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Interfacial analysis and reaction engineering of sucrose ester mediated solution spray synthesis of lead chromate nanorods

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ABSTRACT

Present paper reports coconut fatty acid-sucrose ester mediated coprecipitation synthesis of lead chromate nanocrystals with monoclinic symmetry in the size range of 18–48 nm. Solution spray reactor used for conducting the reactive crystallisation provides falling film mode of contact between atomised reactants. The adsorption density, surface functional groups, lattice parameters, size, morphology and optical properties of the $PbCrO_4$ nanorods were determined by their surface tension, FTIR, XRD, FESEM-EDX and UV–vis analysis, respectively. The concentration and thus surface-active properties of sucrose ester were found to influence the crystallographic parameters, aspect ratio and UV–vis absorption properties of $PbCrO_4$ nanocrystals. The nucleation parameters—induction time and energy barrier were reduced by 72% with increase in surfactant loading from 2 to 10 g/L for given initial supersaturation—200,000 and reaction temperature—303 K. The inter-multilayer and -micelle reactant exchange mechanisms were proposed and established to interpret the role of surfactant aggregation in enforcing the size stabilization, phase uniformity and polymorph selectivity in reference to kinetics and thermodynamics of precipitation of $PbCrO_4$. The investigations are expected to fulfill the growing demand of developing appropriate theoretical principles and modelling methodologies in relation to the rationale control of size, polydispersity and structure of nanopigments.

1. Introduction

Sucrose ester, derived through the exclusive use of renewable resources—carbohydrates and vegetable oils, is a non-ionic surfactant carrying hydrophilic hydroxyl groups and hydrophobic fatty alkyl chains. Its superior emulsifying, foaming, wetting, detergency, stabilizing, and hard water resistance properties are reported [1–3]. The surfactant is receiving considerable attention due to its availability in commercial quantities, together with tasteless, odourless, nontoxic, biocompatible, biodegradable and noncumulative characteristics [4,5]. As a result of these attractive features, its use as template in green synthesis of nanomaterials holds remarkable promise. Nevertheless only limited works on preparing nanomaterials in sugar-ester based templates such as indium sulfide nanorods in water-in-oil microemulsion system [6] and TiO_2 nanoparticles via hydrothermal route [7] have been reported.

The compound lead chromate ($PbCrO_4$) is an important brilliant yellow pigment, photosensitizer and humidity sensing resistor [8,9]. Regulation of the architecture and morphology at the nanoscale through control of size, phase, and polymorphism is essential for the fabrication of nanocrystals such as nanoparticles, nanotubes, nanofibers and nanorods and development of specific physical, optical, magnetic and electronic properties. The traditional nanomaterial synthesis methodologies, however, have limited influence on the crystal morphology of lead chromate (monoclinic vs. orthorhombic). Present study aims to utilize the aggregation properties of amphiphilic sucrose ester in facilitating polymorph selective synthesis of said pigment. Solution spray reactor patented by Mishra et al. [10] was employed in present investigations to accomplish the coprecipitation synthesis of $PbCrO_4$ nanopigments. The objective was thus to conduct coconut fatty acid-sucrose ester mediated solution spray synthesis of $PbCrO_4$ nanorods with well defined morphology and crystal structure. Besides these, present work also reports the evaluations of interfacial properties of coconut fatty acid-sucrose esters as template, establishment of inter-multilayer and -micelle reactant

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exchange mechanism on the basis of FTIR, XRD, FESEM and UV–vis analysis of the products and kinetic and thermodynamic analysis of reactive crystallisation.

2. Experimental

2.1. Chemicals

All chemicals used in this work were analytical grade (Sd Fine Chem., Qualigens) and used as received. Deionised water was used as source of water in all experiments.

2.2. Base catalysed transesterification synthesis of sucrose-coconut fatty acid ester

The method of synthesis is reported elsewhere [11,14]. The fatty acid methyl esters (FAME) were prepared through p-toluene sulphonic acid (PTSA) (1%) catalysed esterification of coconut fatty acids with methanol (20% molar excess) under reflux for 1 h. The crude FAME were purified by performing distillation under reduced pressure of 10 mm Hg. Six station reaction assembly (Carousel 6 plus model, Radleys Tech., US) equipped with magnetic stirring system (RPM = 236), refluxing condenser and electrical heating system (capable of maintaining reaction temperature within ±0.5 °C) was used to carry transesterification between sucrose powder and distilled coconut FAME at molar ratio of 1:1.5 in dimethyl formamide solvent (49.1% by wt). K_2CO_3 was used as the catalyst (2.1% by wt). The reaction mixture was refluxed at 120 °C for 120 min. The progress of the transesterification was monitored by determining the initial and final hydroxyl value (HV) and saponification value (SV). Purification of sucrose ester was accomplished through (i) neutralisation of catalyst using oxalic acid, (ii) precipitation of unreacted sucrose from the reaction mixture by adding toluene, (iii) repeated brine washing for removal of water soluble impurities and (iv) subsequent evaporation of solvent through use of rotary vacuum evaporator.

