NOTES

Purge and trap method to determine alpha factors of VOC liquid-phase mass transfer coefficients

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Abstract A theoretical approach and laboratory practice of determining the alpha factors of volatile organic compound (VOC) liquid-phase mass transfer coefficients are present in this study. Using Purge & Trap Concentrator, VOC spiked water samples are purged by high-purity nitrogen in the laboratory, the VOC liquid-phase mass transfer rate constants under the laboratory conditions are then obtained by observing the variation of VOCs purged out of the water with the purge time. The alpha factors of VOC liquid-phase mass transfer coefficients are calculated as the ratios of the liquid-phase mass transfer rate constants in real water samples to their counterparts in pure water under the same experimental conditions. This direct and fast approach is easy to control in the laboratory, and would benefit mutual comparison among researchers, so might be useful for the study of VOC mass transfer across the liquid-gas interface.

Keywords: mass transfer coefficient, purge and trap, volatile organic compounds, alpha factor.

The process of water-air mass transfer plays an important role in the global cycle and evolution of chemicals, and VOCs transferred from wastewater to the air have been recognized as one of the major sources of atmospheric VOCs[1]. The two-film model was widely used for the study of mass transfer across the water-gas interface[2,3], and mass transfer coefficients, or mass transfer rate constants, are the key parameters for applying the model. The differences between liquid-phase mass transfer coefficients of VOCs in real water, $(K_L)_r$, and their counterparts in pure water, $(K_L)_p$, are reflected by the alpha (α) factors, which equal $(K_L)_r/(K_L)_p$ and are less than 1.0 in value. For this reason the mass transfer parameters obtained in pure water cannot be directly adopted to investigate the real water situations. A great many studies used oxygen as a reference compound, explored theoretical or empirical relationships between mass transfer constants and other parameters like diffusion coefficients, and formulated the relationships of VOC and oxygen interfacial exchange in the same system, thus estimated the VOC interfacial transfer[4-11]. This reference compound method was mainly applied to cases in which mass transfer is controlled by the liquid film resistance. Due to the variation of empirical parameters with compounds and among different authors[12], in practice it is often difficult to choose parameters for studying mass transfer processes.

Many of the previous studies are based on the self-designed devices to survey the liquid-gas interface mass transfer. The purge and trap method is the USEPA standard method for determining VOCs in water matrices. This study is an approach to determine the α factors of VOC mass transfer coefficients by the commercial purge and trap device.

1 Theory

When purging by the high-purity nitrogen or helium in constant flow using the purge and trap device in the laboratory, VOCs are transferred from water to the gas phase. Assuming that the liquid and bubble gas phases are well mixed, and that the surface volatilization is negligible for VOCs entering the gas phase, we have

$$-V_l \frac{dC_l(t)}{dt} = \frac{dM_g(t)}{dt} = Q_g \times C_g(t), \tag{1}$$

where V_l is the liquid volume, L^3; $C_l(t)$ is the homogenous VOC concentration in the liquid phase in purge time t, ML^{-3}; $M_g(t)$ is the total mass of VOC entering the gas phase while purge time t, M; Q_g is

the constant flow rate of purging gas, L^3T^{-1}; and $C_g(t)$ is the bubble gas VOC concentration when the bubble exiting the liquid upper surface, ML^{-3}.

Under the laboratory conditions, the residence time of a bubble in the liquid phase is very short, so the VOC concentration in liquid phase can be considered to be constant during a bubble's rise. According to Matter-Muller's study we can have[13]

$$C_g(t) = H \times C_1(t) \times \left[1 - \exp\left(-\frac{K_L a}{H} \times \frac{V_1}{Q_g} \right) \right],$$ (2)

where H is the Henry's Law constant, dimensionless; K_L is the overall liquid-phase mass transfer coefficients, LT^{-1}. For the very high volatile organic compounds $(H > 0.1)$, interfacial mass transfer is controlled by the liquid film resistance, so overall mass transfer coefficients can be reduced to liquid phase mass transfer coefficients. a is the volume specific interfacial area, L^2/L^3; $K_L a$ is called the liquid phase mass transfer rate constants, T^{-1}.

