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### Facile and economic method for preparation of nano-colloidal Silica with controlled size and stability

#### ABSTRACT

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This study is focused on synthesis of nano-colloidal silica via alkaline water glass solution. Sodium ions of water glass were removed by cation exchanging in a resin column to obtain the silicic acid which was titrated to the solution of sodium silicate. Concentration of the colloidal silica and pH value of the solutions were controlled using different concentrations of alkaline sodium silicate and silicic acid solutions in constant temperature and titration rate. The synthesized colloidal silica was characterized by Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), X-Ray powder Diffraction (XRD), Accelerated Surface Area and Porosimetry analyzer (ASAP) and Gravimetric method. The results showed that the average particle size of colloids and their stability were also influenced by various important factors such as pH, Temperature, Concentrations of alkaline sodium silicate and silicic acid solutions. The results showed that the synthesized nano-colloidal silica suspensions in concentration up to 25 wt.% of SiO<sub>2</sub> with average particle sizes in range of 23 to 100 nm are stable more than one year. Also, surface area and pore volume of the prepared spherical colloidal silica particles were 160 m<sup>2</sup>/g and 0.27 cm<sup>3</sup>/g, respectively.

**Keywords:** *Nano-colloidal silica; Water glass solution; particle size; Silicic acid; Sodium silicate.*

#### INTRODUCTION

Colloidal silica is the dispersion of fine amorphous SiO<sub>2</sub> and typically spherical silica particles in a liquid phase. There are many grades of colloidal silica, but all of them are composed of silica particles ranging in size from about 3 nm up to about 150 nm. They have been known as stable suspensions in water, even at a very dilute concentration, that lasts for more than one-half year. These products are often called precipitated silica or silica sols. Today, colloidal silica dispersions are available in a variety of grades determined by particle size, structure, concentration, pH, surface charge and surface modification[1].

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Colloidal silica is one of the few materials that can enhance glass adhesion in a resin base coating[2]. They are one of the most promising candidates that can be used as high temperature binder for inorganic paint, abrasive particles for mechanical polishing of silicon wafers[3-4], drainage aid in paper making [5] and abrasion-resistant coatings[6]. They can also be applied in model making for investment casting. Furthermore, colloidal silica with high purity and controlled surface area is an ideal component for catalysts. The binding functionality of colloidal silica can be used to increase the hardness of a catalyst. For some catalytic applications, low-sodium colloidal silicas can be used as a particle carrier and reaction site to enhance catalyst surface area[1]. In recent years, extensive studies have been performed on the quality of colloidal silica which is highly dependent on the particle size and size distribution of the particles and their stability in liquid. Depending on the synthesis parameters, the structure of colloidal particles may be spherical or slightly irregular in shape, and they may be present as discrete particles or slightly structured aggregates. These particles may also be present in a narrow or wide particle size range - depending on the process in which they were created. Improvement in colloidal stability and subsequent increases in concentration was due to the advance of ion exchange technology leading to lower levels of destabilizing ions and impurities[7]. Stober and Rang[8] used Tetra ethyl orthosilicate (TEOS), ethanol, ammonium hydroxide and water as raw materials for synthesis mono-disperse silica. Santamaria Razo *et al.*[9] used a sol-gel synthesis procedure based on the Stober method for mono-dispersed silica nanospheres preparation with an excellent control of the particle diameter over a wide range by varying the amount of silicon alkoxide. Yoshida[10] has developed different processes for making colloidal silica that include a peptization [11], his work was based on, an acid-neutralization and an ion-exchange methods, which indicated that homogeneous nucleation and surface growth play an important role in the formation of colloidal silica[10]. Tsai *et al.* [12-13] used KOH and active silicic acid to synthesis the colloidal silica particles via a surface growth process. They found that the particle size of the resulting silica colloids and also the surface growth of the particles are highly

dependent on titrating rate, the formation temperature and especially the concentration of KOH.

In the present paper we reported a facile and economic method for preparing colloidal silica sol using the sodium silicate (water glass) as a precursor. An important goal of this research is to understand the effect of synthesise parameters on the size, concentration and stability of the nanoparticles.

**EXPERIMENTAL**

Water Glass ( $\text{SiO}_2=25.5-28.5$  wt.%,  $\text{Na}_2\text{O}=7.5-8.5$  wt.%) was used as starting material for preparation of silica nanoparticles.

