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Optimization of Amorphous Silica Nanoparticles Synthesis from Rice Straw Ash Using Design of Experiments Technique

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In this study, a chemical method of dissolution-precipitation was applied to produce amorphous silica nanoparticles from rice straw ash (RSA; the waste material of rice cultivation. The morphology, particle size, structure, and area of specific surface of synthesized amorphous silica nanoparticles were evaluated using transmission electron microscopy (TEM), x-ray diffraction analysis (XRD), and BET method to measure the specific surface area of materials. In addition, chemical composition of RSA used and the synthesized silica nanoparticles was studied by x-ray fluorescence (XRF) spectroscopy. The atomic concentration of synthesized silica was determined by x-ray photoelectron spectroscopy (XPS). The effects of sodium hydroxide concentration, precipitation reaction temperature, and precipitation reaction duration on the area of specific surface were determined through design of experiments (DOE) technique. Results depicted that silica nanoparticles with particle size of 10–15 nm were successfully synthesized. Average area of specific surface and purity were 327 m2/gr and 99.5%, respectively. The interactive influence of temperature and duration had the highest effect on the average area of specific surface.

Keywords: Amorphous, design, nanoparticles, optimization, silica, surface, TEM, XRD

1. Introduction

Silica particles have a wide range of applications, including ceramic production, chromatography, electrical and thermal insulations, and catalysts (Iler 1979; Matovic et al. 2009). They are also found in processors for mechanical-chemical polish slurries (Rashad et al. 2011) and composites (Lin et al. 2012), and as filler to reinforce rubber (Mohammadi and Khorsand 2011) and cements (Jo et al. 2007). Since particles at nanoscelae exhibit better properties, such as higher specific surface area (Jo et al. 2007; Ranjbar and Rastegar 2009; Hu et al. 2011; Mohammadi and Khorsand 2011; Rashad et al. 2011; Lin et al. 2012), research has focused on the synthesis of silica nanoparticles using different methods such as sol-gel (Shin et al. 2010), dissolution-precipitation (Liou and Yang (2011), emulsion (Park et al. 2010), self-arrangement (Fan et al. 2001), flame-sprayed pyrolysis synthesis (Schimmoeller et al. 2010), ball milling (Wang and Forssberg 2006), and biologic synthesis (Estevez et al. 2009).

As mentioned above, one of the applications of silica nanoparticles is as an addition to cement to improve its compressive strength (Shih et al. 2006). The research shows that the addition of silica nanoparticles up to 0.6% could increase the compressive strength from 45 MPa to 65.62 MPa, which was attributed to fill into the interstitial spaces inside the skeleton of the hardened microstructure of cement paste to increase its density as well as the strength. Khanzadi et al. (2010) showed similar results in their research, and Zhang and Islam (2012) compared the influence of silica nano- and micro particles on concrete strength and hydration rate; their investigation proved more favorable results with 12 nm silica particles rather than 150 nm silica particles.

As can be seen, research has shown that silica nanoparticles can successfully improve compressive strength of concrete. Today, a major portion of silica is produced from sand mines and, as such, its application in concrete structure is not cost effective. This limitation has persuaded researchers to find new, cost-effective sources of silica.

Rice is basically produced as a source of human food. Rice straw is torched after the rice product is collected, which is due to the increase in soil nutrition elements for the next year of cultivation, as well as removing the necessity for straw storage. In developed countries, however, the concept of "waste material" is no longer valid, as all waste materials are considered as sources for the production of new products and as an increase of added value. Studies have shown that rice straw, the waste material of agricultural processes, may be a potential candidate in producing electricity (Hessien et al. 2009). Besides the added value generated, this will reduce air pollution resulting from the torching of rice straw. However, a major problem is the pile up of rice straw ash (RSA), which is rich in silica (Agbagla-Dohnani et al. 2001; Hessien et al. 2009). The content of silica collected in rice straw is much greater than other plants as the organic constitutes of rice straw are as follows: cellulose: 32–47%, hemicellulose: 19–27%, lignin: 5–24%, ash: 13–20% (Santos et al. 2010).

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RSA has around 60% of silica (Zaky et al. 2008), which, of course, is reported to be different in different climatic conditions, depending on the type of soil, the season of rice cultivation, weather conditions, and geography of the location. Metallic impurities may also be found in the composition due to insertion of chemical fertilizers (Zaky et al. 2008; Chandrasekhar and Pramada 2006; Santos et al. 2010).

