Enhancement of Volumetric Mass Transfer Coefficient for Oxygen Transfer Using Fe₂O₃-Water Nanofluids

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ABSTRACT
Experiments were carried out with Fe₂O₃-water nanofluids to study possible enhancement in volumetric mass transfer coefficient for transfer of oxygen from air bubble to nanofluid, in an agitated, aerated bioreactor. The nanoparticles concentration was varied in the range of 0.022 to 0.065 wt.%, while the reactor was operated at three operating conditions viz. 200 rpm and 1.5 L min⁻¹ of air flow, 100 rpm and 1.5 L min⁻¹ of air flow and 200 rpm and 0.75 L min⁻¹ of air flow. Nanoparticles were found to contribute to enhance oxygen transfer through ‘grazing effect’. An enhancement of 63% was observed for 0.065 wt.% Fe₂O₃-water operated at 200 rpm and 0.75 L min⁻¹ air flow.

Key words: Nanofluid, effective volumetric mass transfer coefficient, grazing effect, bioreactor

INTRODUCTION
Nanofluids are colloidal suspensions of nanoparticles of the size 1-100 nm in a base fluid (Choi, 1995). Addition of nanoparticles to a liquid increases its thermal conductivity and viscosity. Since thermal management is conceived as the major application of nanofluids, thermal conductivity enhancement in nanofluids has been widely studied as evident from reviews (Wang and Mujumdar, 2007; Li and Kleinstreuer, 2008; Bahrami et al., 2007; Yu et al., 2008; Murshed et al., 2008). Relatively fewer studies have focused on viscosity increase (Nguyen et al., 2008; Ko et al., 2007; Phuoc and Massoudi, 2009; Chen et al., 2007; Garg et al., 2009). In aerobic bioreactors, oxygen mass transfer is rate-limiting, compared to oxygen consumption by the microorganisms. Lower oxygen mass transfer rate is attributed to lower solubility of oxygen in water and hence the emphasis is on the improvement of oxygen transfer rate from the air bubble to fermentation broth. This may be achieved by use of surfactants or other additives including fine/ultra-fine particles. This work focuses on the role of Fe₂O₃ nanoparticles in enhancing the volumetric mass coefficient in an agitated, aerated bioreactor.

Kars et al. (1979) discovered ‘grazing effect’, a mechanism by which fine particles in suspension adsorb solute from the gas and rapidly transfer the same to liquid. Zhou et al. (2003) proposed that the mass transfer coefficient may be increased or decreased due to the presence of particles, depending on the dominant of two events: (1) decrease in film thickness due to shearing action by the particles (2) lowering of diffusion coefficient of gas in the liquid owing to increase in viscosity of liquid due to addition of particles. The first study on use of nanoparticles for mass transfer
application seems to be the work of Wen et al. (2005) who investigated the gas–liquid mass transfer in internal loop airlift reactor in the presence of nanoparticles. A strong influence of nanometer sized particles on mass transfer was observed. Krishnamurthy et al. (2005) observed more than one order of magnitude increase in dye diffusion rate using 0.5 vol.% 20 nm Al₂O₃-water nanofluids, compared to that of water. Olle et al. (2006) observed 600% improvement in gas-liquid oxygen mass transfer rate with Fe₂O₃-water nanofluids in an agitated, sparged reactor at nanoparticle concentrations below 1 wt.%. The influence of CuO, Cu, Al₂O₃ nanoparticles on the absorption of ammonia by binary fluid (ammonia-water mixture) has been reported, where in the use of 0.1 wt.% Cu-binary nanofluid led to 321% enhancement in the absorption of ammonia (Kim et al., 2006; Kim et al., 2007). Contrary to the earlier reports on the enhancement of mass transfer due to addition of nanoparticles in an absorption solvent, the non-adsorbing, viscoelastic colloidal silica solution showed lower mass transfer rate and mass transfer coefficient for absorption of CO₂ in 2-amino-2-methyl-1-propanol compared with pure solvent (Park et al., 2006; Park et al., 2008). Kang et al. (2008) reported enhancement in vapor absorption rate by incorporating iron nanoparticles or carbon nanotubes in H₂O/LiBr binary liquid. Vapor absorption rate with 0.1 wt.% CNT was found to be 2.48 times the absorption rate without nanotubes.

MATERIALS AND METHODS
Preparation of nanofluids: Iron oxide nanoparticles (α-Fe₂O₃, 20-50 nm spheres) were purchased from Nanostructured and Amorphous Materials Inc., USA. The nanoparticles, as received were in aggregated form and must be dispersed using milling or probe ultrasonication, as per the guidelines provided by the supplier. A custom-made stirred bead mill was used for dispersing Fe₂O₃ in water at a pH of 8.5. This was followed by dilution to obtain nanofluids of appropriate concentration.