At first, water glass was diluted with different amounts of DI water, then sodium ions were removed from water glass using cation exchange resin (Amberlite IR-120, pH= 2.3) and silicic acid with 2 and 1 wt.% of  $\text{SiO}_2$  and pH=2.5-3.5 were obtained. Then, three alkaline sodium silicate solutions were prepared through diluting water glass with DI water to prepare solutions containing 1- 3 wt.% of  $\text{SiO}_2$ . These three alkaline sodium silicate solutions were heated under the average temperature condition of 84-86°C and titrated by similar volumes of silicic acids with different concentrations at constant rate of 0.85 ml/min. It should be noticed that titration and evaporation rates must be approximately equal to form the colloidal particles and pH value of the solution must be controlled during the process not to decrease below 9, otherwise it would lead the solution to be gelled.

In these set of experiments, the total volume of heating solution during titrating is constant and various concentrations of nano-silica particles were obtained. The experimental flowchart is shown in [Figure 1](#). The surface growth became important as the active silicic acid was continuously titrated to the solution with the new born seeds. The concentration of  $\text{SiO}_2$  (wt.%) in prepared samples were determined via Gravimetric method. Also, the pH values of the colloids were measured by pH meter (Model BLD 8252).

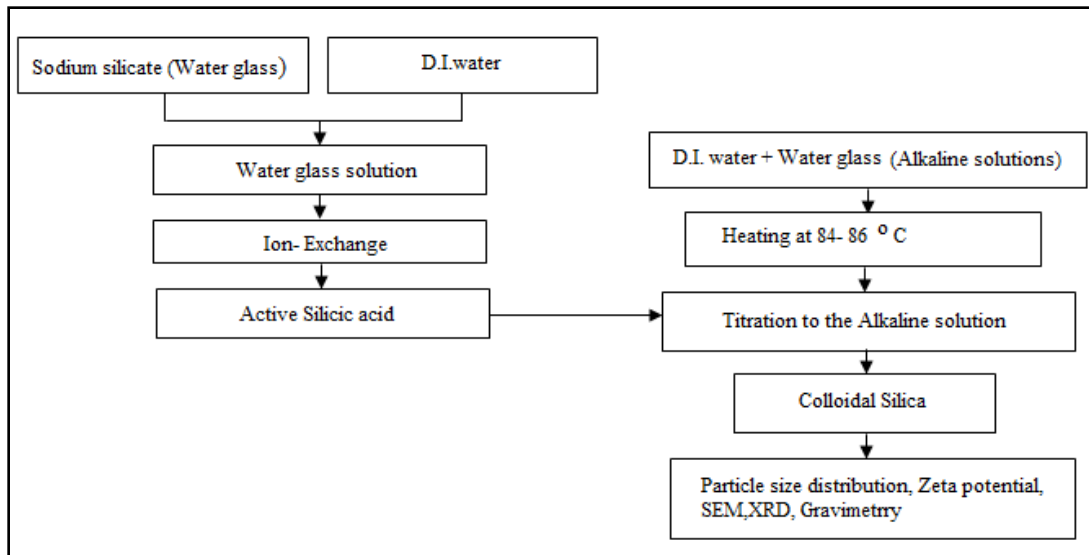


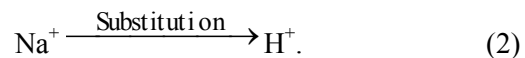
Fig. 1. The preparation flowchart of colloidal silica sol formation

Dynamic Light Scattering (Malvern Zeta Sizer, Nano ZS ZEN 6 3600) were used to characterize zeta potential and particle sizes of the colloidal silica. Philips, XL30 type Scanning Electron Microscope was used to determine the morphology and the shape of particles. Pore structure and Surface area of the samples was measured at 77 K by nitrogen absorption isotherm with a Micromeritics ASAP 2010M, Accelerated Surface Area and Porosimetry Analyzer. TEM image of the samples was recorded on EM208-Philips microscope.

