests that using this strategy for VOC reduction would, however, impose substantial costs, it may be desirable to perform a more thorough study, including an economic comparison with the costs and benefits of other VOC control options.

NOMENCLATURE

C_a	VOC concentration in the off-gas, g/m^3
C_w	VOC concentration in the wastewater effluent, g/m^3
C_{wi}	VOC concentration in the wastewater influent, g/m^3
C^*	equilibrium water phase concentration, g/m^3
H	Henry's law constant, atm. m^3/mol
H_c	dimensionless Henry's law constant, m^3(liq)/m^3(gas)
K_La	overall volumetric mass transfer constant, hr^{-1}
K_s	half saturation constant, g/m^3
k_1	apparent first-order rate constant, m^3/hr.g
$k_{\max}$	maximum specific substrate utilization, g/hr.g_{bio}
k_p	liquid-solid partition coefficient, m^3/g
M_W	molecular weight, g/mol
P_p	partial pressure, atm
Q_w	wastewater flow rate into tank, m^3/hr
Q_a	net air flow rate into tank, m^3/hr
Q_r	recirculating air flow rate, m^3/hr
q	mass of VOC sorbed per mass of solid, g/g
R	universal gas constant, 8.206×10^{-5}, m^3.atm/°K. mol
R_{bio}	fraction of VOC degraded by microorganisms
R_{ads}	fraction of VOC adsorbed
$R_{\text{vol}} = R_{\text{str}}$	fraction of VOC stripped into net off-gas
R_{eff}	fraction of VOC discharged with effluent
r	aeration circulation ratio, dimensionless
r_{bio}	biological reaction rate, g/hr
r_{ads}	rate of VOC removal by adsorption, g/hr
r_{vol}	rate of VOC removal by volatilization, g/hr
T	absolute temperature, °K
V	volume of aeration tank, m^3
X_a	activated biomass concentration, g/m^3

Greek Letters

θ_w	hydraulic residence time of wastewater, hr
θ_a	residence time of aeration gas, hr

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