Enhancement of gas-to-liquid oxygen transfer in the presence of fine solid particles for air-exposed multiphase system

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Abstract

To investigate “particle effect” promoting gas-liquid mass transfer for a better process control, nine species of fine particle ($d_2 = 1-15$ $\mu$m), divided into Group 1 ($\text{SSA} > 65.4$ $\text{m}^2/\text{g}$, termed PAC, $\text{SiO}_2$, $\text{Al}_2\text{O}_3$ and $\text{MnO}_2$) and Group 2 ($\text{SSA} < 9.8$ $\text{m}^2/\text{g}$, termed Biochar, Graphite, $\text{Mg(OH)}_2$, $\text{CaCO}_3$ and $\text{BaSO}_4$), were comparatively introduced for oxygenation tests in an air-exposed stirred system. Group 1 particles with interfacial-cleaning effect facilitated oxygen transfer better than their counterparts of Group 2. For all the particles employed, however, the “particle effect” interestingly presented under control of solid specific gravity, since enhancement factor ($E_f$) globally performed to grow up either when particulate density decreased or liquid density increased ($\text{Pb(NO}_3)_2$ as solute). Moreover, the strength of “particle effect” depends largely on interfacial turbulence, because proper agitation allowed optimal acceleration of oxygen transfer (700 rpm for this work), while either more sluggish or turbulent flow regime would hinder or even eliminate “particle effect”. Consequently, interfacial liquid-entrainment of particle entities was assumed to have played an initiative role for induction of “particle effect”, and this hydrodynamic process was elucidated to be subject to particulate specific gravity as well as interfacial turbulence.

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1. Introduction

Multiphase flow often takes place in chemical and biochemical industries consuming specific gaseous species, where suspended solid media are usually employed as heterogeneous reactant, functionalized catalyst or active substrates (Lindner et al., 1988). Mechanical agitation has been frequently utilized for mixing and mass transfer, because it is simple and flexible in process control. Prior to intense bulk reaction, however, a sufficient gas-to-liquid mass transfer is required to meet its fast consumption which is commonly the overall rate-limiting step (Joly-Vuillemin et al., 1996). For example in environmental practices, the oxygen transfer dominates the aerobic treatment of wastewater in a stirred-tank bioreactor (Zokaei-Kadijani et al., 2013). In fact, fine solid particles, usually present as catalyst or facilitator for bulk reaction, may simultaneously play a role to improve gas-liquid mass transfer (Dagaonkar et al., 2001) that can be labeled as “particle effect”.

The interesting nature of solid particles inducing “particle effect” has drawn a great deal of concern by researchers. It was documented that the addition of fine particles in micron-sized ($\mu$m) level (similar to the order of liquid-film thickness)
could give rise to an enhanced physical gas-absorption rate, whereas particles with larger size almost had no effect (Zhang et al., 2008). The solid loading is one of influencing factors as Smith and Skidmore (1990) have found that volumetric gas transfer coefficient increased with solid fraction of coal up to 2 wt% and then began to decrease, while Hwang and Lu (1997) reported a net reduction of gas transfer rate with an increase in amount of polystyrene particle.

Mechanism study aiming to interpret the particle-induced enhancement effect on gas transfer has been conducted since the original work published by Alper et al. (1980). Some researches attributed the particle effect to an adsorptive transport notion that was called “shuttle and grazing effect”, for which particles were assumed to adsorb an excessive amount of gas at the interface or within liquid film and then release the adsorbed molecules into the liquid bulk (Alper et al., 1980; Tinge and Drinkenburg, 1992; Demmink et al., 1998; Ruchiya et al., 2003). More recently, the effect of solid particles has been suggested due to the adsorptive elimination of trace interfacial “contaminants” such as dust and surfactants that hinder gas-liquid mass transfer (Svitova et al., 2001; Levitz, 2002; González-Garcia et al., 2004; Kaya and Schumpe, 2005; Kordač and Linek, 2006; Rosu and Schumpe, 2007). Kordač and Linek (2006) indicated that the interfacial boundary layer is “rigid” without particles that locally inhibits the mobility of liquid along the interface, while in the presence of particles it is mobile and the surface renewal proceeds (the explanation is very close to that suggested by Kaya and Schumpe (2005)). Yet Garcia-Ochoa et al. (1997) in their research noticed that the presence of pyrite particles (not porous) resulted in higher volumetric mass transfer coefficient compared to fine glass beads, which seems not to be in accordance with the “surfactant grazing” effect. Vinke et al. (1993) proposed a model with assumption of adhering particles relating the enhancement of incipient gas absorption which was verified by fluctuation experiments and gas-absorption measurements. Opposite conclusion against “particle effect” has also been reported as Derksen et al. (2000) observed a diminution of gas-liquid mass transfer coefficient once hydrophobic silica particles (d<sub>50</sub> = 13 μm) were added in a stirred tank reactor which was ascribed to interfacial block effect.