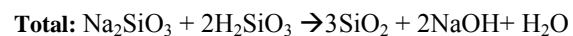
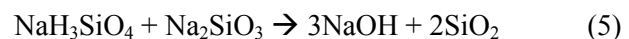
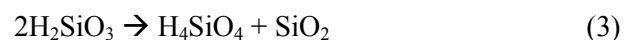
## RESULTS AND DISCUSSION

Colloidal silicas are most often prepared in multi- step process when an alkali-silicate solution is partially neutralized, leading to the formation of silica- nuclei. The initial neutralization step can be accomplished by acidification or electro-dialysis, but it most often achieved by contacting the silicate with hydrogen ions from ion-exchange resin. The neutralization of starting sodium silicate solution to silicic acid must be considered in the context of two different polymeric or monomeric conditions. Despite the differences, most authors agree that polymerization continues until the monomeric silica concentration falls to the solubility of amorphous silica [14]. The neutralization of sodium metasilicate may naively

be written as Eq. (1) and (2), which yielding a monomeric species with the empirical formula  $H_2SiO_3$ .



The maximum concentration of  $SiO_2$  solution for passing from cation exchanger resin is in the range of 7-8 wt.% of  $SiO_2$ . Higher concentration result in gelatin and plugging of the free spaces between of resins. The colloids may deposit to a solid surface driven by transfer processes such as diffusion, flow turbulence and gravity. Colloidal silica particle formation mechanism is described as Equation 3-6.



(6)

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Temperature, pH and evaporation rate of the solution play an important role in colloidal particle formation. The colloidal suspension is stabilized by pH adjustment in the range of 9 - 12.5, storing the solution at temperature of 50 - 150°C, preferably 60 - 95°C and using constant evaporation rate. When the pH is less than 9, polymerization does not progress enough to obtain intended seed. Also when the heating temperature is less than 50°C the homogeneous silica sol is not obtained.

X-ray diffraction patterns of the colloidal silica particles indicated only amorphous SiO<sub>2</sub> phase in any instance. Figure 2 shows the XRD pattern for the sample contains 2 wt.% of SiO<sub>2</sub>.

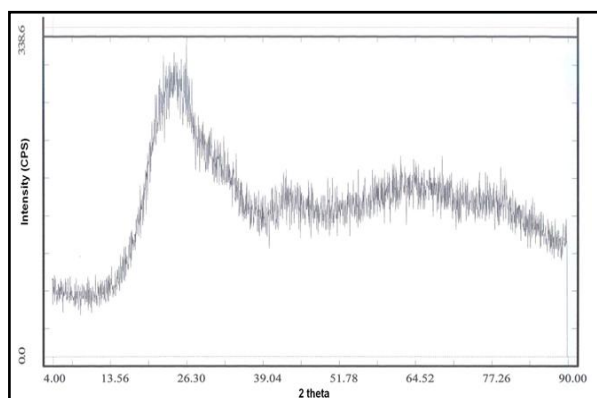


Fig. 2. X-Ray diffraction pattern of colloidal silica contains 2 wt.% of SiO<sub>2</sub>

In general, each dispersed particle in a solution is surrounded by oppositely charged ions called the fixed layer. Outside the fixed layer, there are varying compositions of ions of opposite polarities, forming a cloud-like area. This area is called the diffuse double layer, and the whole area is electrically neutral [15].

The particle size of colloidal silica was found to be dependent on the concentrations of alkaline in the basic solution and the active silicic acid which is titrated into the basic solution. Silicic acids with 2 and 1wt.% of SiO<sub>2</sub> were used to titration of three different concentrations of alkaline solution in the range of 1-3 wt.% of SiO<sub>2</sub>. The effect of silicic acid and alkaline solution concentrations on the particle size of colloidal silica in a constant volume are given in Figure 3. As it is shown in this figure, the ultimate colloidal silica mean particle size increases with increasing the acid concentration from 1 to 2 wt.% in a constant

alkaline solution concentration. It can be explained with rapid decreases of pH in the point the drops contact with alkaline solution which may be an aggregation of seeds due to the pH shock during acid adding. Also, it causes the micro gel formation instead of colloidal particles along the agitator and wall of the vessel. These micro gels would accelerate the reaction of surface growth to form the larger particle colloidal silica. It should be mentioned that, the particle size of forming silica is increased by increasing the additional volume of active silicic acid.