Characterization of nanofluids: The average particle size was determined by Laser Diffraction studies using a particle size analyzer (Blue Wave, Microtrac, Japan). The crystalline/amorphous nature of the as-processed Fe₂O₃ and the milled powders were ascertained using a X-ray diffractometer (D8 Focus, Bruker, Germany). The zeta potential of the nanofluid was determined using a Zetasizer (Nano-ZS, Malvern Instruments, USA). The Viscosity of nanofluids was measured using a viscometer (LVDV II+ Pro, Brookfield Engineering, USA) using an Ultra-low (UL) adaptor with spindle, S00.

Measurement of kₐa in stirred tank reactor: Successful enhancements in mass transfer have been reported with nanofluids containing less than 1 wt.% nanoparticles (Krishnamurthy et al., 2006; Olle et al., 2006; Kim et al., 2006). The viscoelastic nature of 31 wt.% SiO₂-water solution was vastly responsible for reduced kₐa for CO₂ absorption in the study of Park et al. (2006). Hence, experiments were designed in the present study, to utilize very low concentrations of Fe₂O₃-water nanofluids, such that the rheological characteristics of nanofluid are not much different from that of water. The maximum nanoparticles concentration employed here is 0.065 wt.% and hence the viscosity of Fe₂O₃-water nanofluids and that of water would not be much different.

Measurement of kₐa was carried out in a stirred tank bench-top fermentor (BIOFLOW 115, New Brunswick, USA). The fermentor is equipped with sensors for monitoring Dissolved Oxygen (DO), pH and temperature. Air at a controlled flow rate can be supplied through a sparger located below the impeller. In a typical experiment, 1.5-L of Fe₂O₃-water nanofluid was taken in the fermentor followed by the calibration of DO probe at the required air flow rate and impeller speed.
The system was deoxygenated by the addition of sodium sulphite with gentle agitation. Once the percentage oxygen saturation was close to minimum, addition of sodium sulphite was stopped. This was taken as the initial percentage saturation. Air at the required flow rate was supplied, which results in oxygen absorption by nanofluid and hence, an increase in percentage saturation. The percentage saturation was measured at regular intervals of time, till a plateau in percentage saturation was obtained, from which \( k_{1,a} \) was determined.

**RESULTS**

**Characteristics of nanofluid:** The average particle size, as determined by Laser Diffraction (LD), was found to be 120 nm. X-ray diffraction studies revealed the amorphous nature of milled powders, though as-purchased \( \text{Fe}_3\text{O}_5 \) was crystalline. The zeta potential of nanofluid was determined to be -24.3 mV and nanofluids remained stable for more than a week. The viscosity of nanofluids increased linearly with nanoparticle concentration (data not shown for brevity), with the viscosity of 1.3 wt.% \( \text{Fe}_3\text{O}_5 \)-water nanofluid being 7% higher than that of water.

**Influence of nanoparticles mass percentage on percentage saturation:** The comparison of percentage saturation-time data for pure water and that of \( \text{Fe}_3\text{O}_5 \)-water nanofluids of different nanoparticles mass concentration is shown in Fig. 1 for the reactor operating conditions of 200 rpm and 0.75 L min\(^{-1}\) of air flow. It is evident from Fig. 1 that the percentage saturation increases rapidly with time for \( \text{Fe}_3\text{O}_5 \)-water nanofluids compared to that of pure water. This was observed for all the operating conditions investigated, though data are not presented to maintain brevity. This observation hints at enhanced transfer of oxygen from air to \( \text{Fe}_3\text{O}_5 \)-water nanofluids compared to that of pure water.

**Influence of nanoparticles concentration on \( k_{1,a} \):** Volumetric mass transfer coefficient (\( k_{1,a} \)) is normally used in the analysis of mass transport in bioprocess systems. This circumvents the need for the measurement of mass transfer coefficient (\( k_1 \)) and interfacial area (\( a \)) separately and hence used as a convenient parameter for design, analysis and scale up of bioreactor systems. The volumetric mass transfer coefficient (\( k_{1,a} \)) can be obtained from percentage saturation-time data by static method using the following equation:

![Graph showing influence of nanofluids on percentage saturation for reactor operated at 200 rpm and 0.75 L min\(^{-1}\)](image)

*Fig. 1: Influence of nanofluids on percentage saturation for reactor operated at 200 rpm and 0.75 L min\(^{-1}\)*
Where:

- $C_0$ = Oxygen concentration in terms of percentage saturation at the beginning of oxygen supply (%)
- $C_1$ = Oxygen concentration in terms of percentage saturation at any time (%)
- $C_a$ = Oxygen concentration in terms of percentage saturation at the end of oxygen supply (%)
- $k_1a$ = Volumetric mass transfer coefficient (min$^{-1}$)
- $t$ = Time (min)
- $a$ = Interfacial area (m$^2$)

