

Rice Straw Ash- A Novel Source of Silica Nanoparticles

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Abstract: In this study 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 analysis technique for the measurement of the specific surface area of materials (BET). In addition, chemical composition of RSA, used and the synthesized silica nanoparticles was studied by X-ray fluorescence (XRF) spectroscopy. The effects of sodium hydroxide concentration, precipitation reaction temperature and precipitation reaction duration on the area of a specific surface were determined through Design of Experiments (DOE) Technique. Results depicted that silica nanoparticles with particle size of 10-15 nanometers were successfully synthesized. Average area of a specific surface and purity were 327 m²/g and 99.5% respectively. The interactive influence of temperature and duration having the highest effect on the average area of the specific surface.

Keywords: Amorphous Silica, Nanoparticles, Optimization, DOE, TEM, XRD

1. Introduction

Silica particles have wide range of application such as ceramic production, chromatography, electrical and thermal insulations and catalysts [1, 2] as well as processors mechanical-chemical polish slurries [3], composites [4], as filler to reinforce rubber [4] and cements [5]. Since the improvement of properties such as area of a specific surface at nano-scale will lead to higher performance [3-8], researches focus on the synthesis of silica nanoparticles using different methods such as sol-gel [9], dissolution-precipitation [10],

emulsion [11], self-arrangement [12], flame sprayed pyrolysis synthesis [13], ball mill [14] and biologic synthesis [15].

As it is mentioned, one of the applications of silica nanoparticles is as an addition to cement to improve its compressive strength which is studied by Shih et.al. [16]. The research showed that 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 hardened microstructure of cement paste to increase its density as well as its strength. Khanzadi et.al.

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[17] Show the similar results in their research as well. Zhang et.al. [18] compared the influences of silica nano- and micro- particles on the concrete strength and hydration rate. Their investigation proved more favorable results with 12 nm silica particles rather than 150nm silica particles.

As it can be seen investigations have shown that silica nanoparticles can successfully improve compressive strength of concrete. Today, a major portion of silica is produced from sand mines and therefore 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 the 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 increasing of added value. Studies have proven that rice straw, the waste material of agricultural processes, may be a potential candidate in producing electricity [19]. Besides the added value generated, this will reduce air pollution resulting from the torching of rice straw at stead. But a major problem is the pile up of rice straw ash (RSA) which is rich in silica [19, 20]. The content of silica collected in rice straw is much greater than other plants as the organic constitutes of rice straw as follows: Cellulose: 32-47%, Hemi cellulose: 19-27%, Lignin: 5-24%, Ash: 13-20 % [21].

Rice straw ash has around 60% of silica [22], 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 geogra-

phy of place. Metallic impurities may also be found in the composition due to insertion of chemical fertilizers [21, 23].

In 1992, Conradt et. al. [24] evaluated the advantages and limitations of silica nanoparticles synthesis from rice husk. They have faced two problems, first silica affinity towards agglomeration and creation of 30-micron colonies and second, inability to achieve complete oxidation despite the application of enzyme pretreatment and increase of oxygen partial pressure. In 1998, Kamath and Proctor [25], succeeded to extract amorphous silica out of rice husk ash under low temperature and basic conditions. Considering the fact that amorphous silica solubility is quite low under $\text{pH} < 10$ and increases significantly above this level, in 2000 Kalapathy et. al. [26] innovated a simple method to synthesize pure silica from rice husk. Designing Box-Behnken experiments, Zaky et.al [22] 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 ($\text{NaOH}:\text{SiO}_2$) as well as reaction duration and temperature. They showed that the efficiency of silica solubility will reach 99%, if the above-mentioned stoichiometry is 3 and reaction duration and temperature are 4 hours and 100°C , respectively [22].

The purpose of this study was the synthesis of amorphous silica nanoparticles from Iranian RSA through dissolution-precipitation technique and to determine the effects of sodium hydroxide concentration, precipitation reaction temperature and precipitation reaction duration on the area of a 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 Guilan province, having geographical position of 37°, 11" north, width and 50°, 0" east length, with a height of 2 meters above the sea level. The straw selected was 10-15 cm above the bottom of stem. Sodium hydroxide and sulfuric acid 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 a specific surface are evaluated through a computational method rather than experimental, thus reducing of the number of specimens and experiments needed. A triple factorial design was used through Minitab 16. The magnitudes of sodium hydroxide concentration and temperature and duration of precipitation were assigned maximum and minimum values based on the previous works [17, 21, 23-25]. Sodium hydroxide concentration less than 2N and more than 2.5N will lead to reduction on dissolution rate and increase in formed silica particle size, respectively. Other investigations also showed that precipitation temperature of 80-90°C has no effect on formed silica particle size and that precipitation duration of 10-15 min was most efficient with other mentioned parameters. Interpretation of results was per-

formed upon 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 8 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 Phillips PW1800 diffractometer. Phillips PW1480 apparatus was also used to determine the chemical composition of RSA and purity of silica synthesized through X-ray fluorescence (XRF). In order to study the morphology and particle size of silica, Zeiss EM900 transmission electron microscopy (TEM) was used. Finally, BET test was performed to determine the specific surface area.