Conradt et al. (1992) evaluated the advantages and limitations of silica nanoparticles synthesis from rice husk. They faced two problems: silica has an affinity toward agglomeration and creation of 30 μm colonies; silica has an inability to achieve complete oxidation despite the application of enzyme pretreatment and increase of oxygen partial pressure. Kamath and Proctor (1998) succeeded in extracting amorphous silica out of rice husk ash under low temperatures and basic conditions. Considering the fact that amorphous silica solubility is quite low under $pH < 10$ and increases significantly above this level, Kalapathy et al. (2000) innovated a simple method to synthesize pure silica from rice husk. Designing Box-Behnken experiments, Zaky et al. (2008) set a profound investigation to observe solubility of silica in sodium hydroxide in the synthesis process of silica nanoparticles from semi-burned rice straw ash (SBRSA), noticing the effects of parameters like stoichiometry ($NaOH:SiO_2$) as well as reaction duration and temperature. They showed that the efficiency of silica solubility will reach 99%, if abovementioned stoichiometry is 3, reaction duration is 4 h, and temperature is 100°C (Zaky et al. 2008).

The purpose of this study was study the synthesis of amorphous silica nanoparticles from Iranian RSA through the dissolution-precipitation technique and to determine the effects of sodium hydroxide concentration, precipitation reaction temperature, and precipitation reaction duration on the area of specific surface through triple factorial design procedure. The innovative aspect of this investigation is the use of agricultural waste as the primary source for the synthesis of strategic product of silica.

2. Experimental Procedure

2.1 Materials

The straw used in this research was collected from a village in the vicinity of Lahijan city, in the province of Guilan, having geographical position of 37′, 11″ N, width and 50′, 0″ E length, with a height of 2 meters above sea level. The straw selected was 10–15 cm above the bottom of stem. Sulfuric acid and one- molar sodium hydroxide from Merck were used with purity of 99% at the stage of dissolution and 98% at the stage of precipitation, respectively. Deionized water was used in the whole process.

2.2 Experiment Design

Three most efficacious parameters on the characteristics of silica nanoparticles were investigated through a statistical complete triple factorial design procedure in which the spontaneous influences of sodium hydroxide concentration, precipitation reaction temperature and precipitation reaction duration on the area of specific surface are evaluated through a computational method rather than experimental, thus, reducing of the number of specimens and experiments needed. The magnitude of theses parameters were selected based on the previous works (Conradt et al. 1992; Kamath and Proctor 1998; Kalapathy et al. 2000; Zaky et al. 2008; Hessien et al. 2009). Interpretation of results was performed on the measurement of effects and drawing of Pareto graph for parameters and their interactive reactions. To study the magnitude of effects by parameters and their interactions, results of high and low levels were averaged. The effect of each parameter was determined by subtracting average values in high and low levels, denoted by +1 and −1, respectively. The complete triple factorial design procedure was designed for eight experiments detailed in Table 1.

2.3 Apparatus

In this research a double-walled glass reactor with attachments for the adjustment of temperature and pH during the process was applied. To determine the structure, x-ray diffraction (XRD) experiments were performed using Philips PW1800 diffractometer. Philips PW1480 (the Netherlands) apparatus was also used to determine the chemical composition of RSA and purity of silica synthesized through x-ray fluorescence (XRF). Elemental analysis of synthesized silica was also experimented by Kratos XSAM800 (UK) x-ray photoelectron spectroscopy (XPS). In order to study the morphology and particle size of silica, Zeiss EM900 (Germany) transmission electron microscopy (TEM) was

Table 1. Experiment design for the synthesis of silica nanoparticles

No. of experiments	Design of experiments (DOE) code	Temperature (°C)	Concentration of NaOH (N)	Precipitation reaction duration (min)
1	−1,−1,−1	80	2	10
2	+1,+1,−1	90	2.5	10
3	−1,+1,−1	80	2.5	10
4	+1,−1,−1	90	2	10
5	+1,−1,+1	90	2	15
6	−1,−1,+1	80	2	15
7	−1,+1,+1	80	2.5	15
8	+1,+1,+1	90	2.5	15

used. Finally, BET test was performed to determine the area of specific surface.

