Numerical modeling of ferrous iron oxidation in a split-rectangular airlift reactor

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HIGHLIGHTS

- CFD is used to simulate of the iron(II) removal from drinking water.
- Coupled hydrodynamics, gas-liquid mass transfer and reaction kinetics are analyzed.
- Global gas hold-up, liquid recirculation velocity and $k_L a$ are accurately predicted.
- The single-orifice nozzle induced strong heterogeneities of gas holdup and $k_L a$.
- Iron(II) removal was fairly predicted, showing the effect of these heterogeneities.

ARTICLE INFO

ABSTRACT

In this work, CFD is used to simulate the gas-liquid dispersion coupled to the kinetics of the iron(II) removal from drinking water by aeration process in a split-rectangular airlift reactor. The model aims to describe oxidation of iron(II) into insoluble iron(III) species in water treatment, so that hydrodynamics, oxygen mass transfer, chemical reactions, and pH change can be taken into account. In comparison to the abundant literature using CFD on airlift reactors, this work focuses on a particular reactor in which a highly non-uniform primary gas distribution is ensured by a 3.5 mm diameter single-orifice nozzle located at the bottom center of the riser. This makes convergence more difficult, as local gas velocity is high near the nozzle. A multiphase Euler-Euler model with a unique bubble size and a standard $k-\varepsilon$ model of turbulence are used. The 3-D CFD simulations are able to predict the liquid circulation velocity and the average gas holdup both in the riser and the downcomer. The model can also identify the transition from the gas flow regimes without bubbles and with stationary bubbles in the downcomer, while predicted $k_L a$ values agree with reoxygenation experiments. Finally, the simulations also predict accurately the oxidation of iron(II) vs. time without or in the presence of iron(III) as a catalyst, and they are also able to detect where local heterogeneities in dissolved oxygen concentration can emerge when pH and/or the amount of catalyst is increased.

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1. Introduction

Groundwater is a key resource of drinking water. Soluble ferrous iron is probably the most common contaminant of groundwater: It causes unpleasant taste in mouth and anesthetic red or brown stains on clothes and sanitary facilities; it promotes the build-up of deposits that can constrict pipeline and favors the development of iron bacteria that enhance the corrosion of the equipment and make the taste and odor issues worse. Consequently, guidelines for soluble iron are between 0.1 and 0.2 mg/L (European Union Council Directive, 1998). In practice, current iron(II) concentrations in groundwater lie about 0.7 mg/L, but values about 80 mg/L have already been reported.

Iron removal is a conventional operation of water treatment that can be conducted using either a physicochemical or a biological process, each of them with several variants. The common physicochemical pathway consists in an oxidation-precipitation process, followed by either filtration or decantation: soluble iron

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(II) is oxidized into insoluble iron(III) hydroxides, especially ferric hydroxide $Fe(OH)_3$. Among the variants, aeration process is usually applied for oxidizing ferrous iron in water exhibiting iron(II) concentrations higher than 5 mg/L because 1 mg dissolved oxygen is needed to oxidize 7 mg iron. In this case, the biological process may also need aeration and it has been already shown that biological and physicochemical mechanisms usually proceed in parallel and the limitations of the biological process have been reviewed by Sharma et al. (2005). As a result, an accurate description of the kinetics of physicochemical iron(II) removal is required for both pathways. A key issue is that this kinetics is highly sensitive to pH, alkalinity and ionic strength; in addition, an autocatalytic effect of ferric hydroxide has also been highlighted. Consequently, iron removal can sometimes be faster than expected, which results in oversized designs, but opposite trends have also been reported.

In the last decade, gas-liquid reactors such as bubble columns and airlifts have been shown to be versatile tools for iron(II) removal in groundwater because they combine good mixing, low energy consumption, gas-liquid mass transfer and pH control properties (El Azher et al., 2008; Mousavi et al., 2008). The hydrodynamics, mass transfer and chemical reactions in multiphase airlift reactors are complex and they are strongly coupled. A main issue of two-phase flow process in airlifts reactor is, therefore, to predict accurately these three aspects, which requires fundamental understanding and modeling of the underlying mechanisms. The potential of CFD for simulating hydrodynamics and gas-liquid mass transfer in the design and scale-up of multiphase airlift reactors has been established by several authors, for example (Mudde and van den Akker, 2001; Oey et al., 2003; van Baten and Krishna, 2003; van Baten et al., 2003; Blažej et al., 2004; Sokolichin and Eigenberger, 1999; Sokolichin et al., 2004; Dhanasekharan et al., 2005; Talvy et al., 2007a; Luo and Al-Dahhan, 2008; Huang et al., 2010; Šimčík et al., 2011; Bannari et al., 2011; Mohajerani et al., 2012; Vial and Stiriba, 2013; Law and Battaglia, 2013). CFD is a cost-effective tool that can simulate the flow pattern, local hydrodynamics and other characteristics of multiphase reactors. The reactor geometry and scale up are automatically accounted, and heterogeneities in local concentrations or reaction rate can be easily detected. However, very few CFD studies and models that tackle the oxidation of soluble ferrous iron species in drinking water have been reported.