With respect to “particle effect” in a stirred system actually, explanations made solely by physicochemical properties of particles may not be comprehensive enough, since the motion of solid suspensions influenced by liquid turbulence should be considered as well, for which a transient impact of particles accumulating at gas-liquid interfacial region may be evoked affecting gas transfer. Roizard et al. (1999) observed that under flow conditions activated carbon (≤20 μm) investigated could not adhere steadily at the gas-liquid interface, and they made a recommendation that enhancement of mass transfer cannot be simply explained by stagnant adhesion of particles. That is to say, the hydrodynamic behavior of solid individuals should be taken into consideration on interpreting the “particle effect”. Similarly, Kluytmans et al. (2003) postulated that the solid particles should have played a back-mixing role on boundary layer thus improved gas transfer. They suggested that the increment of stirring intensity was not favorable for “particle effect” (using activated carbon), since in response the ratio of mass transfer coefficient with and without particles would began to decrease. All the scientific efforts indicated that a more likely explanation for “particle effect” should be a collection of influencing factors including both the relevant particulate properties and hydrodynamics, and on this regard, the controlling parameters accounting for “particle effect” needs to be further specified and investigated in multiphase flow.

In this paper, comparative investigation on kinetics of oxygen transfer was conducted using nine species of fine particle (deliberately selected), for which main purposes were (1) to extract the controlling factors for occurrence of “particle effect”, and (2) to make further discussion on possible mechanism interpreting the functionalization of fine particles as promoter for gas-liquid mass transfer.

2. Materials and methods

2.1. Materials

Powdered activated carbon (PAC), calcium carbonate (CaCO₃, analytical reagent) and manganese black (MnO₂, analytical reagent) were purchased from Keremel Reagent Co. Ltd. (Tianjin, China). Fine graphite powder (Graphite, analytical reagent) and aluminum oxide (Al₂O₃, analytical reagent) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Magnesium hydroxide (Mg(OH)₂, analytical reagent) was obtained from Fuchen Chemical Reagent Factory (Tianjin, China). Barium sulfate (BaSO₄, analytical reagent) was provided by Silian Chemical Plant Co. Ltd. (Shanghai, China). Silicon dioxide (SiO₂, analytical reagent) was bought from Ruijintie Chemical Reagent Co. Ltd. (Tianjin, China). Biochar particles were produced in laboratory by means of hydrothermal carbonization according to Xiao et al. (2012), for which poplar sawdust was utilized as raw material. Plumbous nitrate (Pb(NO₃)₂, analytical reagent) was purchased from Kaixin Chemical Reagent Co. Ltd. (Tianjin, China). Purified water was employed as liquid phase that was prepared by local tap water undergoing filtration and ion exchange (resin column).

2.2. Oxygen transfer experiments

Oxygen transfer tests were performed in a cylindrical glass reactor (unbaffled) with internal diameter of 120 mm containing 1L liquid as illustrated by Fig. 1. Digital tachometer magnetic stirrer (Jiangsu, China) was utilized to control the stirring speed in the range from 100 to 1000 rpm. Prior to each oxygen transfer test, a preset amount of solid sample used was milled using agate mortar, ultrasonically dispersed in water for 5 min, and then kept immersed for 1 h to ensure a complete wetting. The de-oxygenation as a preparation step for oxygen transfer was accomplished by bubbling of pure nitrogen gas. It should be addressed that for all the tests in the presence of
particles, there was no apparent sediment of particle clusters at the bottom of reactor within experimental time period, indicating the homogeneously fluidized state of solid suspensions being employed. For measurement of surface conductance, a thin-walled cell made of quartz glasses was dipped into the liquid surface and then quickly withdrawn as a sample of supernatant mixture. All experiments were performed at ambient temperature (23–25°C) and atmospheric pressure.

