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A feasibility study of the biologically inspired green manufacturing of precipitated silica

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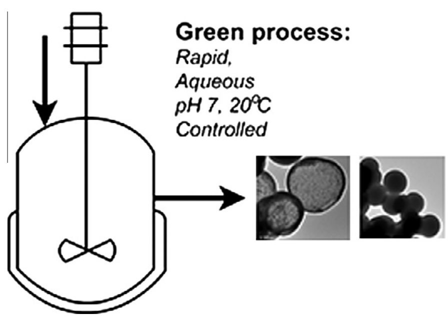
HIGHLIGHTS

- A new bioinspired green method for the preparation of silica is proposed which is environmentally friendly and rapid.
- The green process could prove to be economically favourable to current methods.
- The carbon footprint of bioinspired process is an order of magnitude less than current processes.
- Minimum conversion required for profitable operation of the green process can be easily achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents a possible industrial scale design for biologically inspired (bioinspired) 'green' production of precipitated silica using either batch or continuous processing. This design allowed a comparison based on the economic and environmental factors between the proposed green process and an existing process for the production of precipitated silica. The proposed green process uses an additive which allows rapid silica formation to occur in laboratory experiments in less than five minutes at room temperature and neutral pH. The green process hence offers significant advantages in terms of production capacity and no heat requirements, therefore reducing both running costs and carbon dioxide emissions. From the preliminary feasibility study reported herein, it appears that the green route may prove economically comparative to current processing techniques, especially noting that this process can be easily adapted to unit operations in the existing silica production, without the need for additional capital investment. A sensitivity analysis was conducted which identified that the most crucial factors affecting the process economics were the raw material costs and the conversion. Furthermore, we have examined and compared properties of commercially available precipitated silica samples with those obtained by the green process. It appears that the green method provides an additional advantage: it can create products with a much more diverse range of properties, which can be readily controlled, thus allowing them to enter new and unique markets.

1. Introduction

Specialty silicas, obtained by processing low valued silica sand and quartzite, are generally classified based on their properties and methods of production and include fumed silica, precipitated

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silica, silica gels and sols, and micro-silica [1]. The estimated 2012 global annual production for specialty silica was 2.4 million tonnes, which corresponds to a market value of around $3.6 billion [2]. The specialty silica market has shown strong growth over the past decade, leading to an estimated production of 2.7 million tonnes of specialty silica by 2014 [2]. Precipitated silicas are expected to enjoy the most rapid growth and are expected to remain as the largest segment of the specialty silica market over the next decade [2]. These quantities illustrate the importance of the industries and processes dealing with precipitated silica.

1.1. Current process for the production of precipitated silica

Precipitated silica is commercially produced by neutralizing sodium silicate in multiple steps with sulphuric acid to form a slurry of silica, see Fig. 1 [1,3]. Typically, a pre-heated reactor containing water, sodium silicate (water glass) as the silica precursor is loaded. Sulphuric acid is then introduced to reach a desired pH, followed by periods of either simultaneous or sequential additions of sodium silicate and sulphuric acid while maintaining the set pH. The mixture is allowed to age and agitated intermittently in order to avoid gelation [3]. The chemical properties of the product silica are significantly affected by the conditions inside the precipitation vessel. The most important factors affecting silica properties are the pH, the temperature, the residence time, the solid concentration, the rate of addition of raw materials, the stirring intensity and the feed position of the raw materials [3]. Examples of typical process conditions used in silica manufacturing processes are listed in Table 1. Most plant designs utilise either a batch or, more commonly, a semi-batch system [4–9]. Although continuous processing has been demonstrated [10,11], the yield is greatly reduced and it has not proven to be economic to date. Following precipitation, the silica is separated out of the suspension typically by filtration [3], washed to remove any impurities and dried at 250 °C to the desired moisture content using a spray, belt or rotary drier [3] before finishing by milling, granulating, pelleting [4] and switching to hydrophobicity [12].

Actual processing conditions currently used for producing precipitated silica vary slightly from process to process and due to confidentiality issues actual designs or economics for processes are not published. For this reason a most-representative route was chosen from the literature and a silica production plant was designed for comparative purposes [5].

