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Aqueous process intensification through enhanced oxygen mass transfer using oxygen vector: An application to cleaner leaching

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ABSTRACT

Intensification of chemical processes has surfaced many challenging but promising areas. Enhancement of Oxygen Mass Transfer (OMT) is one such area in aqueous chemical processes. Several attempts made to alleviate OMT limitation, however, remains futile in lowering energy and material requirement. In this regard, the use of *n*-Dodecane, an Oxygen Vector, could be a radically promising route for enhancing OMT. The present work explores the use of *n*-Dodecane (Oxygen Vector) for the enhancement of OMT, corroborated with the Classical Molecular Dynamic (MD) simulations. The results showed that 2.5% (v/v) *n*-Dodecane addition in aqueous systems ('Na_2SO_3 solution – *n*-Dodecane' and 'H_2O – *n*-Dodecane') would lead to enhancement up to 750%. MD simulation results confirm the transfer of oxygen from *n*-Dodecane-to-aqueous medium with diffusivity of 10^{-8} m^2/s, thus becomes the dominating route for the enhancement in OMT. In addition, it has been found that *n*-Dodecane fraction, temperature and the rate of oxygen consumption reaction are the dictating parameters for enhancement. The concept of Oxygen Vector for enhancing OMT has been successfully exploited for cleaner leaching of metals (>95 % Cu, Ni and Co) from refractory complex sulfides at moderate temperature-pressure conditions (T~ 95 °C and pO_2~3 Bar), which would have otherwise been possible at $T > 200\,°C$ and $pO_2 > 10$ Bar. In addition, recyclability of *n*-Dodecane, Oxygen Vector, in leaching system is an added advantage. Thus, this study offers a promising route in enhancing kinetics of oxidative aqueous processes and provides suggestive insights for lowering the material and energy requirements.

1. Introduction

Oxygen mass transfer (OMT) has always been a vastly garrulous area in the biochemical, petrochemical and, in particular, chemical aqueous processes. The gained momentum of this topic arises from the empirical evidence that oxygen is sparingly soluble in an aqueous system, which, in consequence, limits the oxygen mass transfer in an aqueous system (Truesdale et al., 1955; Weiss, 1970; Wilhelm et al., 1977). Further, the processes encountering such limitations have always been addressed through parameters like high requirement of temperature, pressure, and stirring rate, for the enhancement of oxygen mass transfer (Akita and Yoshida, 1973; Chern et al., 2001; Lewis and Whitman, 1924; McClure et al., 2015; Vogelaar et al., 2000). As a matter of fact, modulating these process parameters could facilitate enhancement up to certain limits, however, these methods are material and energy intensive in nature. Interestingly, the point that remains concealed in the backdrop of aforementioned parameters is that, it is the localized oxygen availability which defines the OMT efficacy and hence, the process efficiency. In this regard, a radical departure from the predominant advances could be the use of 'Oxygen Vectors'. These are the organic liquids, which have manifold higher oxygen solubility than aqueous system, which on mechanical emulsification in an aqueous system is expected to directionally transfer oxygen via persistent chemical potential gradient (driving force for mass transfer) and high interfacial area. Therefore, Oxygen Vector will result in higher local oxygen concentration, hence improves process efficiency at comparatively lower energy requirement. Thus,

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avoids the use of energy intensive alternatives. The term 'Vector' connotes the directional transfer of oxygen. The plausible pathways for oxygen mass transfer (OMT) are shown in Fig. 1. Oxygen Vector (alias organic liquid) is used as an attractive feedstock of oxygen in bioconversion, primarily in fermentation-based-bioprocess, for ensuring optimum yields (Clarke and Correia, 2008). Organic liquids, like *n*-Hexane, *n*-Heptane, Toulene, PCF-40, Ethanol, Heptanol, Octanol, Hexanol, Oleic acid, Kerosene, and *n*-Dodecane were used in enhancing OMT in fermentation medium (Bi et al., 2001; Cesário et al., 1997; Clarke and Correia, 2008; Dumont et al., 2006; Jia et al., 1997; Jianlong, 2000; Koide et al., 1985; Kundu et al., 2003; Yoshida et al., 1970). However, the systems wherein they had been explored are having following conditions: low electrolyte concentration, ambient temperature, use of emulsifiers, air flow based stirring conditions; as because use of aggressive conditions (high temperature, pressure, and stirring rate) for OMT would adversely affect the bio-process. However, there are no reported literature on the use of organic liquid for enhancing OMT for the system like stirred tank based leaching reactor. In addition, leaching conditions are very aggressive in nature viz. use of high electrolytic concentration, high temperature and pressure, high stirring rate etc. Therefore, it is essential for Oxygen Vector to be inert, stable, and immiscible in the leaching medium such that it can be easily reused and recycled in the subsequent leaching trails. Amongst the aforementioned Oxygen Vectors, *n*-Dodecane found to be suitable based on highest boiling point, immiscibility, and oxygen solubility. Therefore, *n*-Dodecane has been chosen to carry out the present study. Herein, the present study vividly attempts to advantageously exploiting 'Oxygen Vector' in the enhancement of OMT in oxidative aqueous process, which will led to cleaner production of several important metals such as Ni, Co, Cu etc., from their complex sulfide ores.