2.3. Analytical methods

The profile of particle size distribution was obtained by Laser Particle Size Analyzer Mastersizer2000 (Lasentec, Redmond, Washington), and the Sauter mean diameter \( d_{32} \) was automatically calculated according to \( d_{32} = \sum_{i=1}^{n} d_i^3 / \sum_{i=1}^{n} d_i^2 \). Material texture properties were measured using Autosorb-1 (Quantachrome, USA), where the specific surface area (SSA) and total pore volume \( (V_{\text{total}}) \) were determined by multi-point Brunauer-Emmett-Teller (BET) model based on the adsorption-desorption isotherms of \( N_2 \) at \(-196.15 \)°C. Contact angle characterizing the wettability of particle was detected by the Drop Shape Analyzer (DSA100, KRÜSS, Germany) and values were acquired through Drop Shape Analysis software. The density of solid phase \( (\rho_s) \) was determined by means of pycnometer. The liquid dynamic viscosity was detected by NDJ-1 rotary viscometer (Shanghai, China).

Concentration of dissolved oxygen \( (C_{O_2}) \) was measured by YSI 550A Handheld Dissolved Oxygen and Temperature System (USA, \( t_{63%} < 5 \) s). The volumetric mass transfer coefficient \( (k_l a) \) was calculated following Equation (1), and it is normalized with respect to a slight temperature change by Eq. (2).

\[
\frac{dC_{O_2}}{dt} = k_l a (C_{O_2}^* - C_{O_2})
\]  

(1)

\[
k_l a_{(20)} = \frac{k_l a_{(77)}}{\theta - 77}
\]  

(2)

Where \( C_{O_2}^* \) is the saturated concentration of dissolved oxygen, \( T \) is the liquid temperature, \( k_l a_{(20)} \) represents the normalized volumetric mass transfer coefficient at \( 20 \)°C, and \( \theta \) is the correction coefficient with generally accepted value of 1.024 (Stenstrom and Gilbert, 1981).

The specific interfacial area, namely “a” in Eq. (1), is a variable in response to mechanical agitation, for a cone-shaped vortex emerged at the centre of reactor and gradually grew with increasing stirring speed. Noting there was no bubble enmeshment within the covered intensity of stir, the lateral area of cone was taken into consideration for determination of specific gas-liquid contact area. Detailed information for determination of “a” is presented in Fig. 1.

Eventually, the normalized oxygen mass transfer coefficient can be obtained by Eq. (3).

\[
k_{L(20)} = \frac{k_l a_{(20)}}{a}
\]  

(3)

3. Results and discussion

3.1. Effect of particle species

Fine particle with potentiality to cause an enhancement of gas-liquid mass transfer is an interesting research topic for engineered applications. For a rational control of the “particle effect,” the implication of solid particle property with kinetics of gas absorption needs further investigation. In this section, nine species of fine particle were deliberately selected for comparative study (see Table 1 for detailed information), and enhancement factor of gas transfer \( (E_f) \) was introduced as reference for evaluation of “particle effect”. The \( E_f \) is defined as the ratio of normalized oxygen transfer coefficient determined in the presence and free from solid particles following Eq. (4).

\[
E_f = \frac{k_{L(20,P)}}{k_{L(20,NP)}}
\]  

(4)

Where \( k_{L(20,P)} \) and \( k_{L(20,NP)} \) represent respectively the normalized oxygen mass transfer coefficient with and without particle.

Result of \( E_f \) for different particle systems are illustrated by Fig. 2. The grain size is known to be a confining factor since particles over hundreds of microns level always lose their interfacial impact for an occurrence of “particle effect” (Zhang et al., 2008). It appeared in Fig. 2 that dimensionless value of \( E_f \) all surpassed 1.0 with particle addition, showing the presence of selected tiny solid species had made “particle effect” and they are suitable in size \( (d_{32} = 1–15 \mu m) \) for conductance of comparative study.

It is known that surface-adsorptive particles tend to sweep air-diffused “contaminant” residing in gas-liquid interfacial region, and in turn the gas absorption will be accelerated due to a lowered interfacial rigidity (Kordač and Linek, 2006). For a better evaluation, we therefore divided the particles into two series named Group 1 and Group 2. Particles of Group 1 with SSA higher than 65.4 m²/g were more surface-active than that of Group 2 (SSA < 9.8 m²/g), and were regarded to have more adsorption sensitivity toward interfacial “contaminant” (more possibly some polarized tiny dusts diffused from air).

