Mass Transfer Characteristics of an Airlift Contactor with a Semipermeable Membrane, Containing Aqueous Hydrocarbon Solution

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Abstract

The effect of hydrocarbon contaminants on gas-liquid mass transfer coefficient, \( K_La \), was studied in a 25 L concentric cylindrical airlift contactor with a semipermeable membrane. A specific form of the continuity equation was combined with gas holdup values in order to derive an expression for calculating the experimental mass transfer coefficient. A new surface renewal-stretch model was developed to correlate experimental data for the time-average overall mass transfer coefficient, \( K_{La,av} \), in the airlift contactor. This model was modified in order to predict the effect of hydrocarbon dissolution on mass transfer coefficient. Water with different hydrocarbon concentrations of 0-200 mg/L p-Xylene and 0-25 mg/L Naphthalene was used as liquid media, under varying superficial gas velocities. The results indicated that deviation of mass transfer coefficient could go either way when hydrocarbons were present in water: the most significant reduction in \( K_La \) occurred at the concentration of 37 (mg/L) for p-Xylene while \( K_La \) could be slightly recovered thereafter. A less severe depression of \( K_La \) was observed for Naphthalene.
Introduction

Airlift reactors are a special type of multiphase pneumatic contactors widely used in chemical and biotechnological process industries. The design of airlift contactors has undergone extensive modifications by proposing a myriad of configurations to improve the hydrodynamic and mass transfer characteristics. Airlift contactors are generally distinguished by two vertical sections: aerated and nonaerated zones. One of these zones sparged by a gas is called riser in which higher gas holdup leads to a difference in the bulk density of gassed liquid compared to that of downcomer and induces fluid circulation: upflow in the riser and downflow in the downcomer. In a development the impermeable membrane was replaced with a semipermeable one (permeable to liquid and impermeable to gas bubbles) in order to improve the rate of mass transfer and reduce the mixing time by producing the both vertical (upward in the riser and downward in the downcomer) and horizontal flow pattern through the draft tube from the downcomer to the. The resulting airlift contactor shows great significance for biotreatment of recalcitrant pollutants dissolved in water owing to the capability of immobilizing microorganisms to the porous membrane and improved rate of oxygen mass transfer.

Biotreatment technique in such a airlift contactor is based on activation of a presumably well-adapted microbial consortium in contaminated soil. Attachment of particles to a fixed support minimizes the friction between them and prevents them from leaving the reactor while it makes the stimulation of the indigenous microorganisms much easier (higher metabolic activity) by introducing nutrients and oxygen into the attached soil particles. Moreover, several layers of immobilized cells on a support provide greater resistance to toxicity.

Petroleum-based products are widely used in many industrial processes and accidental discharge of these chemicals may cause water and groundwater contamination. When these chemicals enter the surface or subsurface environment, some components dissolve and leach out of the slick, some evaporate, and the majority may eventually be biodegraded. Due to immediate detrimental effects in aqueous systems that cause substantial mortality of biota, the hydrosphere is the most heavily affected environmental
compartment by hydrocarbon components. The ecotoxicity of oil fractions including soluble aromatic compounds (PAHs) and BTEX is higher to aquatic organism. Knowledge of effects of dissolution of potentially water-soluble hydrocarbon pollutants on oxygen mass transfer behavior is important for assessing the potential of water-based technologies in biotreatment of crude and fuel oil contaminated waters. Improving oxygen supply in cell culture systems has been a central topic for many biochemical processes.

Spills of hydrocarbon compounds spread out almost immediately in water to form a semi-rigid film (slick) on the surface. When studying the thermodynamic behavior of surface films on liquid substrates, the solution properties are not usually of much interest. However, on the environmental side, a belief that a slight change in solution concentration can affect the transport of mass of various species, such as nutrients, oxygen, and chemicals shifts emphasis to the latter. The change in surface tension, though imperceptible, is believed to be the measure of impact on mass transport. The influence of dissolved hydrocarbons on oxygen mass transfer in aqueous systems has not been fully assessed to date. Certain observations reported in the literature support the hypothesis that dissolution of contaminants in general may significantly affect oxygen mass transfer rates in water. The main purpose of this study is to evaluate the effect of two chemical-constituents, namely p-Xylene and Naphthalene on oxygen mass transfer characteristics in a novel airlift contactor. The results are of importance in extending the influence of any surface contaminant including surfactants on oxygen mass transfer characteristics in gas-liquid contactors.
**Theoretical Development**