Also, Figure 3 shows that the average particle size of colloidal silica decreases with increasing the alkaline solution concentration up to 2 wt.% in a constant silicic acid concentration (1 and 2 wt.% of SiO<sub>2</sub>) and then increases in this point. The first decrease can be explained according to the of titration theories which indicates that the ultimate particle size decreases with increasing the concentration of the reactants, because nuclei growth rate is less than the nuclei formation. However, with increasing the alkaline solution concentration more than 2 wt.% the ionic binding strength increases and the primary silica particles attach each other easier due to the effect of opposite charges of the solution and decreasing the electrical double layer thickness of silica particles. In this case, the nuclei growth exceeds the nuclei formation rate so the size of the colloidal particles increases[12].

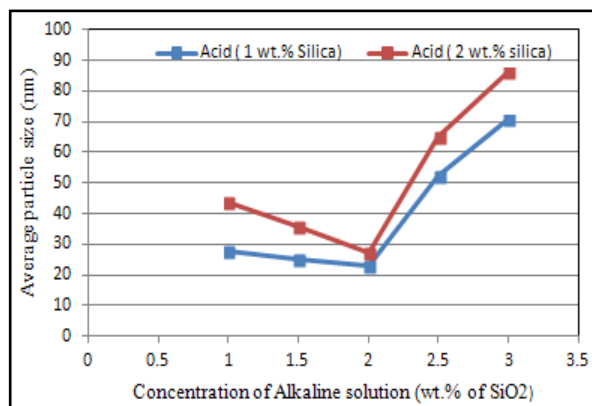


Fig. 3. The influence of silicic acid and alkaline concentrations on the average particle size of colloidal silica.

The appearance of colloidal silica dispersion depends greatly on weight fraction of

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silica and the particle size of the colloidal particles. Dispersions with small silica particles (< 10nm) are normally quite clear. Midsize dispersions (10-20 nm) start to take on an opalescent appearance as more light is scattered. Dispersions containing large colloidal silica particles (> 20nm) are normally white and opaque [1]. The weight fraction of silica in the dispersion is limited to the particle size. The mean particle size of colloidal silica with different wt.% of SiO<sub>2</sub> is shown in Figure 4. As it can be seen, the mean particle size of the colloidal silica is increased as the sol concentration increased from 9 to 11 wt % of SiO<sub>2</sub>. At this point, by increasing the concentration of sol up 12 wt.% of SiO<sub>2</sub>, the average particle size is decreased. But with increasing the sol concentration more than 12 wt.% of SiO<sub>2</sub>, the particle size is increased, because most of the added active silicic acid would be absorbed onto the surface of the seeds to increase the particle size, and only some of the silicic acid would be homogeneously nucleated to form new nuclei.

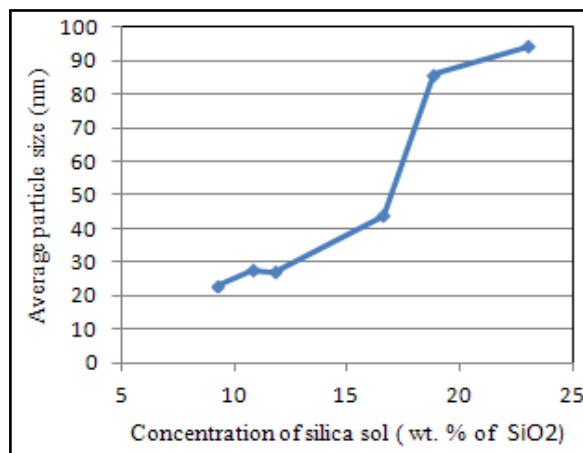


Fig. 4. The effect of silica sol concentration on the average particle size of the particles.

The conductivity and zeta potential of colloidal silica solutions in various concentrations of SiO<sub>2</sub> are shown in Figures 5 and 6, respectively. As it can be seen in figure 5, the minimum conductivity is appeared in 11.8 wt. % of SiO<sub>2</sub>, which is the most stable silica sol with zeta potential equal to -58.7 in Figure 6.

In this experiment, in order to enhance colloidal silica concentration, with constant concentrations of alkaline sodium silicate solution

and the active silicic acid (3 and 2 wt.% of SiO<sub>2</sub>, respectively), volume of the titrated silicic acid was increased and the titration rate decreased. Results showed a large concentration of SiO<sub>2</sub> (about 34 wt.%) in colloidal silica solution. In addition, the average particle size and Zeta potential of the solution increased up to 321nm and -12.7 mV which show less stability in comparison with the solutions with lower concentration of SiO<sub>2</sub> (Figure 6).