Surface-active carbon is frequently used as catalyst (Sánchez-Polo et al., 2005) in scenarios of three-phase reaction, and meanwhile referring to Fig. 2, it can promote gas transfer since PAC at concentration of 4 kg/m³ remarkably accelerated oxygen absorption with \( E_f \) up to 4.37 (close to that of 4.71 reported by Klytmans et al. (2003)).
Table 1 – Relevant properties of fine solid particles used. Type $\rho_L$ (g/cm³) $d_{32}$ (μm) Size distribution (μm) Contact angle (°) $S_{BET}$ (m²/g) $V_{total}$ (cm³/g)

<table>
<thead>
<tr>
<th>Type</th>
<th>$\rho_L$ (g/cm³)</th>
<th>$d_{32}$ (μm)</th>
<th>$D_{50}$</th>
<th>$D_{10}$</th>
<th>$D_{90}$</th>
<th>Contact angle (°)</th>
<th>$S_{BET}$ (m²/g)</th>
<th>$V_{total}$ (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>1.72</td>
<td>2.199</td>
<td>2.135</td>
<td>3.243</td>
<td>5.145</td>
<td>30.6</td>
<td>413.569</td>
<td>0.615</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.687</td>
<td>14.713</td>
<td>7.607</td>
<td>48.541</td>
<td>107.682</td>
<td>17.43</td>
<td>72.029</td>
<td>0.0593</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.566</td>
<td>4.093</td>
<td>1.533</td>
<td>8.358</td>
<td>54.231</td>
<td>14.78</td>
<td>275.949</td>
<td>0.470</td>
</tr>
<tr>
<td>MnO₂</td>
<td>4.55</td>
<td>1.379</td>
<td>1.336</td>
<td>31.914</td>
<td>92.818</td>
<td>20.14</td>
<td>65.457</td>
<td>0.0495</td>
</tr>
<tr>
<td>Biochar</td>
<td>1.205</td>
<td>10.359</td>
<td>4.769</td>
<td>25.198</td>
<td>101.234</td>
<td>73.63</td>
<td>8.855</td>
<td>0.0514</td>
</tr>
</tbody>
</table>
their enhancements were not reached such an extent as PAC, since $E_I$ differentiated significantly following the order of $E_{(PAC)}(4.37) > E_{(SiO_2)}(2.96) > E_{(Al_2O_3)}(1.98) > E_{(MnO_2)}(1.69)$. Actually, SiO$_2$, Al$_2$O$_3$, and MnO$_2$ are all good surface-active materials that are believed to be capable for induction of interfacial-cleaning, e.g., MnO$_2$ particles have been proved to be effective sorbent in removal of dissolved organics (Singh et al., 2010) or heavy metals such as arsenate ion (Liu et al., 2010). However, $E_I$ of MnO$_2$ system exhibited to be far less than PAC system. The comparative outcome revealed that, the interfacial-cleaning process contributing to “particle effect” should not be regarded as the controlling factor, due to the significant discrepancy of $E_I$ obtained by Group 1 particles. Interestingly, $E_I$ for Group 1 particles globally performed to increase as the solid density decreased (see Fig. 2), which had shown a reverse relationship between the extent of “particle effect” and particulate specific gravity.

Graphite powder (abbreviated as Graphite) is composed of crystalline carbon with little adsorption capacity for oxygen. It can be seen in Fig. 2 that the presence of Graphite, as Group 2 member, could also induce a sound enhancement of oxygen transfer with $E_{(Graphite)}$ of 2.89. Four other samples in Group 2, namely Biochar, Mg(OH)$_2$, CaCO$_3$ and BaSO$_4$, were introduced respectively as inert particles for comparison. The $E_I$ for Group 2 particles also made clear difference, following the order of $E_{(Biochar)}(3.45) > E_{(Graphite)}(2.89) > E_{(Mg(OH)_2)}(2.04) > E_{(CaCO_3)}(1.46) > E_{(BaSO_4)}(1.05)$. It was noticed that, quite coincide with the trend of Group 1, $E_I$ of Group 2 particles likewise presented to be reversely correlated with material density. To wit, the “particle effect”, for all the solid candidates in Group 1 and Group 2, expressed to be subject to particulate specific gravity.