2.4 *Procedure*

Raw rice straws were washed thoroughly with running tap water followed by distilled water to remove adhering soil and other contaminants present in them and then dried in the sunlight for 24 h. After proper cleaning, rice straw was heat treated at 600°C for 6 h in air to remove organic compounds. Each specimen contained 10 grams of RSA, weighed to the accuracy of 0.001 gram. Sodium hydroxide solutions of 2 and 3 N were also prepared. In basic leaching, the temperature of reactor containing sodium hydroxide was kept at 100°C. While sodium hydroxide was stirred at 700 RPM, RSA was added. Basic leaching performed at 100°C for a period of 4 hat a stirring speed of 700 rpm. The resulted solution was then filtered by Whatman No. 41 incinerator to separate sodium silicate from undesirable residuals. This was followed by the addition of 20% sulfuric acid to the extracted sodium silicate in the process of dissolution to achieve a pH of 7, while the contents of reactor were still stirring at the mentioned rate. A concentration of sodium silicate solution was selected to be 30% based on previous researches (Khanzadi et al. 2010). The temperature of precipitation process was selected to be 80°C and 90°C, as well as its duration on 10 and 15 min. The extracted solution from the dissolution-precipitation processes was then centrifugally separated and rinsed by 300 ml of deionized water to remove sulfate compounds. Final product was dried at ambient temperature for 18 h.

3. Results and Discussion

Figure 1 shows the XRD pattern of RSA in which amorphous silica is observable due to the presence of wide peak of $\theta = 22°$. This pattern also reveals the presence of potassium as potassium chloride, known to be an impurity. XRD pattern is in good agreement with previous works (Kalapathy et al. 2000; Zaky et al. 2008), but it does not show the existence of sodium in RSA.

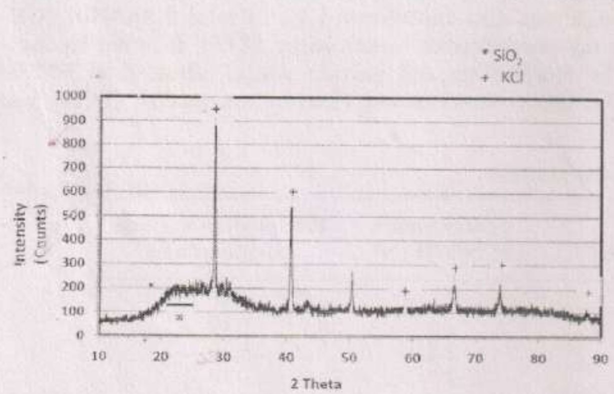

Fig. 1. Rice straw ash XRD pattern.

An XRF experiment of RSA (Table 2) depicts the existence of negligible amount of sodium as an impurity. As sodium has been reported to exist as an impurity in the final product of silica nanoparticles (Kalapathy et al. 2000; Zaky et al. 2008) very little amount of it in the RSA used, will help synthesize pure silica.

Images obtained from TEM of specimen 2 prove the successful synthesis of silica nanoparticles from RSA through dissolution-precipitation technique. As observed in Figure 2, spherical silica nanoparticles of around 10–15 nm were synthesized. Results of chemical composition analysis of specimen 2 are shown in Table 3. Besides, as seen in Figure 3, XRD patterns of synthesized silica nanoparticles reveal a wide peak of $\theta = 22°$, corresponding to amorphous silica. The purity of silica nanoparticles synthesized in this process is higher than 85–96% purity silica from silica ash. Table 4 shows the results of XPS experiment of synthesized silica. Considerable portion of synthesized silica comprised of silica and oxygen, while sodium, potassium and titanium were detected at very low concentrations. Higher purity silica will improve its performance as processors mechanical-chemical polish slurries, composites and cements.

The results of BET experiment are shown in Table 5. As mentioned before, the average value of low- and high-level results are calculated and subtracted to be used in the investigation of effects of each parameter. The subtraction integer shows its influence on the target variable which is area of specific surface in this study.

Figure 4 shows the Pareto plot showing the effects of different parameters on the area of specific surface. It is clear from the plot that interactive effect of precipitation reaction duration and temperature has greatest influence on area of specific surface with sole effect of temperature and sole effect of duration coming in the next orders. Besides, the effect of temperature and duration are almost the same.