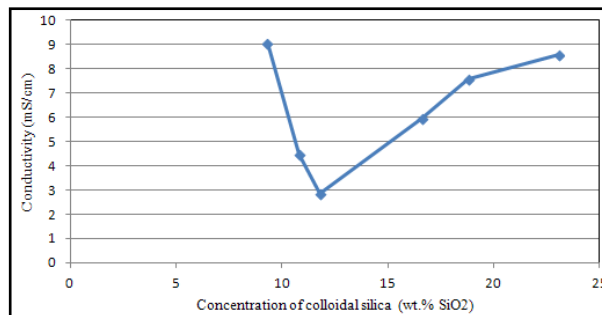


Fig. 5. The effect of silica sol concentration on the Conductivity of sols.

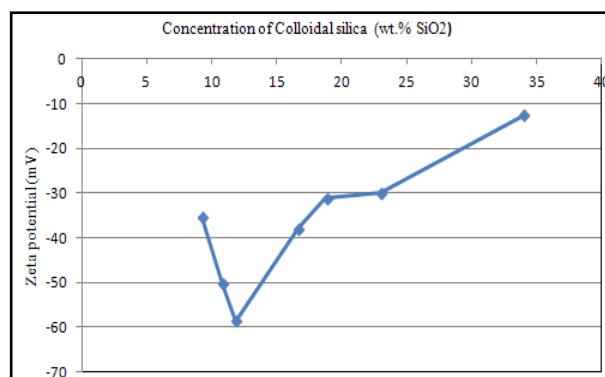


Fig. 6. The effect of silica sol concentration on the zeta potential of sols.

Figure 7 shows the zeta potential of formation colloidal silica in various pH values. When a voltage is applied to the solution in which particles are dispersed, particles are attracted to the electrode of the opposite polarity, accompanied by the fixed layer and part of the diffuse double layer, or internal side of the "sliding surface". Zeta potential is considered to be the electric potential of this inner area including this conceptual "sliding surface"[16]. As this electric potential approaches zero, particles tend to aggregate. The most

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important factor that affects zeta potential is pH value of the solution. If the alkaline solution concentration increases then the particles will tend to acquire more negative charge and the zeta potential increases toward positive values. At the same time if acid silicic concentration increases then a point will be reached where the charge will be neutralized and further increase of acid silicic concentration will cause a buildup of positive charge which led to zeta potential decrease. In general, a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. Particles with zeta potentials more negative than  $-30\text{mV}$  are normally considered stable. So it can be seen that all the colloidal silica solutions are stable. The minimum zeta value is appeared in the most stable sol in pH value of less than 10. It should be noticed that pH value of the solution must be controlled during the process; otherwise it would lead the solution to be gelled.

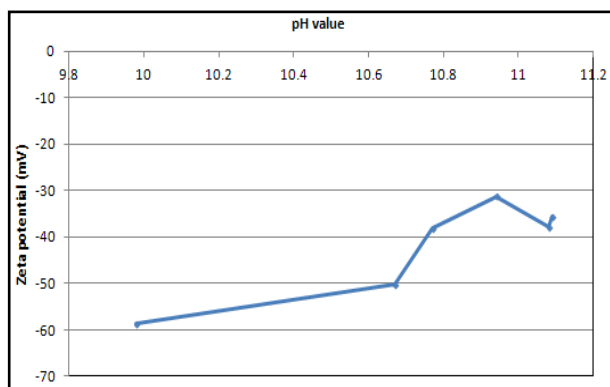


Fig. 7. Dependence of the zeta potential to the pH value of silica sols.

Figure 8(a-b) illustrates the scanning electron microscope (SEM) images of silica particles from two different colloidal concentrations of 10.8 and 16.6 wt. % of  $\text{SiO}_2$ . It can be seen the relative uniformity of spherical particles with 27.71 nm and 43.90 nm average diameters (from Dynamic Light Scattering results) for the samples with 10.8 and 16.6 wt.% of  $\text{SiO}_2$ , respectively.

Figure 9 shows TEM images of the synthesized samples with various magnifications. These images indicate the structure of colloidal particles may be spherical or slightly irregular in shape, and they seem to be present as slightly structured aggregates.

