Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Application of fractional factorial design for green synthesis of cyano-modified silica nanoparticles: Chemometrics and multifarious response optimization

Marwa S. Elazazy *, Ahmed A. Issa, Maha Al-Mashreky, Maetha Al-Sulaiti, Khalid Al-Saad

Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, Doha 2713, Qatar

ARTICLE INFO

Article history:
Received 31 August 2017
Received in revised form 6 February 2018
Accepted 8 February 2018
Available online xxxx

Keywords:
Silica nanoparticles
Cyano-functionalized
Fractional factorial design
Multiple responses
Derringer's function

ABSTRACT

Cyano-functionalized spherical silica nanoparticles (SNPs) were synthesized via Stöber method. A $2^{k-p}{}_{IV}$–fractional factorial design ($2^{k-p}{}_{IV}$–FFD) was used to smartly prepare monodispersed evenly distributed SNPs. Six factors were considered; concentrations of tetraethylorthosilicate (TEOS), 3-Cyanopropyltriethoxysilane (CPTS), water, and ammonia, reaction time (RT) and stirring time (ST). Two responses; particle size (PS, measured by SEM) and particle-size distribution (PSD, calculated as standard deviation, ±SD) were measured. Control charts were used to decide on impacts of linear and two-way interactions on both responses. Derringer's function was used to consolidate these multifarious responses into a uniform execution characteristic. Both screening and optimization were always accompanied by ANOVA testing at a 95.0% confidence interval (CI). The ideal synthetic conditions were obtained from the composite desirability plots. Cyano-functionalized SNPs with an average PS of 474.04 ± 86.71 nm were produced. Raman spectroscopy and FTIR were used to confirm the functionalization process. Thermogravimetric analysis (TGA) was used to evaluate the thermal behavior of synthesized particles.

1. Introduction

Nanotechnology is a conception that was introduced in 1959 by the scientist Richard Feynman in his lecture "*There is Plenty of Room at the Bottom*" [1]. Having an adaptable particle size (PS), substantial surface area and narrow particle size distribution (PSD), silica (SiO_2) nanoparticles (SNPs) are amongst the most extensively investigated nanomaterials [2–6]. Having a uniform size and compatibility with living tissues, SNPs play a substantial role in alleviating cancer, for example [7].

Several applications that target removal of pesticides utilized inorganic nanoparticles (NPs) [8–10]. Yet, being unstable (iron NPs) or costly (gold and silver NPs), usage of inorganic NPs becomes unfeasible and restricted to only narrow scale applications. The predominant alternative in this case is the functionalized SNPs [11–13]. SNPs can be readily functionalized with groups such as silane/amine or Fe_3O_4 in a core–shell arrangement with a subsequent improvement in their efficiency in detecting pesticides.

Being inexpensive and simply obtainable via uncomplicated synthesis, SNPs are considered as an ubiquitous substitute for other inorganic NPs in production of stationary phases both for packed (silica microspheres) and monolithic columns (porous silica) [14–18]. Splitting the PS might augment the separation performance. However, one problem with small sized SNPs is the back pressure in packed columns [17,18]. Core-shell NPs conversely would be a remedy for such a challenge by offering an effectual separation with a fast flow rate and small back pressure [17–19].

The quality of many applications involving functionalized and/or magnetic SNPs is greatly dependent on having monodispersed (a uniform PS) and evenly distributed (narrow PSD) NPs. Management of the synthesis route of SNPs is crucial in achieving the desirable features in terms of PS, PSD, porosity and surface area [5,6]. With no doubt, and by offering a controllable PS and PSD, customizable morphology, and a feasibility of functionalization, the sol–gel based approach (Stöber synthesis) remains the most common technique adopted for this process so far [20–23].

Tetraethoxy silane (TEOS), a common precursor in the production of SNPs is a metal alkoxide that reacts with water in presence of a catalyst forming a single-phase solution (sol). The later, in turn goes through phase transition to form a gel which can be simply viewed as a two phases system that has a firm network of solid metal oxide in the liquid phase [2]. Ammonia is a usually used

* Corresponding author.
E-mail address: marwasaid@qu.edu.qa (M.S. Elazazy).

https://doi.org/10.1016/j.apt.2018.02.012
0921-8831/

catalyst that boosts a hydrolysis reaction to produce silanol groups and condensation reaction to form siloxane bridges [24–27].

Synthesis of SNPs is affected with several variables. Exploring the literature revealed that inspected parameters usually include the concentration of TEOS, concentration and type of catalyst (base/acid), alcohol type, water concentration, and temperature. Yet, different procedures have reported different PS and PSD. This contradictory PS and PSD patterns were usually attributed to the different water/ alcohol/ ammonia/ TEOS concentrations (alone or combined) [24–27].

This inconsistency in the reported procedures might be also attributed to the usage of the traditional OVAT "one-variable-at-ti me" analysis. Such a concern has created the need for an optimized and trustworthy technique for the synthesis of functionalized SNPs. One of the crucial difficulties accompanying the OVAT is the large number of experiments needed with incapability to mediate the appropriate system implementation with a high degree of conviction. Factorial design (DOE) would be the optimal solution then. With less number of experiments and depletion of resources, massive data, and an excellent competency to study variable–variable interactions, DOE is the approach of choice [28–34].