Table 2. Results of rice straw ash XRF experiment

Chemical composition	Weight percent
SiO_2	61.39
Al_2O_3	0.22
Fe_2O_3	0.14
CaO	2.78
Na_2O	0.15
K	12.94
MgO	1.72
TiO_2	0.006
MnO	0.371
P_2O_5	0.882
Cl	4.35
S	0.632
L.O.I	14.13
Ba,Sr,Cu,Zn,Pb,Ni,Cr,V,Ce La,Rb,W,Zr,Y,Co,As,U,Th	Ppm

ppm: part per million; LOI: loss on "eye" ignition

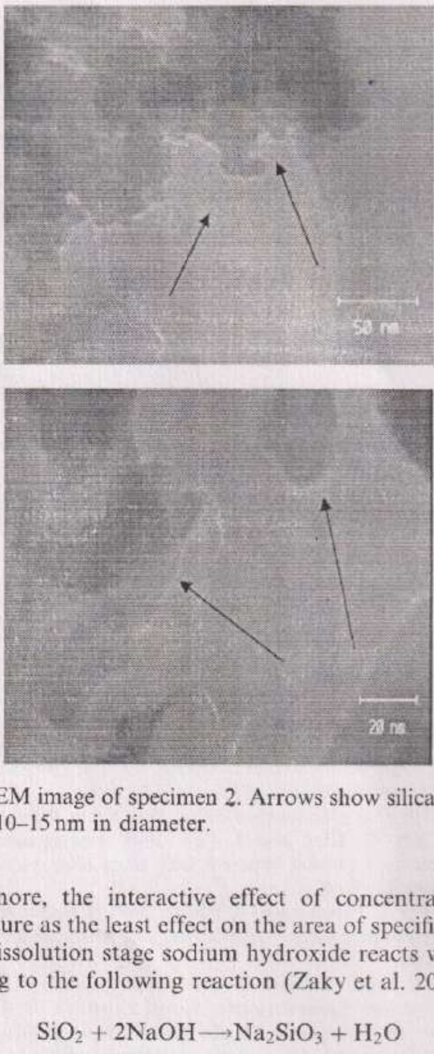

Fig. 2. TEM image of specimen 2. Arrows show silica nanoparticles of 10–15 nm in diameter.

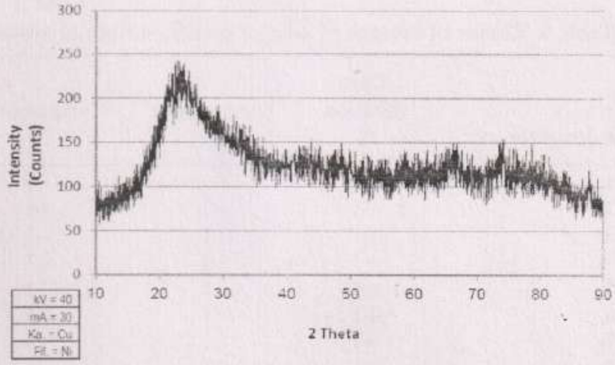

Fig. 3. Synthesized silica nanoparticles XRD pattern.

Table 4. Elemental content of synthesized silica as determined by XPS

Element	Atomic concentration%
Silicon	27.4
Oxygen	60.1
Carbon	3.4
Sodium	2.7
Potassium	3.5
Titanium	1.8

Furthermore, the interactive effect of concentration and temperature as the least effect on the area of specific surface. At the dissolution stage sodium hydroxide reacts with silica according to the following reaction (Zaky et al. 2008):

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

The mechanism can be so described that silica dissolution takes place by the diffusion of hydroxide in to the silica and is controlled by the diffusion rate on the solid surface. Hydroxide diffusion increases with increasing pH and solution ionic strength. At a specific pH and solution ionic strength, hydroxide surface adsorption decreases with increase in the size of hydrated cations (Wang and Gillot 1991).

Table 3. Results of specimen 2 XRF experiment

Chemical composition	Weight percent
SiO_2	99.95
Al_2O_3	0.002
Fe_2O_3	0.001
CaO	0.002
Na_2O	0.001
K	0.005
MgO	0.001
TiO_2	0.004
P_2O_5	0.002

Thuadaij and Nuntiya (2008) reported a considerable increase in area of specific surface with increase in the concentration of sodium hydroxide from 2 to 25 N. In another study Zaky et al. (2008) also reported higher efficiency of silica dissolution with increase in sodium hydroxide concentration. The present study also proves the effect of sodium hydroxide concentration on area of specific surface of nanosilica; however, this effect is much weaker than the influence of interactive effect of temperature and duration of precipitation reaction.