*Mass transfer in pure water*—Unsteady circulation with rocking motion of fluid particles increases the intensity of turbulence, which in turn changes incessantly the conformation, and position of eddies and exposes fresh surfaces to fluid particles. At the same time bulk motion also drives eddies and liquid particles in a continuous circulation. Surface renewal-stretch model was introduced by Jajuee et al. (2005a) on the assumption that diffusion happens in the same direction as convection, i.e. $z$ in the presence of both turbulent and convective motion. This model expresses the local velocity $v_z$ in time-dependent interface surface $A$, and gives the continuity equation a new form:

$$-z\left(\frac{\partial \ln A}{\partial \theta}\right)_{x,y} + \frac{\partial A}{\partial z} + \frac{\partial A}{\partial \theta} = D \frac{\partial^2 c_A}{\partial z^2}$$

(1)

The solution of Eq. (1) gives the time-dependent molar concentration of species $A$:

$$C = \frac{\text{erf}\left(\frac{Z A(T)}{\sqrt{4 \int_0^T A^2(\theta)d\theta}}\right)}{\text{erf}\left(\frac{Z A(T)}{\sqrt{4 \int_0^T A^2(\theta)d\theta}}\right)}$$

(2)

where $C = \frac{c_A - c_{A,i}}{c_{A,0} - c_{A,i}}$, $Z = -\frac{z}{\sqrt{D \theta_0}}$, $T = \frac{\theta}{\theta_0}$ and $A(\theta) = A_0 \left(1 - e^{-s \theta}\right) + A_0$, in which $s$ is the fractional rate of surface renewal.

The average flux over the time of exposure per unit area of turbulent surface is

$$N_{A,av} = (c_{A,i} - c_{A,0}) \int_0^\infty K_L(T)dT = K_{L,av}\left(c_{A,i} - c_{A,0}\right)$$

(3)

thus,

$$N_{A,z} = \Delta c \int \frac{D_A}{A_0^2 \pi \theta_0} \int_0^\infty \frac{A(T)}{\sqrt{A^2(\theta)dT}} \frac{\text{d}A(T)}{dT}dT$$

(4).
Solving the integrand of the second part of Eq (4) gives the time-average overall mass transfer coefficient as follows

\[ K_{L,\text{av}} = \sqrt{\frac{4D_s}{\pi}} \]  

(5)

Substituting \( s = \sqrt{\frac{U_g s g}{K}} \) in gaslift systems and

\[ a = \left( 0.5 \times 5000^{1-n/10} \right) C_7 \frac{\rho^{0.4} U_g^{(8-n)} / 10}{\sigma^{0.6} K^{0.1}} \left( \frac{\mu_s}{\mu_c} \right)^{0.25} \]

in Eq (5) yields the following correlation for Sherwood number

\[ Sh = 5000 \frac{(1-n)}{10} C_8 \frac{Sc^{0.5} Re^{10(n+2)}/(8n+17.5)}{Bo^{0.6} Fr^{5n-2}/(15(n+1))} \]  

(6)

Figure 1 & 2 show the experimental results obtained by various authors for Newtonian and non-Newtonian fluids vs the proposed correlation, Eq (6), with the average absolute deviation of 25% & 19%, respectively.

**Figure 1** - Experimental Sherwood number for Newtonian fluids vs. predicted Sherwood number from Eq. 6.
Figure 2- Experimental Sherwood number for non-Newtonian fluids vs. predicted Sherwood number from Eq. 6.

Eq. (5) can also predict mass transfer between drops, as the dispersed phase, and bulk of liquid. Experimental data has been correlated for $K_{L,av}/\sqrt{DN}$ values, in which $D$ & $N$ are molecular diffusivity and impeller speed in an agitated vessel, respectively, as illustrated in Fig. 3.
Mass transfer in the presence of dissolved hydrocarbons-

The change of mass transfer has been ascribed to interfacial motion, which in turn is attributed to hydrodynamic and molecular effects. It may be of value to show that how interfacial flows affect the overall exposed surface area for mass transfer and change mass transfer behavior.

According to surface renewal-stretch model:

\[
\left( N_{A,z} \right)_h = 2\sqrt{2} \Delta c A_d \left( \frac{D_A}{A^2 \pi \theta_0} \right) \int_0^{\infty} \left( \frac{dA}{dz} \right)^2 \frac{dz}{dT} \, dz
\]  

where subscript \( h \) designates the presence of contamination in general, and \( z_h \) is the depth in which the concentration of contaminants is equal to that of bulk concentration.