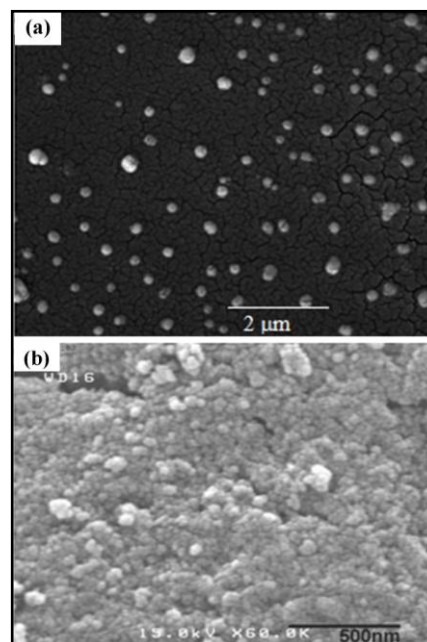


Fig. 8. SEM images of colloidal silica with (a) 16.6 wt.% of  $\text{SiO}_2$  (25000 $\times$ ), (b) 10.8 wt. % of  $\text{SiO}_2$  (60000 $\times$ )

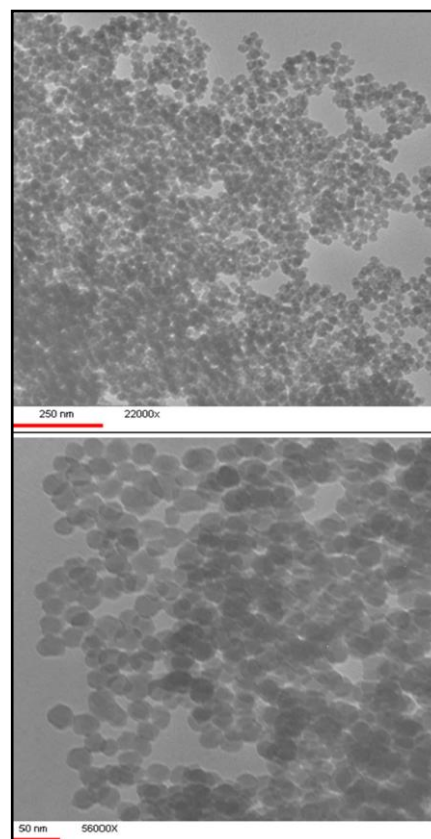


Fig. 9. TEM images of as-synthesized colloidal silica with 16.6 wt.% of  $\text{SiO}_2$  in different resolutions.

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Isotherm absorption/desorption curves of the silica with concentration of 10.8 wt.% of SiO<sub>2</sub> is demonstrated in Figure 10.

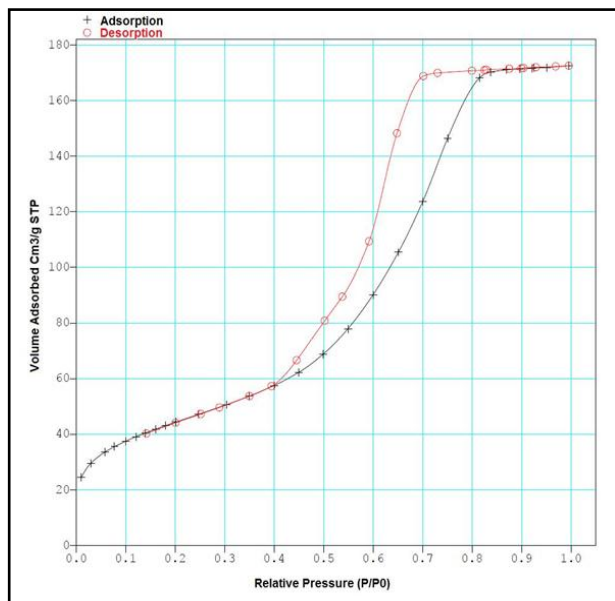


Fig. 10. Isotherm curves of the silica with concentration of 10.8 wt.% of SiO<sub>2</sub>.