The precipitation reaction which is the acidic neutralization of sodium silicate by a protonated acid is performed under (Hessien et al. 2009):

$$Na_2SiO_3 + H_2SO_4\ SiO_4 \longrightarrow H_2O + Na_2SO_4$$

It seems that temperature and duration of precipitation reaction are solely more effective on the area of specific surface in comparison with the concentration of sodium hydroxide in dissolution reaction. This is attributed to the influences of temperature and duration as being been more significant.

Increasing the surface in nanoscale particles, makes silica nanoparticles very suitable at applications like fillers in composites, catalysts and electronic devices (Iler 1979), whereas high area of specific surface of silica nanoparticles synthesized in this research, makes it an acceptable alternative for silica ash in comments.

Table 5. Results of average of area of specific surface of synthesized silica based on Table 1

No. of experiments	Time duration C	Temperature B	Concentration A	BC	AC	AB	ABC	Average of surface area (m^2/gr)
1	−1	1−	−1	+1	+1	+1	−1	151
2	−1	+1	+1	−1	−1	+1	−1	325
3	−1	+1	−1	−1	+1	−1	+1	327
4	−1	−1	+1	+1	−1	−1	+1	150
5	+1	−1	+1	−1	+1	−1	−1	260
6	+1	−1	−1	−1	−1	+1	+1	260
7	+1	+1	−1	+1	−1	−1	−1	293
8	+1	+1	+1	+1	+1	+1	+1	290
$\sum Y^+$	1103	974	1025	884	1028	1026	1027	
$\sum Y^-$	953	821	1031	1172	1028	1030	1029	
$\bar{Y}^+$	275.75	243.50	265.25	221	257	256.5	256.75	
$\bar{Y}^-$	238.25	205.25	257.75	293	257	257.50	257.25	
$\bar{Y}^- - \bar{Y}^+$ effect of	37.5	38.25	7.5	−72	0	−1	−0.5	

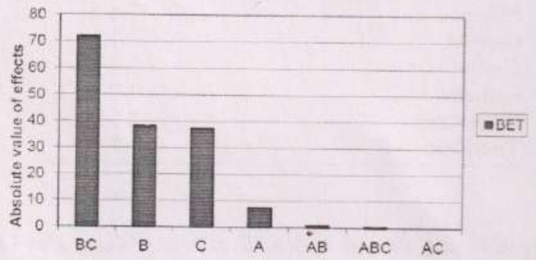

Fig. 4. Pareto plot showing the sole and interactive effects of involving parameters.

4. Conclusion

In this study, amorphous silica nanoparticles were successfully synthesized through dissolution- precipitation reaction from RSA collected from the rice steads of Iran, left as waste. Synthesized silica nanoparticles were 10–15 nm in diameter with the parity of 99.95% and area of specific surface of $327\,m^2/gr$. At constant pH, sulfuric acid concentration and string speed, temperature and duration of precipitation reaction had great influence on the area of specific surface of silica particles, with the interactive influence of temperature and duration having the highest effect. The final product possessed very little amount of sodium impurity, which helps improve the efficiency of product.