Contaminants with the greatest effect on the interface mobility, thus on mass transfer, are hardly soluble. When dealing with bubble swarms released from a submerged sparger, it is plausible to assume that a thin film of contaminants is formed at the gas-liquid interface as though contaminant molecules are exchanged between interface and bulk of liquid in equilibrium. The stagnant cap model describes how interfacial tension gradients act on surface flow with a force balance at any point in which equilibrium exists on the interface. Behavior of contaminants in vicinity of gas bubbles is in such a way that adsorbed concentration
is lower at the top than at the bottom of rising bubbles, because their molecules are dragged by adjacent liquid. We assume the same model for hydrocarbon components being the source of contamination in aqueous systems, in the sense that these contaminants are incessantly transferred from the bulk to the top of bubbles and leave from the bottom of bubbles to the bulk of the liquid. When the concentration of contaminant hydrocarbons in the bulk of the liquid is different from that at the gas-liquid interface, the net mass flux of the contaminant for the top of bubbles becomes

$$N_{H,z} = \sqrt{2} \frac{D_H}{A_0 \pi\theta_0} \frac{\Delta c_{Hi}}{d\theta} \int_0^T \frac{\left(\frac{dA}{d\theta}\right)^2}{(d\theta)^2} d\theta \int_0^T \left(\frac{dA}{d\theta}\right)^2 d\theta - 2\sqrt{2} \frac{D_H}{A_0^2 \pi\theta_0}
\times \int_0^\infty \frac{d\Delta c_{Hi}}{dz} \left(\int_0^T \left(\frac{dA}{d\theta}\right)^2 d\theta\right) dz \quad (8)$$

where $\Delta c_{Hi} = c_{bulk} - c_{Hi}$, in which $c_{Hi}$ is the interfacial concentration of contaminants and $c_{bulk}$ is the concentration far enough from the surface region so the bulk phase properties prevail. Solving Eq (8) and substituting in Eq. (7) gives the overall flux of oxygen relative to a phase boundary as follows (Jajuee et al. 2005b)

$$\left(\frac{N_{A,z}}{N_{A,z}}\right)_h = N_{A,z} \left[1 - C_6 c_{Hi} \left(\frac{d\gamma_{W(H)}}{dc_{Hi}}\right)^2\right] \leq N_{A,z} \quad (9)$$

Figure 4 shows the measured values compared with the calculated values of $N_{A,z} \left[1 - 1.6 c_{Hi} \left(\frac{d\gamma_{W(H)}}{dc_{Hi}}\right)^2\right]^{0.5}$ as a function of the concentration of p-Xylene. The experimental data were obtained by Jajuee et al. 2005c. Figure 5 shows the same values as a function of the concentration of Naphthalene when the concentration of p-Xylene remained constant at 76 mg/L.
Concentration of p-Xylene (mg/L)

Volumetric mass transfer coeff., $K_{La}$ (s$^{-1}$)

Figure 4- Volumetric mass transfer coefficient, $K_{La}$, in a membrane airlift contactor as a function of p-Xylene concentration in water at zero Naphthalene concentration and superficial gas velocities $U_{sg} = 4.24 \times 10^{-3}$ m/s and $U_{sg} = 2.10 \times 10^{-3}$ m/s.

Concentration of Naphthalene (mg/L)

Volumetric mass transfer coeff., $K_{La}$ (s$^{-1}$)

Figure 5- Volumetric mass transfer coefficient, $K_{La}$, in a membrane airlift contactor as a function of Naphthalene concentration in water at 76 mg/L p-Xylene concentration and superficial gas velocity $U_{sg} = 2.10 \times 10^{-3}$ m/s.
Conclusion

Satisfactory agreement between theory and experiment remains elusive for models that cannot predict a reduction in $K_{L}a$ followed by a softer trend of $K_{L}a$ increase. No adequate theory has been developed as yet to study the effect of hydrocarbon contaminants on mass transfer. Contributions made by experimental studies suggest that, however, deviation from mass transfer behavior caused by dissolved hydrocarbon components is a forgone conclusion. In brief, the extent to which the overall exposed interfacial surface area of mass transfer might be stretched is contingent upon the shape of gas bubbles, which in turn depends on gravity and surface tension effects. Therefore, changes in gas-liquid interface mass transfer resulting from surface contaminants are due to the reduction in surface tension. The model employed in this study could fully predict the effects of surface contaminants on gas-liquid oxygen mass transfer coefficient and satisfactorily fit experimental mass transfer data obtained from hydrocarbon contaminated aqueous systems.

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