The objective of this work is to synthesize uniform-sized; monodispersed, cyano-functionalized spherical SNPs with a narrow particle size distribution employing Stöber synthesis (sol–gel). Optimum synthetic conditions will be controlled using the experimental design approach. Fractional factorial design will be employed as a screening design. Considering PS and PSD as two responses, composite desirability function will be employed where the different responses will be consolidated in one optimal response. To the best of our knowledge, synthesis of cyano-modified SNPs via an optimized experimental design has not been reported before.

Table 1
Vetted continuous variables and response levels for a two-level ($2^{6\text{-}2}$) fractional factorial design (FFD) scrutinized for the synthesis of *cyano*-modified silica nanoparticles.

Screened factors	Code	Level	
		Low (−)	High (+)
TEOS (TEOS, M)	X_1	0.10	0.50
Reaction time (RT, min)	X_2	5	25
CPTS (CPTS, M)	X_3	0.05	0.20
Water (Water, M)	X_4	1	15
Concentration of ammonia (Ammonia, M)	X_5	0	4
Stirring time (ST, min)	X_6	15	60
Responses	Y1, Y2	Smallest PS, Narrowest PSD	

Table 2
The $2^{6\text{-}2}$ Fractional Factorial Design for coded variables. Factor domains are represented as (−1, lower domain) and (+1, upper domain). Actual domain levels are given beside each domain code.

Run #	$2^{6\text{-}2}$ basic design in coded units					
	X_1 (M)	X_2 (min)	X_3 (M)	X_4 (M)	X_5 (M)	X_6 (min)
1	−1(0.10)	+1(25)	−1(0.05)	+1(15)	+1(4)	−1(15)
2	+1(0.50)	+1(25)	−1(0.05)	+1(15)	−1(0)	−1(15)
3	+1(0.50)	−1(5)	+1(0.20)	+1(15)	−1(0)	−1(15)
4	+1(0.50)	−1(5)	−1(0.05)	−1(0)	+1(4)	−1(15)
5	+1(0.50)	−1(5)	−1(0.05)	+1(15)	+1(4)	+1(60)
6	−1(0.10)	−1(5)	−1(0.05)	−1(0)	−1(0)	−1(15)
7	−1(0.10)	−1(5)	+1(0.20)	+1(15)	+1(4)	−1(15)
8	−1(0.10)	−1(5)	+1(0.20)	−1(0)	+1(4)	+1(60)
9	+1(0.50)	+1(25)	+1(0.20)	−1(0)	+1(4)	−1(15)
10	−1(0.10)	−1(5)	−1(0.05)	+1(15)	−1(0)	+1(60)
11	+1(0.50)	+1(25)	−1(0.05)	−1(0)	−1(0)	+1(60)
12	−1(0.10)	+1(25)	+1(0.20)	+1(15)	−1(0)	+1(60)
13	+1(0.50)	−1(5)	+1(0.20)	−1(0)	−1(0)	−1(15)
14	−1(0.10)	+1(25)	+1(0.20)	−1(0)	−1(0)	+1(60)
15	+1(0.50)	+1(25)	+1(0.20)	+1(15)	+1(4)	+1(60)
16	−1(0.10)	+1(25)	−1(0.05)	−1(0)	+1(4)	+1(60)

Y1(PS, nm): Average size of 100–200 particles; Y2 (PSD, ±SD): SD = Distribution of 100–200 particles.

Table 3
Details of the synthetic procedure. Ethanol volume was calculated to keep the total volume constant, 25 mL.

#	Ethanol (mL)	Water (mL)	Ammonia (mL)	RT (min)	TEOS (mL)	CPTS (mL)	ST (min)
1	13.26	4.269	6.62	25	0.558	0.3	15
2	15.181	6.73	0	25	2.791	0.3	15
3	14.283	6.73	0	5	2.791	1.2	15
4	15.29	0	6.623	5	2.791	0.3	15
5	11.082	4.29	6.623	5	2.791	0.3	60
6	23.72	0.423	0	5	0.558	0.3	15
7	12.353	4.269	6.623	5	0.558	1.2	15
8	16.689	0	6.623	5	0.558	1.2	60
9	14.456	0	6.623	25	2.791	1.2	15
10	17.414	6.73	0	5	0.556	0.3	60
11	21.487	0.423	0	25	2.791	0.3	60
12	16.516	6.728	0	25	0.558	1.2	60
13	20.588	0.423	0	5	2.791	1.2	60
14	22.821	0.423	0	25	0.558	1.2	15
15	10.16	4.269	6.623	25	2.791	1.2	60
16	17.587	0	6.623	25	0.558	0.3	60

Please cite this article in press as: M.S. Elazazy et al., Application of fractional factorial design for green synthesis of cyano-modified silica nanoparticles: Chemometrics and multifarious response optimization, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.02.012