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Experimental and numerical study of iron pyrite nanoparticles synthesis based on hydrothermal method in a laboratory-scale stirred autoclave

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ABSTRACT

In this paper, the synthesis of iron pyrite nanoparticles (FeS_2) is investigated both experimentally and numerically through facile hydrothermal route in a laboratory-scale stirred autoclave reactor equipped with a 4-bladed 45° pitched-blade turbine (PBT) impeller. An elaborated CFD model is also adopted which accounts for the governing transport phenomena, namely mass, momentum, energy and species equations to investigate flow behavior as well as mixing patterns and chemical reactions for the synthesis of iron pyrite nanoparticles in the autoclave reactor. The iron pyrite reactor is described as an incompressible, single-phase, liquid mixing regime undergoing chemical reactions via integrating with an appropriate proposed kinetics model obtained experimentally. Power consumption and mixing time of the autoclave reactor are measured experimentally to assess the validity of the CFD model. Besides, the effect of temperature and reactant molar ratio as two important key parameters in the synthesis reaction is evaluated both numerically and experimentally, and the products in each scheme are characterized by X-ray diffraction (XRD) analysis. Both cold and reactive simulated results are in good agreement with experiments carried out in this work. Moreover, the reactive simulated results in conjunction with the XRD measurements illustrate that temperature is not an influential parameter in the synthesis of iron pyrite; whereas, an appropriate value of the reactants molar ratio is required to obtain a more purified product. The present developed CFD model is anticipated to help researchers in better understanding of the synthesis process, and to be useful as a bridge to the pilot-plant design in a cost-effective way.

1. Introduction

Iron pyrite (FeS_2) is an earth-abundant, inexpensive and environment-friendly material, which has long been a material of interest as a motivating candidate for high-tech fields such as electrochemical energy storage and solar energy conversion technologies. A combination of several unique features such as high absorption coefficient (5.5×10^5 cm^{-1} for $\lambda \leq 700$ nm), desired band gap (E_g = 0.95 eV) as well as a remarkable quantum efficiency above 90%, makes iron pyrite an ideal option for photovoltaic applications. It has been pointed out that a very thin film of synthesized iron pyrite (10–20 nm) can result in 500 mV voltages [1–3]. Despite being earth-abundant, natural iron pyrite has a few main deficiencies such as existing impurity and undesirable crystal shape and size, which makes its direct application in solar cell technology impossible. Among all the metal sulfides that are used as the cathode material in lithium-ion batteries, iron pyrite has received special attention due to its peerless characteristics [4]. An improvement in output voltage in lithium-ion batteries has been reported using synthesized iron disulfide as the cathode material. This enhanced voltage is attributed to the smaller size of crystals and its modified structural shape. Further, the amount of impurities is much lower in the iron pyrite structure produced synthetically [5,6]. Much attention has been devoted to synthesize iron pyrite nanoparticles by controlling the particles morphology, size distribution as well as the structural stability [4]. To date, several methods have been conducted for the iron pyrite synthesis, which among them, thermal sulfuration [7,8], mechanical milling [9,10], wet chemical synthesis [11] as well as the recently reported method, i.e., mechanical alloying [4] are of the mainly known methods of preparing iron pyrite nanoparticles. Wet chemical synthesis, which occurs in an aqueous solution, in essence, consists of hydrothermal [12,13] and solvothermal routes [14,15], both have been studied by several researchers. In recent years, the hydrothermal synthesis of iron pyrite has gained much attention due to its facile process, low operating temperature as well as inexpensive reactants (i.e., water is used as the main

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solvent). Due to the use of hydrothermal route in the present work to prepare the nanocrystals of iron pyrite, a review of the recent investigations on the synthesis of iron pyrite conducted by hydrothermal method is then necessary. One of the first studies on the hydrothermal synthesis of iron pyrite has been carried out by Wu et al. [16]. They conducted a series of experiments by single-stage hydrothermal route using $FeSO_4$, $Na_2S_2O_3$ and pure sulfur, S in a temperature range of 90–280 °C for 24 h. The resulting iron pyrite has nanoparticles with an average size of 500 nm. They also proposed a detailed mechanism for the synthesis of the nanoparticle iron pyrite [16]. In a more recent study on the hydrothermal synthesis of iron pyrite, Gartman et al. investigated the influential factors affecting the size and morphology of iron pyrite with a range size of micrometer to nanometer to shed light on the formation processes of these micro and nanoparticles by conducting more than 50 pyrite syntheses [17]. Yang et al. prepared single-phase flake-like pyrite particles in the range of micro-to-nanometer, which were synthesized hydrothermally. They also employed the synthesized pyrite in a single-cell thermal battery and observed an enhanced performance compared with the natural pyrite-base thermal battery [18]. Liu et al. studied the process of preparing phase-pure, single crystalline pyrite nanoparticles in hydrothermal route. They also investigated the effects of molar ratio and reaction time on the quality and morphology of FeS_2 nanocrystals [19]. Bai et al. successfully developed a synthetic approach for preparing single-phase pyrite nanoparticles with an average diameter of 2–5 nm in polar solvent and aqueous dispersions. They also pointed out that their methodology is a universal approach, and can be modified to produce both types of iron pyrite, i.e., nanowires and nanosheets [20].