In the purging device, if the surface volatilization of VOCs is negligible, that is, VOCs enter the headspace via the bubble-liquid mass exchange, therefore from eqs. (1) and (2) we have

$$-V_1 \frac{dC_1(t)}{dt} = Q_g \times H \times C_1(t) \times F,$$ (3)

where $F = 1 - \exp[-(K_L a/H) \times (V_1/Q_g)]$ reflects the VOC saturation degree in the bubble gas phase[13]. Eq. (3) leads to

$$C_1(t) = C_1(0) \exp\left(-(Q_g/V_1) \times H \times F \times t \right).$$ (4)

In the purge and trap concentrator, VOCs purged out of water are carried by nitrogen to the trap where they got adsorpted onto the adsorbents. Noticing that $M_g(0)$ is zero, combining eqs. (2) and (4), we have

$$M_g(t) = Q_g \int_0^t C_g(t) dt = V_1 \times C_1(0) \times \left[1 - \exp\left(-\frac{Q_g}{V_1} \times H \times F \times t \right) \right].$$ (5)

For initial total mass of VOC in liquid phase $M_1(0) = V_1 \times C_1(0)$,

$$-\frac{Q_g}{V_1} \times H \times F \times t = \ln\left(1 - \frac{M_g(t)}{M_1(0)} \right).$$ (6)

$M_g(t)$ can be obtained by gas chromatography analysis of VOC after thermo-desorption from the trap. By plotting the diagram of $\ln(1 - M_g(t)/M_1(0))$ vs t, we can obtain the slope $-(Q_g/V_1) \times H \times F$, given the Q_g, V_1 and H values, we can calculate F and $K_L a = -(HQ_g/V_1) \times \ln(1-F)$. The bubble's residence time in the liquid phase is very short, and Q_g is controlled to be relatively high. So for the organic compounds with high volatility, they are far from saturation in the bubble, and F can be reduced to $(K_L a/H) \times (V_1/Q_g)$, hence eq. (6) can be reduced to

$$-\ln\left(1 - \left(M_g(t)/M_1(0) \right) \right) = (K_L a) \times t.$$ (7)

This indicates that the slope of $-\ln[1 - M_g(t)/M_1(0)]$ to t is approximately the mass transfer rate constants $K_L a$. In the laboratory the determining of VOC mass transfer rate constants was performed under the same conditions for the real water samples and the pure water, as the definition of α factor is

$$\alpha_{VOC} = \frac{(K_L)_{VOC}^{real\ water}}{(K_L)_{VOC}^{pure\ water}} = \frac{(K_L a)_{VOC}^{real\ water}}{(K_L a)_{VOC}^{pure\ water}}.$$ (8)

Therefore, after determining the $K_L a$ in real water and pure water, from the above equation α factor can be calculated.

2 Experimental

Wastewaters from an aeration tank in a municipal wastewater treatment works were sampled for the determination of α factors of benzene, carbon tetrachloride and 1,1,1-trichloroethane in the wastewater matrices.

Standard dolution: 80 mL methanol was added to a 100 mL volumetric flask, using micro-volume syringe 100 μL of benzene, carbon tetrachloride and 1,1,1-trichloroethane were injected into the methanol in the flask respectively, and then methanol was added to the flask until the solution volume read 100 mL. The standard solution was capped and kept at 4°C for over 12 h before use.

Sample preparation: Wastewater was prepared in a 1.0 L volumetric flask. 0.5 g $CuSO_4$ $5H_2O$ and 0.5 mL above standard solution were added to the flask during the wastewater sample preparation. The target VOCs contained in the wastewater before adding standards did not interfere with the determination of α factor in our study, so if the target VOCs in the wastewater were in very high level, it was unnecessary to add standard solution to the wastewater for the determination. Pure water sample was prepared in a 1.0 L volumetric flask with double-distilled water and 0.5 mL standard solution adding to the flask. The wastewater sample and pure water sample were prepared before use and shaken for well mixing.

Laboratory determination: Tekmar 3000 Purge & Trap Concentrator with Tekmar 2016 Autosampler was coupled with a Hewlett Packard 5972 GC/MSD to measure VOCs purged out of the water phase. The GC column type was HP-VOC (30m× 0.25mm× 0.5μm). The GC temperature program was set initially to 40 °C for 2 min, then at 8°C/min to 180°C and kept for 5 min. The Tekmar 3000 was at first set to perform USEPA 524 standard method, and the purge gas flow and purge time were set to 40 mL/min and 11 min respectively. The target VOCs' $M_l(0)$ in the wastewater were first determined by USEPA 524 standard method, then regulated the purge gas flow to 5.0 mL/min. Injecting 5.0 mL wastewater samples once a time, $M_g(t)$ was measured while purge time t was set to 0, 0.5, 1.0, 2.0, 4.0 and 8.0 min respectively. The $M_g(t)/M_l(0)$ in eq. (7) could be calculated by the ratio of peak areas in total ion chromatography. For pure water samples the same procedures were followed as for wastewater samples.