Facts demonstrated a dominative role of solid specific gravity on the profile of $E_I$, which should be underlined as a controlling aspect accounting for the extent of “particle effect”, though the interfacial-cleaning can made appreciable contribution as $E_I$ of PAC (4.37) was higher than that of Graphite (2.89) with quite similar solid density.

Here the authors take the assumption that an entrainment of fine solid particles (by liquid micro-elements) might have took place, inducing instantaneous fast-moving of particles from bulk into gas-liquid interfacial region (performed as particle-collision toward the liquid film). In response, the boundary film-layer inhibiting gas transfer was deformed or disrupted by particle intervention, leading to an enforcement of interfacial turbulence that benefits gas-to-liquid oxygen penetration. Efforts to describe hydrodynamic effect of particles have also been made by researchers, since Zhang et al. (2008) mentioned that small particles would produce a reduction of “internal diffusion resistance” thus favoring the isobutene hydration, and Kluytmans et al. (2003) presumed a back-mixing effect of particles facilitating gas-liquid mass transfer. But a convincing detection on the precise functional way for moving particles at gas-liquid interfacial region is still very hard to realize.

Based on assumption of particle entrainment, the motion of fine particles at gas-liquid interface should be dictated by interfacial liquid fluctuation as a consequence of dissipated stirring power (700 rpm for this section). Fine particles of higher specific gravity own stronger inertial force against any driving energy of liquid, and in correspondence, will be less sensitive to an instantaneous entrainment by tiny fluid-elements occurring in or adjacent to the gas-liquid interfacial region. Thus the physical deformation of liquid film
by momentary particle-induced collision would be impaired. Moreover, fine particles with lower specific gravity are more prone to accumulate at the region very close to film zone, making an easier and more active interfacial-collision by local liquid entrainment for “particle effect”. For outcome of Group 2 in Fig. 2 accordingly, the enhancement of $E_t$ with decreasing solid density could be attributed to an improved process of particle collision toward liquid film. Simultaneous with the intensified particle-to-film collision, the interfacial-cleaning effect assigned to Group 1 particles will correspondingly got promote as a result of enhanced interfacial particle-intervention, giving rise to the dual-benefit for “particle effect” if a lower solid density can be controlled. Then it is not difficult to understand the profile of $E_t$ for Group 1 particles (see Fig. 2).

Consequently, both the behavior of particle-collision and “interfacial-cleaning” (if any) should account for “particle effect” in air-exposed multiphase system with time-lasting diffused “contamination”, and interfacial liquid-entrainment of low-density particles should be emphasized as paramount important for the occurrence of interfacial particle-intervention and the subsequent “particle effect”.

The density of liquid phase is closely coupled to specific gravity of particle, and it is often the variation in the case of salty solutions or organic-loaded matrix. Then the character of “particle effect” for salty solution was examined taking Graphite as model particle and Pb(NO$_3$)$_2$ as the solute. Results are shown in Fig. 3. In cases free from particle, mass transfer coefficient slightly decreased with increasing Pb(NO$_3$)$_2$ amount in a similar trend as Sergio et al. (2014), because the presence of electrolytes in water enhanced liquid viscosity that impaired oxygen diffusion (Jammongwong et al., 2010). More specifically, the detected dynamic viscosities were respectively 1.02, 1.31, 1.45 and 1.72 mPa$s, corresponding to the liquid density containing Pb(NO$_3$)$_2$ of 0, 10, 30 and 50 wt%.

Upon addition of Graphite, however, mass transfer coefficient gradually grew up with increasing Pb(NO$_3$)$_2$ concentration reading the inset of Fig. 3. This interesting phenomenon conform the idea that a proper diminution on particulate specific gravity will benefit “particle effect”. van der Zon et al. (1999) in hydrogenation process observed that higher concentration of methyl acrylate tend to weaken the agglomeration of Pd/C catalyst, for which the effective particle diameter accordingly decreased leading to an increment in conversion rate of organic solutes. Yet taking stagnant images of particle population could not well delineate the fast-moving state of particles that were believed to be in homogeneous phase during stirred reactions. A more acceptable explanation may be that, the salty liquid phase had reduced the specific gravity of particle, making more fine individuals available and vigorously collided at the film zone that benefited gas-liquid mass transfer.