In this figure the adsorption/ desorption isotherm of a nonreactive gas (N<sub>2</sub> at 77 K), at the temperature of 300°C with 1 hour heat treatment is determined as a function of the relative pressure, i.e. ratio of the applied pressure and the saturation pressure of the gas. It indicates a departure of absorption and desorption plot, forming a so called “absorption circuitry” at relatively high pressure region which is due to the attribution of mesoporous structure. It starts at low relative pressure. At a certain minimum pressure, the smallest pores will be filled with liquid nitrogen. As the pressure is increased further, larger pores are filled, and near the saturation pressure, all pores are filled. The total pore volume is determined by the quantity of gas absorbed near saturation pressure. Desorption occurs when the pressure is decreased from the saturation pressure downward [17]. A linear increase of the absorbed volume at low pressures was followed by a steep increase in nitrogen uptake at a relative pressure of  $0.4 < P/P_0 < 0.8$  which was due to capillary condensation inside the mesopores. Pore size contribution of the silica (10.8 wt.% of SiO<sub>2</sub>) was calculated by BJH

method from the corresponding isotherm curve presented in Figure 11.

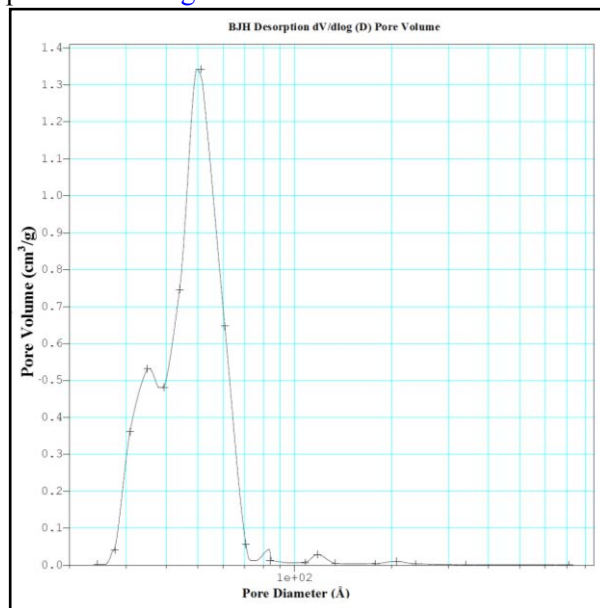


Fig. 11. Pore size distribution of colloidal silica (10.8 wt % SiO<sub>2</sub>)

BJH curve of the colloidal silica with concentration of about 10.8 wt.% of SiO<sub>2</sub> indicates two mainly grades of pore distribution, one concentrated around 20 Å, the other around 45 Å. Average pore diameter, BET surface area and total pore volume of the colloidal silica were 5.59 nm, 161.08 m<sup>2</sup>/g and 0.27 cm<sup>3</sup>/g, respectively.

## CONCLUSIONS

In this paper nano-colloidal silica was successfully prepared by titrating active silicic acid into alkaline sodium silicate solutions at 84-86 °C. The effect of process parameters such as silicic acid concentration, alkaline sodium silicate concentration and pH value of the solution on the properties of the colloidal silica at constant formation temperature, titration rate and volume of titrated silicic acid were investigated. The seed concentration, particle sizes and also the stability of colloidal particles are highly dependent on pH and temperature of the process. The results showed that with controlling these parameters in pH value of 9.5-11, stable colloidal silica dispersions can be prepared, altering the pH value can change the zeta

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potential of the samples, and thereby the stability of the particles in the liquid.

Ultimate colloidal silica mean particle size increased with increasing the active silicic acid concentration from 1 to 2 wt.% in a constant alkaline solution concentration and decreased with increasing the alkaline solution concentration up to 2 wt.% in a constant silicic acid concentration (1 and 2 wt.% of SiO<sub>2</sub>) and then increased again. Generally, the synthesized nano-colloidal silica suspensions in concentration up to 25 wt.% of SiO<sub>2</sub> have average particle sizes lower than 100 nm, which all of these sols are stable more than one year.

In addition, investigation of sol conductivity and zeta potential versus sol concentration showed that the minimum conductivity was appeared in 11.8 wt.% of SiO<sub>2</sub>, this sol was the most stable silica sol with zeta potential equal to -58.7 mV. It was shown that the zeta potential increased toward positive values with increasing the alkaline solution concentration. Also the prepared spherical colloidal silica particles showed a fairly large surface area of 160 m<sup>2</sup>/g.

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