2.4. Procedure

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 the 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 hours at a stirring speed of 700 RPM. The resulted solution was then filtered by Whatman No. 41 incinerator to separate sodium silicate from residual organics and RSAs. This was followed by the addition of 20%-sulfuric acid to the extracted sodium silicate in the process of dissolution to

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

achieve a pH of 7, while the contents of reactor were still stirring at the mentioned rate. The temperature of precipitation process was selected to be 80 and 90°C, as well as its duration in 10 and 15 minutes. The extracted solution from the dissolution-precipitation processes was then centrifugally separated and rinsed by 300ml of deionized water to remove sulfate compounds. Final product was dried at ambient temperature for 18 hours.

3. Results and discussion

Fig. 1 shows the XRD pattern of RSA in which amorphous silica is observable due to the presence of wide peak of $2\theta=22^\circ$. This pattern also reveals the presence of potassium as potassium chloride, known to be an impurity. XRD pattern is in good agreement with pre-

vious works [22, 26], but it does not show the existence of sodium in RSA.

An XRF experiment of RSA, shown in 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 [22, 26], very little amount of it in the RSA used, will help synthesize pure silica.

Images obtained from TEM of specimen No. 2 prove the successful synthesis of silica nanoparticles from RSA through dissolution-precipitation technique. As observed in Fig. 2, spherical silica nanoparticles of around 10-15 nm were synthesized. Results of chemical composition analysis of specimen No. 2 are shown in Table 3. Besides, as seen in Fig. 3, XRD patterns of synthesized silica nanoparticles reveal a wide peak of $2\theta=22^\circ$, corresponding to amorphous silica.

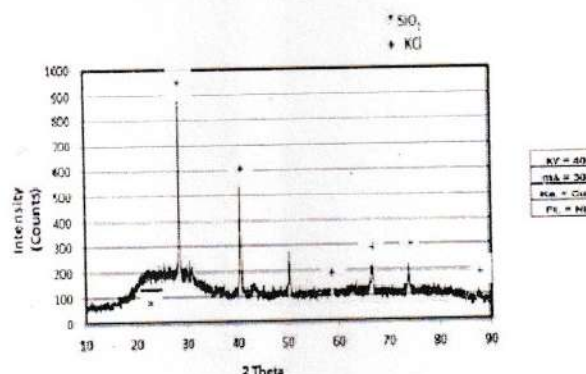


Fig. 1. Rice straw ash XRD pattern.

The purity of silica nanoparticles synthesized in this process is higher than 85-96% purity silica from silica ash. Higher purity silica improves performance of processors mechanical-chemical polish slurries, composites and cements.

After the entry of results of BET into Minitab 16, DOE designed Table 4. In this table parameters of concentration, dissolution temperature and its duration are indicated by A, B, C, respectively. AB, AC, BC and ABC also show the effects of parameters one another. 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 a specific surface in this study.

Fig. 4 shows the pareto plot showing the effects of different parameters on the area of a specific surface. It is clear from the plot that interactive effect of precipitation reaction duration and temperature has greatest influence on area of a 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. Furthermore, the interactive effect of concentration and temperature as the least effect on the area of the specific surface. At the dissolution stage sodium hydroxide reacts with silica according to the Eq. (1) [22]:



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 an in-

crease in the size of hydrated cations [27].

Thuadaij et al. [28] reported a considerable increase in area of specific surface with an increase in the concentration of sodium hydroxide from 2 to 25 N. In another study Zaky et al. also reported higher efficiency of silica dissolution with increase in sodium hydroxide concentration [22].