Generally, the “particle effect” for a stirred reactor followed an opposite trend to the variation of solid specific gravity, and this interesting phenomenon may be attributed to the implication of material specific gravity with its interfacial motion driven by liquid entrainment. It should be reminded that production of floating particles with specific gravity lower than 1.0 is not advisable, since a stagnant solid layer would be formed undesirably on surface of liquid phase as a barrier inhibiting gas transfer (Tagawa et al., 2012).

3.2. Effect of interfacial turbulence

In stirred multiphase system, the motion of fine solid particles could be globally simplified as the centripetal gyration and perpendicular transport to gas-liquid interface, and their collective hydrodynamic impacts are considered to arouse the “particle effect”. The stirring intensity, being the source power of dissipated flow energy, will control the state of convective particle motion at gas-liquid interface and thus may have certain association with “particle effect”. Accordingly, the evolution of $E_t$ as a function of stirring speed was experimented in the presence of solid particles, for which PAC and Graphite, with quite similar specific gravity, were chosen as typical particle species respective for Group 1 and Group 2. Results were recorded in Fig. 4.

For stirring speeds lower than 400 rpm, either PAC or Graphite can hardly show “particle effect” on kinetics of oxygen transfer. This phenomenon was possibly because the power dissipated is not sufficient enough to realize effective liquid enmeshment of fine particles into the interfacial region.
that inhibits gas transfer. As stirring speed elevated from 400 to 700 rpm, the selected particles began to functionalize as promoter for oxygen transfer, and this ameliorative effect became increasingly evident. Meanwhile, the PAC of Group 1 always performed better “particle effect” than Graphite of Group 2, reflecting partial but not decisive contribution of interfacial-cleaning effect (see discussion in Section 3.1). It is necessary to address that the solid loading should affect the extent of “particle effect”. Read inset of Fig. 4, the optimal concentration allowing “particle effect” was about 4 kg/m³ for both PAC and Graphite, while either insufficient or excessive loading of solid phase will not produce more positive contribution. Regarding the assumption of this work, reasonable explanation on concentration impact is that the effective collision (between particles and liquid film) was subject to the abundance of fine solid individuals and microscopic space provision, and the corresponding mathematical descriptions has been established in the authors’ previous work (Zhang et al., 2013).

Turning back to Fig. 4, once the stirring speed increased over 700 rpm, 𝐸₁ of both PAC and Graphite systems suddenly began to drop down, demonstrating that the state of hydraulic agitation thereafter is no more suitable for induction of “particle effect”. The violence of energy dissipation is directly linked to flow regimes with different character of interfacial turbulence. Driven by violent agitation, the interfacial hydrodynamics would conceivably be converted from laminar-like flow to a turbulent regime, and in response, the interfacial gas-liquid convection got gradually intensified and performed to overshadow the hydrodynamic perturbation by local particles. As a consequence of turbulent flow regime, the “particle effect” on deformation of boundary liquid film was largely confined or even eliminated (see Fig. 4).

To verify the transformation of flow regime considered to take place as a function of stirring speed, here the authors tried to use a calculative method with respect to the profile of transferred oxygen mass. The process of gas transfer depends both on molecular thermal diffusion and turbulent mixing as can be expressed by Eq. (5).

\[ M_T = M_C + M_D \]  

(5)

where, \( M_T \) represents the total transferred mass, \( M_C \) is transferred mass induced by interfacial gas-liquid convection, and \( M_D \) is the transferred mass by molecular diffusion.

The unsteady-state molecular diffusion is an entropy-driven spontaneous process. According to the Fick’s second law, mass transfer induced simply by molecular diffusion can be written in parabolic type as expressed by Eq. (6).

\[
\frac{\partial C_A}{\partial t} = D_{O2} \frac{\partial^2 C_A}{\partial z^2}
\]  

(6)

where, \( C_A \) is oxygen concentration at gas-liquid interface, \( t \) represents the time, \( D_{O2} \) is the diffusion coefficient for oxygen with average value of 2.095 × 10⁻⁵ m²/s at 20°C referring to literatures (Bouwer et al., 1997; van der Zon et al., 1999; El-Din and Smith, 2003; Linek et al., 2008), and “z” axis direction is perpendicular to water surface.