Computational fluid dynamics (CFD) technique is a valuable numerical tool, which has served in chemical reactors engineering as a bridge between preliminary assessments and final, optimum designs. In fact, CFD works as a virtual laboratory to mitigate the severity of carrying out numerous experimental measurements, and to provide a better understanding of complex transport phenomena of chemical processes in a cost-effective way.

Stirred reactors are the most commonly used reactors, which play a key role in many chemical processes to enhance mixing, gas dispersion, solid suspension, reactive crystallization as well as heat and mass transfer [21]. Over the past two decades, CFD techniques have been widely used in stirred reactors to shed light on the complex phenomena emanating from hydrodynamics, mixing and reactive flow processes, in addition to finding the optimal design. Although achieving a uniform mixing is the main purpose of employing impellers in stirred tank reactors, however, the importance of local mixing and flow patterns induced by impellers that can affect the final product quality—e.g., particles size, has also been emphasized [22]. Besides, the effect of impeller shape, vessel size and Reynolds number on reactor performance and final product in reactive crystallization process has been discussed [23]. CFD tool can be employed here to divulge this intricate relationship, and to help better understand the flow structure and mixing behavior in an effective way. One of the most full-fledged reviews has been done on stirred tanks equipped with axial impeller (axial impeller is used in this work) presented by Joshi and his co-workers where several important issues such as the selection of appropriate turbulence models, employing multiple impellers and application in multiphase flows has been addressed [24].

In view of the literature review that has been conducted here and to the best of the authors' knowledge, no investigation is reported in literature on using a stirred reactor to synthesize iron pyrite nanoparticles. Furthermore, the long time of the reaction is another issue that provides the motivation for the present work to make it shorter via the improvement of reactant mixing by an impeller. Therefore, in the present work, the use of computational fluid dynamics techniques is evaluated to predict both local velocity and instantaneous reactants concentrations profile inside a laboratory scale stirred autoclave by investigating the reaction of iron pyrite synthesis. Thus, appropriate set of governing conservation equations including continuity, momentum and species as well as energy transport equation are formulated, coupled and finally solved numerically by incorporating these with a simple empirical kinetics model extracted from our previous work [25]. Furthermore, the computed results for both hydrodynamic and reactive flows are validated against experimental campaign carried out in this research.

The layout of this paper is as follows: first, experimental setup and measurements are discussed in Section 2. The framework of the elaborated CFD model for the stirred autoclave reactor employed in the present study for the synthesis of iron pyrite is elucidated in Section 3. Section 4 discusses the results obtained from the simulation studies. In the end, the main conclusions of the present work are outlined in Section 5.

2. Experimental section

The experimental measurements carried out in the present study consist of three parts, which are described here.

2.1. Measurement of mixing time

According to Fig. 1, an experimental set-up was established to measure the values of mixing time. An unbaffled flat-bottom and transparent-glass-type tank with similar size and dimensions was constructed and employed in this study, since mixing time measurements was impossible via the stainless steel autoclave reactor. Particular attention was paid to ensure the similarity of the geometry, dimensions and specifications between the stainless steel reactor and the glass-type one. A 4-bladed 45° pitched-blade turbine (PBT) impeller similar to the one employed for the stainless steel reactor was mounted on a mechanical mixer type RZR 2041 equipped with a precise control system to set the impeller rotation. In all experiments, the tank was filled with distilled water with a height of 120 mm. All set-up specifications comprising the tank and impeller dimensions, which were employed as experimental rig, are presented in Table 1.

A colorization–decolorization technique based on a fast acid–base reaction proposed by Lamberto et al. [26] was conducted for the mixing time measurements. The tracer solution was prepared with water and purple bromocresol as an indicator for base to acid and acid to base reaction schemes. In the basic medium, bromocresol is purple and it turns

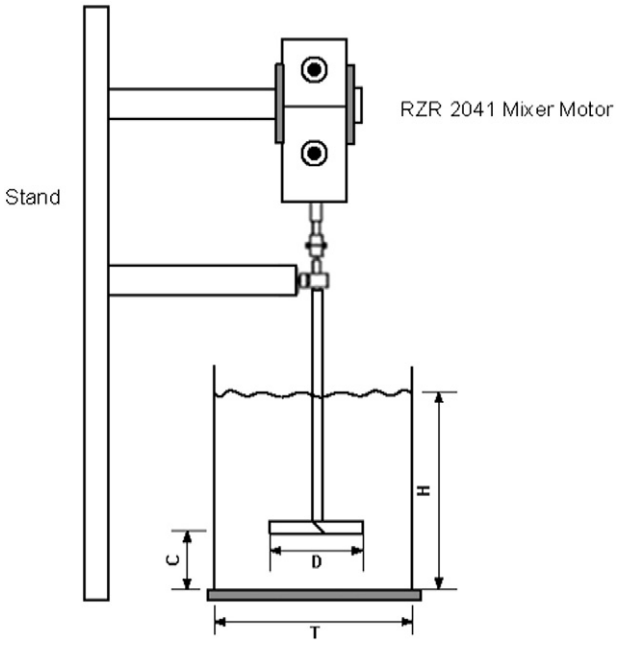

Fig. 1. Schematic of the experimental rig established for measuring mixing time.