Alkoxysilane compounds may be also used as silica precursors in sol–gel synthesis, which typically occur at high or low pH and often in the presence of an alcoholic solvent [17,18]. However, this process provides poor control over the resulting silica morphology, requires excessively long reaction time and has an increased environmental concern than the aforementioned processes, and hence it is outside the scope of this investigation.

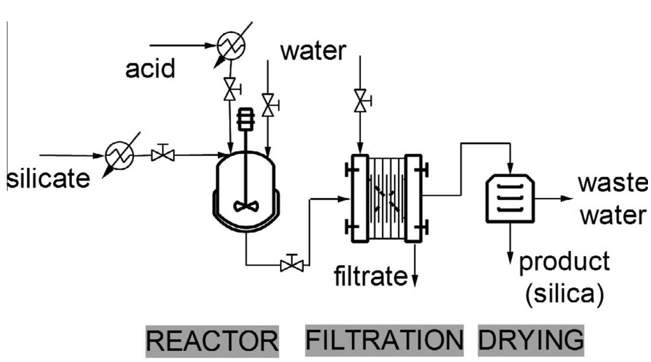

Fig. 1. Typical PFD for current industrial silica production process.

1.2. Proposed green process for the production of precipitated silica

Current processing techniques discussed above for the production of precipitated silica are typically complex, multistep and energy intensive, often requiring relatively harsh conditions including high temperatures (>60 °C) and extremes of pH. The energy costs and capital costs due to the need for specialised handling are also concerning. As awareness of carbon dioxide emissions increases, the development of an economically competitive process with a reduced environmental impact is of significant importance. It is therefore clear that greener alternatives are urgently required to replace these processes.

To this end, in the recent past, we have developed a new bioinspired green method for the preparation of silica that is gaining attention due to the ease of application, the use of environmentally friendly conditions of neutral pH, room temperature and all aqueous synthesis, one step reaction and rapid preparation times (1–15 min) (this has been extensively reviewed recently in Ref. [16]). It appears that biology produces large quantities of silica, which is facilitated by the use of biomolecules (e.g. proteins, polysaccharides and small amines) [16,19]. The understanding of the roles these biomolecules play *in vivo* has led to the invention of lab-scale bioinspired silica synthesis processes by utilising cheaper and readily available analogues of the biomolecules, called “additives”. An additive is mixed during the precipitation reaction and has various functions: it acts as a catalyst reducing the reaction time allowing the reaction to occur at much milder conditions, and it also helps self-assemble primary silica particles (building blocks) [19]. There is a wide range of additives available which can provide most promising controls over the reaction time, produced silica properties and cost [16,19]. Furthermore, the understanding of the role of these additives in silica formation and their interactions with solution silicate species is maturing [20,21]. Other advantages of this new process route include the ability to use a much wider variety of silicate sources and to produce, in a controlled fashion, silica with wide ranging particle sizes, porosities, morphologies and structures [16]. In addition, hybrid compounds can also be produced in one step through the addition of a dopant during the precipitation reaction, thus leading to, for example, the preparation of biocatalysts, catalysts, separation media and biomaterials [16,22–24].

The bioinspired silica process has to date remained at chemistry bench-tops as a small-scale synthesis (typically produced in μg-mg quantities). However, recently we have demonstrated that this process has the potential for producing silica at larger scale in a continuous production [25]. In that report, we proposed a simple process as shown in Fig. 2, which essentially is similar to the traditional process, with two exceptions: missing heating for the reactants and the reactor, and a pre-neutralisation step for silicate stream. This implies that the proposed green process may require reduced capital costs for a new plant instalment or can be easily adapted to an existing silica production facility. These possibilities are further discussed in the Results and Discussion section below. Following precipitation, the silica can be separated out and treated in the same way as in the traditional process.

Noting that typically there are a number of challenges to overcome before a new process can be ready for industrial production, we take the first step here and aim to investigate the feasibility of the green process as an alternative to existing silica production processes. We hope that this study will produce a clear indication of the viability of the new process and furthermore identify key advantages and challenges that can be addressed in future research. In particular, we aim to design and evaluate economics of three processes: an existing (batch) silica production process, a proposed batch green process and a proposed continuous green process. For both green processes, three scenarios were considered