For \( z = 0 \) and \( t ≥ 0 \), the parameter \( C_A \) can be replaced by the saturated dissolved concentration “\( C_{O2}^r \)”. Assuming if \( z → ∞ \), the dissolved concentration of oxygen will be close to zero. Then dissolved gas concentration can be written by Eq. (7) as a result of Eq. (6), where the bulk concentration of oxygen is preset at zero at the beginning of mass transfer.

\[
C_{A(z,0)} = C^r[1 - \text{erf}(\frac{z_0}{\sqrt{4D_{O2}t}})]
\]  

(7)

where, \( C_{A(z,0)} \) is oxygen concentration at \( z = z_0 \), and \( \text{erf} \) is the error function can be found in many mathematical tables. Based on film theory, \( z_0 \) indicates the thickness of liquid-film layer for oxygen transfer and can be approximately determined by \( \frac{D}{v_t} \).

Then the molar amount of transferred gas for time interval “\( t \)” can be evaluated by Eq. (8) taking into consideration the Fick’s first law \( (N_0(t) = -D_{O2} \frac{\partial C_A}{\partial z}|_{z=z_0} dt) \) in which \( N_0(t) \) denotes the total mass transfer flux for each unit time.

\[
M_{O2(0)} = S_A D_{O2} \int_0^t \frac{\partial C_{A(z,t)}}{\partial t}|_{z=z_0} dt
\]  

(8)

where, \( M_{O2(0)} \) is total transferred mass (or molar amount) by diffusion over time interval “\( t \)”, and \( S_A \) is the apparent gas-liquid contact area.

Accumulation of aqueous oxygen over time will add extra influence for local concentration gradient at \( z_0 \), and hereby the authors choose very short time interval of 10 s to ensure the accuracy in determination of \( M_{O2(0)} \). Then the contribution of interfacial convection to total mass transfer based on Eq. (5) can be evaluated by Eq. (9), where \( M_T \) can be obtained by extrapolation method based on kinetics of oxygenation.

\[
\alpha = \frac{M_{T(10s)} - M_{O2(10s)}}{M_{T(10s)}}
\]  

(9)

where, \( \alpha \) represents the contribution of interfacial turbulence to total amount of aqueous oxygen transferred from gas to liquid.

All the computations involved were completed by software MATLAB 7.0, and the result of \( \alpha \) is illustrated by Fig. 5. Due to gradual thinning of boundary layer, the \( \alpha \) smoothly grow up with increasing stirring speed for moderate agitation (lower than 700 rpm). This result also reflected information that the dissipated agitation power could be flexibly regulated just by altering the stirring speeds in equidifferent range of 100 rpm.

![Fig. 5 - Evolution of normalized mass transfer coefficient and \( \alpha \) as a function of stirring speed (solid concentration: 4 kg/m³).](image-url)
Once stirring speed climbed up to 700 rpm and went on elevating, $\alpha$ sharply enhanced as can be seen in Fig. 5, indicating that the surface hydrodynamics has probably transformed into turbulent regime. That is to say, the interfacial gas-liquid convection was substantially intensified and become the dominant influence on oxygen transfer. Correspondingly, oxygen transfer coefficient (i.e., $R_{O2G}$) for pure water with no solid phase largely increased upon stirring speed over 700 rpm (see Fig. 5). In contrast, $R_{O2G}$ for Graphite system almost stopped growing in turbulent regime. This was because the fast liquid renewal severely deformed or even disrupted the liquid film, whereas this “hydrodynamic effect” should principally be assigned to particles in moderate flow patterns (less than but close to 700 rpm). Consequently, the particle-induced hydrodynamic effect at gas-liquid interface was in discount once turbulent regime was formed and developed. As for the presence of PAC, the contribution of interfacial-cleaning to “particle effect” simultaneously improved with an enhanced interfacial entrainment of particle. Once turbulent regime was formed, however, $k_{O2PAC}$ for PAC unexpectedly began to decline as can be seen in Fig. 5. Possible explanation may be that, the reinforced gas-liquid convection had induced an intense flush to surface of particles enriched in situ at interface, resulting in (1) destruction of the balanced physical-adhesion of trace dust-contaminants at particle surface and (2) restriction of continuous settlement of dust-contaminants onto particle surface. Thus for PAC, the action of interfacial-cleaning was impaired in turbulent regime, for which a significant decline of $k_{O2PAC}$ accordingly took place. Then it is no surprising that both the $E_{PAC}$ and $E_{Graphite}$ enhanced with increasing stirring speed up to a peak value around 700 rpm, while afterwards their “particle effects” began to drop down (see Fig. 4).