2.3. Sucrose ester mediated solution spray synthesis of lead chromate nanorods

The experimental procedure for synthesis lead chromate is based on the process reported elsewhere [12]. The solution spray reactor assembly, as shown in Fig. 1, incorporates two external mixing nozzles with 1 mm orifices (No. 14; Fig. 1) and uses 20 kgf/cm^2 air pressure by reciprocating compressor (No. 1) to cause the atomizations of solutions of equimolar (0.1 M) solutions of $Pb(NO_3)_2$ precursor and K_2CrO_4 precipitant. Both solutions carry loading of 2 g/L of sucrose ester. The atomised streams of

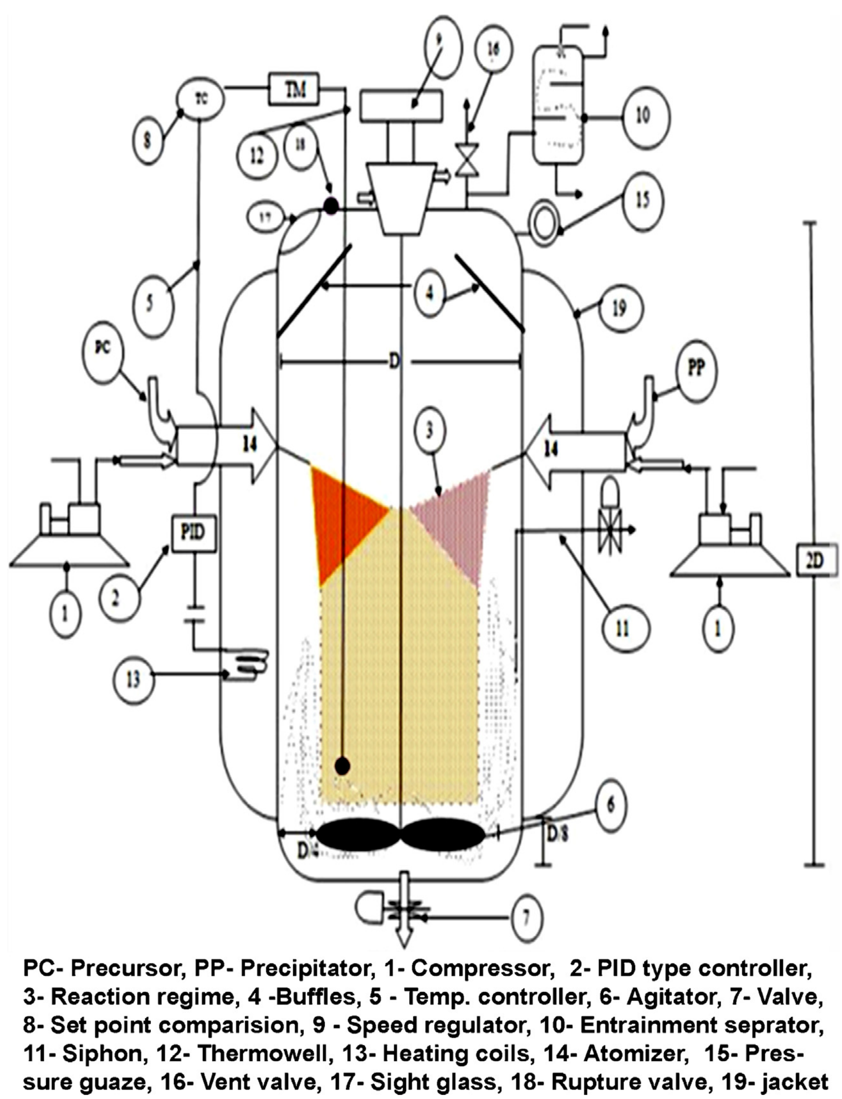

Fig. 1. Solution spray reactor for synthesis of nanomaterials (Indian Patent No. 235186).