The present study also proves the effect of sodium hydroxide concentration on the area of the specific surface of nano silica; 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 Eq. (2) [19]:



Table 2. Results of rice straw ash XRF experiment

Chemical Composition	Weight Percent
SiO ₂	61.39
Al ₂ O ₃	0.22
Fe ₂ O ₃	0.14
CaO	2.78
Na ₂ O	0.15
K	12.94
MgO	1.72
TiO ₂	0.006
MnO	0.371
P ₂ O ₅	0.882
Cl	4.35
S	0.632
L.O.I*	14.13
Ba, Sr, Cu, Zn, Pb, Ni, Cr, V, Ce	ppm†
La, Rb, W, Zr, Y, Co, As, U, Th	

* Loss on ignition

† part per million

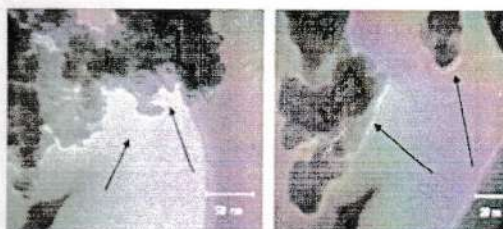


Fig. 2. TEM image of specimen No. 2. Arrows show silica nanoparticles of 10-15 nm in diameter.

Table 3. Results of specimen No. 2 XRF experiment

Chemical Composition	Weight Percent
SiO ₂	99.95
Al ₂ O ₃	0.002
Fe ₂ O ₃	0.001
CaO	0.002
Na ₂ O	0.001
K	0.005
MgO	0.001
TiO ₂	0.004
P ₂ O ₅	0.002

It seems that temperature and duration of precipitation reaction are solely more effective on the area of a specific surface in com-

parison with the concentration of sodium hydroxide in dissolution reaction. This is attributed to the greater influences of temperature and duration have been more significant.

Increasing the surface in nano- scale particles, makes silica nanoparticles very suitable at applications like fillers in composites, catalysts and electronic devices [1], whereas high area of specific surface of silica nanoparticles synthesized in this research, makes it an acceptable alternative for silica ash in comments.

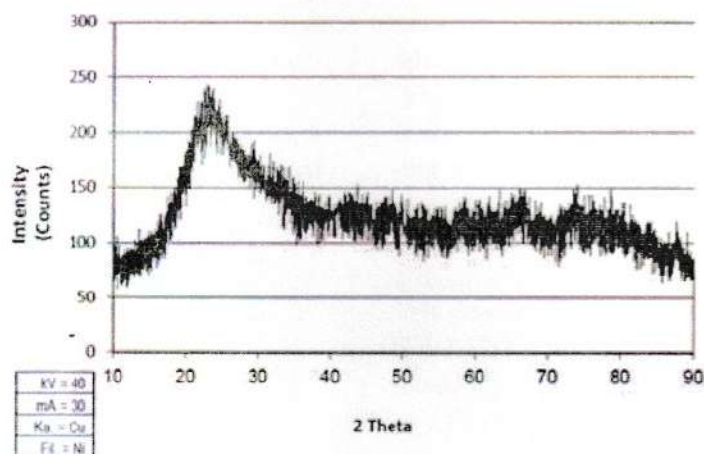


Fig. 3. Synthesized silica nanoparticles XRD pattern.

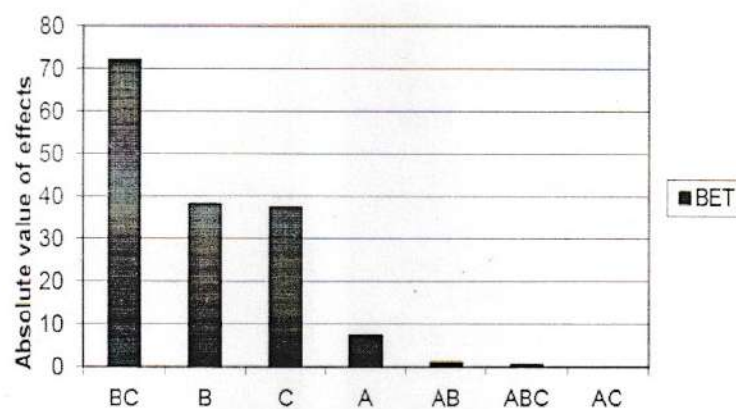


Fig. 4. Pareto plot showing the sole and interactive effects of involving parameters.

Table 4. Results of average of area of specific surface of synthesized silica based on table 1

No. of Experiments	Time duration	Temperature	Concentration	BC	AC	AB	ABC	The average of surface area (m ² /g)
	C	B	A					
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
ΣY^+	1103	974	1025	884	1028	1026	1027	
ΣY^-	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	
$\bar{Y}^- - \bar{Y}^+$	37.5	38.25	7.5	-72	0	-1	-0.5	

4. Conclusions

In this study, amorphous silica nanoparticles were successfully synthesized through dissolution- precipitation reaction from rice straw ash 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 m²/g. At constant pH, sulfuric acid concentration and string speed, temperature and duration of precipitation reaction had great influence on the area of the 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.

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