The Reynolds number (Re) was examined following Eq. (10) (Arratia et al., 2004), though for a stirred reactor it may not be a very precise dimensionless parameter.

$$\text{Re} = \frac{d^2 np \rho}{\mu}$$

(10)

Where $d$ is the diameter of magnetic stirrer, $n$ is the rotational speed, $\rho$ is the solid density, and $\mu$ is the dynamic viscosity in the presence of particles.

It should note that the values of $\mu$ detected in the presence of particle species are quite close to water (all within 1.0–1.25 mPas). Then we may take the case of Graphite as model particle representing Group 2 or the analogous particles. Under stirring speed of 700 rpm where Graphite particles optimally worked for “particle effect”, the Re was calculated to be $1.05 \times 10^8$ that appreciably coincides with the empirical minimum for engineered hydraulic design (Re $\geq 10^4$) for stirred reactors. This outcome suggested that proper regulation of agitation for air-diffused multiphase reactor could satisfy both the requirement of a complete mixing as well as an optimal particle effect on gas-liquid mass transfer. For surface-active Group 1 particles, nevertheless, it is not convincing enough to use Reynolds number as the controlling hydrodynamic parameter, because the process of interfacial-cleaning will add more complexity to “particle effect” (further investigation will need to be done).

To seek further evidence for interfacial entrainment of particles, the authors tried to investigate the profile of supernatant conductance in stirred multiphase flow. Here Graphite and BaSO$_4$ were deliberately selected as the solid phase due to their electric sensitivity, chemical stability (insoluble) as well as material purity. As shown by Fig. 6, surface conductance of Graphite mixtures exhibited to ascend as stirring speed grew up within the range allowing “particle effect”, which probably reflected the entrainment of particle entities into the interfacial region deforming boundary layer (illustrated by inset of Fig. 6). For BaSO$_4$ system in contrast, the surface conductance was almost unchanged as agitation intensity varied, implying possibly the absence of BaSO$_4$ particles at gas-liquid interface. This analysis is in accordance with the fact that BaSO$_4$ particles could hardly improve oxygen transfer referring to Fig. 2. It should note that lower conductivity for BaSO$_4$ compared to Graphite did not mean a lower concentration of particles (both are set at 4 kg/m$^3$), but was just due to the natural conductivity of these fine solid material. Comparative results on the profile of supernatant conductance in response to interfacial turbulence, therefore, may serve as detectable evidence supporting the assumption that, interfacial entrainment of particle should be a decisive process for development of “particle effect”, for which the initiation step was mainly subject to particulate specific gravity and interfacial turbulence.

4. Conclusions

Particle-induced intensification of gas-liquid mass transfer in multiphase flow is an interesting research topic for many chemical engineering sectors. Abstraction of main aspects affecting the “particle effect” is of practical importance for better process control, though actually some dynamic parameters is still very difficult to detect, like the dimension of film zone between phases, particle-adhesion of trace interfacial “contaminant” such as dust (diffused from air), a precise trajectory of particle populations driven by mechanical agitation, etc. In order to gain more process information accounting for “particle effect”, the authors conducted comparative study using nine kinds of fine solid particle that were divided into adsorptive group with SSA higher than 65.4 m$^2$/g (Group 1) and a priori sorption-inert group with much less SSA (Group 2). Due to interfacial-cleaning behavior, Group 1 particles always show better “particle effect” than their counterparts of Group 2. However, the performance of “particle effect” for all the particle species was predominately controlled by solid specific gravity, rather than a simple surface-adhesion effect.
Consequently, liquid entrainment of particles allowing intercollison with “film zone” was assumed to play a decisive role for induction of “particle effect”, which was further validated to be subject to both the particulate specific gravity and interfacial turbulence. The authors tentatively examined supernatant conductance of Graphite and BaSO₄ systems in response to interfacial turbulence, and comparative results may be recommended as supportive evidence for occurrence of particle-intervention at interfacial region as the initiative step for “particle effect”.

The conclusions obtained are believed to have guiding significance for engineered process control of gas transfer by virtue of “particle effect”, such as a more rational selection/preparation of solid phase and regulation of stirring energy for air-exposed stirred reactors.

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References