In this work, we have focused on the use of 'Oxygen Vector' *i.e. n*-Dodecane for the enhancement of OMT in oxidative aqueous systems. 'Water-*n*-Dodecane' and 'Sodium sulfite solution-*n*-Dodecane' emulsion systems have been explored, wherein quantification of enhancement of OMT has been made using Enhancement factor 'E'. The experimentally obtained E values with *n*-Dodecane addition, indicates its efficacy (up to 7.5 times or 750% with 2.5% (v/v) *n*-Dodecane addition) in enhancing OMT. MD simulation results also confirm *n*-Dodecane-to-water, would be the dominant pathway for enhancing OMT. In addition, the stability, inertness, and immiscibility of *n*-Dodecane in the aqueous system allows its easy separation and subsequent use, which makes the use of *n*-Dodecane, a promising pathway for enhancement of OMT. Furthermore, *n*-Dodecane has been advantageously explored in process intensification of aqueous dissolution (leaching) of metals from sulfide minerals, where OMT is of critical importance. Generally, this process operates at very high temperature (>200 °C) - oxygen pressure condition (>10 Bar) (McDonald and Muir, 2007; Padilla et al., 2007), in contrast, the use of *n*-Dodecane allows it to function at temperature (~95 °C) and pressure (~3 Bar) coupled with easy use and recycling of *n*-Dodecane. In fact, companies like Sherritt International, INCO etc. are looking forward for an alternative and immensely working to lower the material and energy requirement for an autoclave aqueous dissolution of metals from sulfide minerals. Therefore, this study could also provide significant contribution in this regard. Thus, this study not only offers a promising route for enhancing OMT but also offers profound insights for process intensification, which holistically tells and complements the significance of *n*-Dodecane as Oxygen Vector.

2. Experimental

2.1. Materials

De-ionized water having pH ~5.5 and excel grade N_2/O_2 gasses supplied by Linde, India were used in all the experiments. Sodium sulfite, cobalt sulfate, and sulphuric acid (98%) were used of analytical grade (E-Merck, India); *n*-Dodecane used for enhancement of oxygen mass transfer was also of analytical reagent grade, supplied by HiMedia®.

The complex metal sulfide sample used for leaching studies was synthesized in our laboratory by melt sulfiding Cu—Ni—Co—Fe alloy inside an induction furnace. The alloy was obtained *in-house* through large-scale reduction (500 kg/batch) smelting of polymetallic sea nodules or manganese nodules. The chemical composition of this complex sulfide was found to be: Cu = 27%, Fe = 27%, Co = 1.78%, Ni = 23.76% and S = 20.55%. XRD analysis indicated the following major phases: Pentlandite ($Fe_{4.6}Ni_{4.4}S_8$, $Fe_{4.4}Co_{0.03}Ni_{4.57}S_8$), Bornite ($Cu_5FeS_4$), Sugakite ($Cu(Fe, Ni)_8S_8$), and Talnakhite ($Cu_9(Fe, Ni)_8S_{16}$).

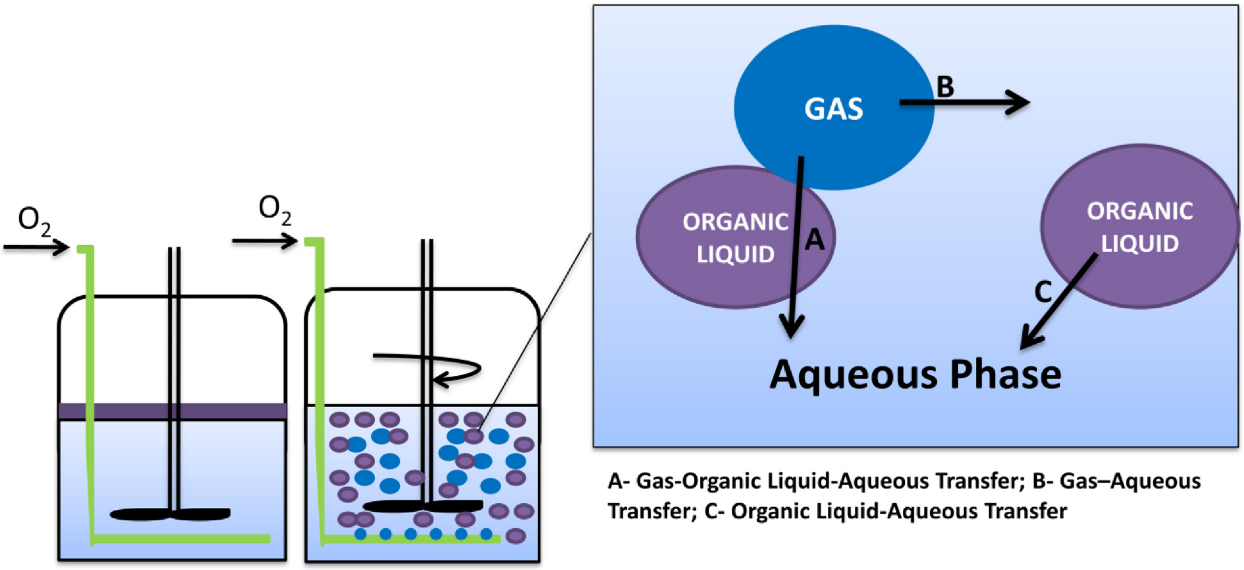

Fig. 1. Plausible pathways for O_2 transfer from gas to aqueous phase in an emulsified system.