The volumetric mass transfer coefficient determined from Eq. 1 for different operating conditions and nanoparticles concentration is shown in Fig. 2. An increase in volumetric mass transfer coefficient with increase in nanoparticles concentration can be observed for the two operating conditions: 100 rpm and 1.5 L min$^{-1}$ and 200 rpm and 0.75 L min$^{-1}$. When the reactor was operated at 200 rpm with 1.5 L min$^{-1}$ of air flow, there seems to be an optimum nanoparticles concentration at which the $k_1a$ was maximum. However, for all the operating conditions, $k_1g$ using nanofluids was higher than those with water, indicating enhancement in $k_1a$ for all the cases. At the highest nanoparticles concentration, $k_1a$ is independent of operating conditions.

**Influence of nanoparticles concentration on effective volumetric mass transfer coefficient:** Effective volumetric mass transfer coefficient ($E$) is defined as the ratio of volumetric mass transfer coefficient obtained with nanofluids to the volumetric mass transfer coefficient obtained with pure water (Olle et al., 2006). This parameter is an indicator of enhancement in mass transfer coefficient. Figure 3 shows the influence of nanoparticles mass percentage on $E$ at two different operating conditions. It can be observed from Fig. 3 that the effective $k_1a$ increases with nanoparticles mass concentration. An effective $k_1a$ of 1.63 has been obtained for 0.065 wt.% Fe$_3$O$_4$-water nanofluids at 200 rpm and 0.75 L min$^{-1}$ air flow, representing 63% enhancement in oxygen transfer from gas to liquid using these nanofluids. It is also evident that the nanoparticles are more effective in enhancing $k_1a$' at lower air flow rate.

![Fig. 2: Influence of nanoparticles mass concentration on $k_1a$](image-url)
Fig. 3: Influence of nanoparticles mass concentration on enhancement in $k_c a$

DISCUSSION

An enhancement in volumetric mass transfer coefficient may be attributed to either an increase in mass transfer coefficient ($k_c$) or an increase in interfacial area ($a$) or both (Olle et al., 2006). In gas-liquid mass transfer operations, the total surface area of all the bubbles is taken as interfacial area. Hence, higher number of smaller bubbles provides higher interfacial area as compared to lower number of larger bubbles. In a stirred tank reactor, bubbles are broken upon contact with impeller, leading to higher number of small bubbles, irrespective of bubble size at the sparger. This is evident from the correlations for $k_c a$ proposed in the literature for stirred tank reactors that do not take into account of bubble diameter or bubble frequency. Hence, change in interfacial area ($a$) due to the use of nanofluids can be expected to be negligible. Also, the physical properties of such low concentration nanofluid systems do not differ appreciably from that of base fluid and hence, this enhancement in a stirred tank reactor cannot be explained by traditional theories of gas-liquid mass transfer.

While searching for a plausible mechanism for this enhancement, we wish to recall the following significant conclusions of earlier investigations on mass transfer studies using nanofluids: Krishnamurthy et al. (2006) attributed the mass transfer enhancement to 'nanoscale stirring' of the liquid by Brownian motion. The role of 'nanoscale stirring' in an agitated aerated reactor may be negligible owing to the prevalence of highly turbulent environment. Under these circumstances, either grazing effect or reduction in film thickness by shearing action may be responsible for the observed enhancement.

Fluid-solid interactions are influenced largely by surface area of particles (Rajan et al., 2006; Rajan et al., 2007; Rajan et al., 2008). The nanoparticles utilized in the present study had BET surface area of 30 m² g⁻¹, which is sufficient for reasonable adsorption rates. The higher effectiveness of nanofluids in increasing $k_c a$ at lower air flow rate (from Fig. 3), along with a constant $k_c a$ at highest nanoparticles concentration (from Fig. 2), suggest that a nanoparticles concentration-dependent phenomenon plays a role in oxygen mass transfer. Hence, the enhancements in $k_c a$ of the present study may be attributed to 'grazing effect' of nanoparticles.

CONCLUSIONS

Stable Fe₃O₅-water nanofluids were prepared by stirred bead milling and utilized for study of mass transfer of oxygen from air to nanofluid in an agitated, aerated bioreactor. Enhancement in oxygen mass transfer was observed for all concentrations of Fe₃O₅-water nanofluids as observed
from percentage saturation-time data and volumetric mass transfer coefficient. The maximum $k_e/a$ enhancement of 63% has been obtained at the reactor operating condition of 200 rpm and 0.75 L min$^{-1}$ of air flow for 0.065 wt.% Fe$_3$O$_4$-water nanofluid. The mass transfer enhancement is attributed to ‘grazing effect’.

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