3 Results and discussion

For benzene, carbon tetrachloride and 1,1,1-trichloroethane, the relationship of the $-\ln(1-M_g(t)/M_l(0))$ vs t in the wastewater and pure water is shown in fig. 1. The slopes of $-\ln(1-M_g(t)/M_l(0))$ to t in wastewater and pure water were k_w and k_p respectively, and from eqs. (7) and (8) α factor could be calculated by k_w/k_p. In our study the α factors of mass transfer coefficients in the studied wastewater are 0.62, 0.71 and 0.66 respectively for benzene, carbon tetrachloride and 1,1,1-trichloroethane.

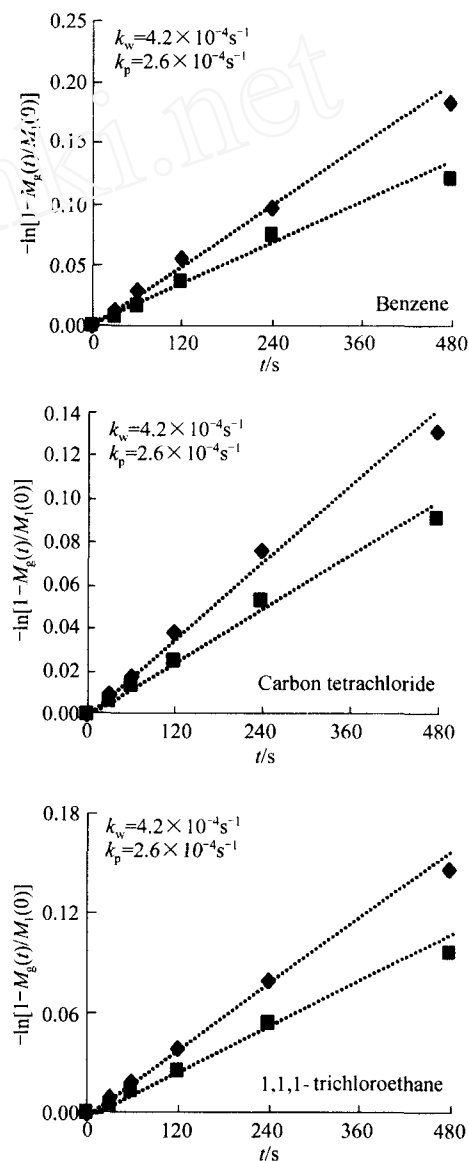The VOC mass transfer rate constants in pure water are unchanged if the laboratory

Fig. 1. $-\ln[1-M_g(t)/M_l(0)]$ vs t. ◆, Pure water; ■, wastewater.

operation conditions remain the same. So if the VOC mass transfer rate constants in real water samples are determined under the same operation conditions in the laboratory, from eq. (8) we can directly calculate α factors without repeating the test of mass transfer rate constants in pure water. With the α factor available, laboratory simulation with pure water matrices can be extended to the study of VOC mass transfer processes in real water matrices. Therefore in case of reference compound method impossible or inconvenient to be used, the α factor determination plus laboratory simulation might be a substitute for mass transfer investigation. Moreover, the method can determine alpha factors of many VOCs at one time, and its operation conditions are easy to be controlled, so in some cases the method might not only be more accurate and convenient, but benefit the comparison among different researchers.

In our study we have used some widely adopted assumptions: i) the mass transfer coefficient is constant over the wastewater depth range; ii) the liquid phase and bubble gas are well mixed; iii) the temperature is constant; iv) the equilibrium at the bubble-liquid interface obeys Henry's Law. What might be also noticeable is the possible variance of Henry's Law constants with the real water matrices. Many tests in wastewater revealed oxygen's β factor (the ratio of Henry's Law constants in real water to that in pure water) to be approximately 0.99[14], so the influence of this variance might be negligible. In our study volatilization from water column upper surface was also neglected, for the samples were analyzed just after the sample injection and the purge gas went through the water column in fine bubbles that had comparatively large surface areas, thus transfer through upper surface volatilization might be minor.

4 Conclusion

The purge and trap method was adopted to determine the VOCs' alpha factor of liquid-phase mass transfer coefficients. The easy control of laboratory test conditions will make access to mutual comparison among different researchers. The method might give helps to the study of mass transfer across water-gas interface for organic compounds with high volatility.

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