References

Agbagla-Dohnani, A., P. Nozière, C. Clément, and M. Doreau. 2001. Chemical and morphological composition of 15 varieties of european rice straw. *Animal Feed Science and Technology* 94: 15–27.
Chandrasekhar, S., and P. N. Pramada. 2006. Rice husk ash as an adsorbent for methylene blue-effect of ashing temperature. *Adsorption* 12: 1227–1243.
Conradt, R., P. Pimkhaokham, and U. Leela-Adisorn. 1992. Nano-structured silica from rice husk. *Non-Crystalline Solids* 145: 75–79.
Estevez, M., S. Vargas, V. M. Castaño, and R. Rodriguez. 2009. Silica nano-particles produced by worms through a bio-digestion process of rice husk. *Non-Crystalline Solids* 355: 844–850.
Fan, H., F. Van Swol, Y. Lu, and C. J. Brinker. 2001. Multiphased assembly of nanoporous silica particles. *Non-Crystalline Solids* 285: 71–87.
Hessien, M. M., M. M. Rashad, R. R. Zaky, E. A. Abdel-Aal, and K. A. El-Barawy. 2009. Controlling the synthesis conditions for silica nanosphere from semi-burned rice straw. *Materials Science and Engineering B* 162: 14–21.
Hu, H., L. Chen, and G. Chen. 2011. Reinforcement of epoxy with graphite oxide nanoparticles prepared via electrochemical route. *Materials and Manufacturing Processes* 26: 618–622.
Iler, R.K. 1979. *The Chemistry of Silica*. New York: Wiley.
Jo, B. W., Ch. H. Kim, and J. Lim. 2007. Investigations on the development of powder concrete with nano SiO_2 particles. *Civil Engineering* 11: 37–42.
Kalapathy, U., A. Proctor, and J. Shultz. 2000. A simple method for production of pure silica from rice hull ash. *Bioresearch Technology* 73: 257–262.
Kamath, S. R., and A. Proctor. 1998. Silica gel from rice hull ash: Preparation and characterization. *Cereal Chemistry* 75: 484–487.
Khanzadi, M., M. Tadayon, H. Sepehri, and M. Sepehri. 2010. Influence of nano-silica particles on mechanical properties and permeability of concrete. Second International Conference on Sustainable Construction Materials and Technologies, Ancona, Italy, June 28–30.
Lin, W., T. Zhu, Q. Li, Sh. Yi, and Y. Li. 2012. Study of pervaporation for dehydration of caprolactam through PVA/Nanosilica composite membranes. *Desalination* 285: 39–45.
Liou, T. H., and C. C. Yang. 2011. Synthesis and surface characteristics of nanosilica produced from alkali-extracted rice husk ash. *Materials Science and Engineering* 176: 521–529.
Matovic, B., B. Babic, A. Egelja, A. Radosavljevic-Mihajlovic, V. Logar, A. Saponjic, and S. Boskovic. 2009. Preparation of Porous silica ceramics using the wood template. *Materials and Manufacturing Processes* 24: 1109–1113.
Mohammadi, M., and H. Khorsand. 2011. Evaluation of optimum parameters in the reaction of precipitated nanosilica using different surfactants. In *Proceedings of the National Conference on Recent Advances in Modern Communication Systems and Nanotechnology*, Rajasthan, India, January 6–8.
Park, Ch. Y., Y. G. Lee, Ch. Oh, and S. G. Oh. 2010. Preparation of poly-(NIPAM) grafted hybrid silica particles with hollow structure in emulsion. *Industrial and Engineering Chemistry* 16: 32–38.
Ranjbar, Z., and S. Rastegar. 2009. The influence of surface chemistry of nano-silica on microstructure, optical and mechanical properties of the nano-silica containing clear-coats. *Organic Coatings* 65: 125–130.

Rashad, M. M., M. M. Hessien, E. A. Abdel-Aal, K. El-Barawy, and R. K. Singh. 2011. Transformation of silica fume into chemical mechanical polishing (CMP) nano-slurries for advanced semiconductor manufacturing. *Powder Technology* 205: 149–154.

Santos, M. B., G. A. Nader, P. H. Robinson, D. Kiran, U. Krishnamoorthy, and M. J. Gomes. 2010. Impact of simulated field drying on in vitro gas production and voluntary dry matter intake of rice straw. *Animal Feed Science and Technology* 159: 96–104.

Schimmoeller, B., Y. Jiang, S. E. Pratsinis, and A. Baiker. 2010. Structure of flame-made vanadia/silica and catalytic behavior in the oxidative dehydrogenation of propane. *Catalysis* 274: 64–75.

Shih, J. Y., T. P. Chang, and T. Ch. Hsiao. 2006. Effect of nano silica on characterization of portland cement composite. *Materials Science and Engineering A* 424: 266–274.

Shin, K., J. J. Kim, and K. D. Suh. 2010. Facile process for generating monolithic-structured nanosilica/polystyrene multi-core/shell microspheres by a seeded sol–gel process method. *Colloid and Interface Science* 350: 581–585.

Thuadaij, N., and A. Nuntiya. 2008. Preparation of nanosilica powder from rice husk ash by precipitation method. *Chiang Mai Journal of Science* 35: 206–211.

Wang, H., and J. E. Gillot. 1991. Mechanism of alkali-silica reaction and the significance of calcium hydroxide. *Cement and Concrete Research* 21: 647–654.

Wang, Y., and E. Forssberg. 2006. Production of carbonate and silica nano particles in stirred bead milling. *International Journal of Mineral Processing* 81: 1–14.

Zaky, R. R., M. M. Hessien, A. A. El-Midany, M. H. Khedr, E. A. Abdel-Aal, and K. A. El-Barawy. 2008. Preparation of silica nanoparticles from semi-burned rice straw ash. *Powder Technology* 185: 31–35.

Zhang, M. H., and J. Islam. 2012. Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag. *Construction and Building Materials* 29: 573–580.