The present work focuses on the oxidation of ferrous iron in water, with levels of iron(II) concentration, typically between 5 and 20 mg/L, in a split-rectangular airlift reactor. The objective is, therefore, to develop a computational fluid model to study hydrodynamics, gas-liquid mass transfer, pH change coupled to chemical reaction processes that govern the reactor behavior, so that robust scale-up and performance can be achieved. The numerical solutions for the equations model are obtained using the ANSYS Fluent 15.0 software package and the Gambit mesh generator. The experimental data from Gourich et al. (2005, 2006) and El Azher et al. (2008) are used to validate the CFD model. In these works, experiments were carried out in a split-rectangular internal airlift using real drinking water spiked with various amounts of soluble ferrous iron and insoluble iron hydroxide. Water properties were varied as a function of pH and of the initial concentrations of soluble iron(II) and insoluble iron(III) hydroxide, the latter playing the role of a catalyst. In these works, a single-orifice nozzle was used for the primary gas distribution. This differs from literature data in which the primary gas distribution is often uniform. It must, however, be pointed out that the gas distribution is often non-uniform in industrial water/wastewater bubble column reactors. In addition, Gourich et al. (2006) had shown that using such a distributor enhanced gas-liquid mass transfer due to the higher recirculation of small bubbles in the downcomer, which makes this design attractive. Due to the presence of fine solid particles of ferric

hydroxide that induced turbidity and color, local hydrodynamics and bubble size could not be measured and hydrodynamic data only consisted of average gas hold-up in both sections, and overall liquid recirculation velocity. For gas-liquid mass transfer, only the volumetric mass transfer coefficient k_La on the reactor was determined. In this work, the general features of the flow field such as gas holdup, oxygen concentration, overall volumetric mass transfer coefficient and liquid velocity are calculated from first principles and compared with experimental data. Then, the computational model is used to simulate iron(II) oxidation from drinking water in the aerated airlift reactor, so that hydrodynamics, gas-liquid mass transfer and pH change can be taken simultaneously into account. Finally, the effect of operating conditions including pH and initial concentrations of ferrous iron $[Fe(II)]_0$ and ferric hydroxide $[Fe(III)]_0$ are investigated with an emphasis on the development of local heterogeneities and on the respective roles of the riser and the downcomer.

2. Simulation setup

The internal-loop airlift reactor simulated in this work had been investigated experimentally by Gourich et al. (2005, 2006), while El Azher et al. (2008) studied the aeration process for the removal of iron(II) from drinking water with a batch liquid phase, so that their data can be used to validate CFD modeling. Their experimental setup was a split-rectangular internal airlift reactor of 63 L, consisting of a square column (0.20 m × 0.20 m) of 2 m height, divided equally into a riser and a downcomer section by a baffle (Fig. 1). Available data describes the respective influence of superficial gas velocity from 0.01 to 0.08 m/s and of water properties on hydrodynamics, mass transfer and reaction using Casablanca drinking water spiked with various amounts of soluble ferrous iron and insoluble iron hydroxide. Water properties were varied as a function of pH and of the concentrations of soluble iron(II) and insoluble iron(III) hydroxide. The computational fluid dynamic (CFD) model developed in this work to describe the local, hydrodynamic, the mass transfer properties, and the kinetics of iron(II) removal in this airlift reactor is summarized below.

2.1. Kinetic model

El Azher et al. (2008) carried out experiments on waters exhibiting various levels of iron(II) concentrations close to those of ground waters rich in iron, typically between 5 and 20 mg/L. The oxidation of ferrous iron into ferric iron in aeration process can be described by the following stoichiometry:

$$4Fe^{2+} + O_2 + 8OH^- + 2H_2O \rightarrow 4Fe(OH)_3 \tag{1}$$
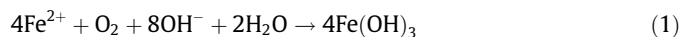
Thus, 1 mol of oxygen will oxidize 4 mol of iron(II) under ideal conditions. Additionally, 2 mol of acidity are produced per mol of iron(II) converted into iron(III). The reaction rate was expressed by Stumm and Lee (1961) and verified by Sung and Morgan (1980):

$$r_{(Fe(II))} = K[Fe(II)][OH^-]^2[O_2] \tag{2}$$

For a batch liquid phase, at constant pH and oxygen partial pressure, and when gas-liquid mass transfer is rapid in comparison to the reaction rate, this gives:

$$\frac{d[Fe(II)]}{dt} = -k[Fe(II)] \tag{3}$$

El Azher et al. (2008) determined the kinetic constants K and k by fitting experimental data with Eqs. (2) and (3) for a range of gas flow rate, pH, and initial concentrations of ferrous iron $[Fe(II)]_0$. However, an autocatalytic effect due to ferric hydroxide formed