

Chemical synthesis of nanostructured silica from Algerian diatomite

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Abstract

In this research, we reported chemical and soft method for the purification of Algerian diatomite. We discussed the effect of different parameters such as the temperature, pH and acid leaching, on the purity of purified diatomite. We carried out comparative study by analyzing the morphology, the crystal quality and the chemical composition of the raw and purified diatomite using scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray (EDX), respectively. We succeed, to purify the raw diatomite which contains 86% of silica to nanostructured silica with purity of 99,092%. Suggested technic allowed the synthesis of nanostructured silica at slightly low temperature of 80°C using facile chemical method. The resulting nanostructured silica has potential application for many applications.

Keywords: Diatomaceous Earth; Alkaline Dissolution; Nanostructure Silica Gel.

1. Introduction

Diatomite (Diatomaceous Earth) is a natural clay composed mainly of geological fossilized skeletons of unicellular organisms [1]. It is known that there are over 100,000 different species of diatomite and each having a unique morphology [2]. The diatomite consists typically of 86 to 94% of silicon dioxide (SiO₂) and little amounts of metal oxides. It is characterized by specific properties, such as high silica content, high porosity, low density, etc. [3]. In 2016, the united states of America (USA) was the largest producer of diatomite with 832 thousand metric tons (TMT) of world production, followed by Denmark with 440 TMT, China with 420 TMT, Argentina with 200 TMT, Peru with 150 TMT, France with 75 TMT, Russia and Korea with 70 TMT, and Algeria with 2 TMT [4].

Silica, which is the major component in the diatomite, is used in wide range of applications, such as in swimming pool filters, glass fabrication, food additives, optical fibers technology, cosmetics, pharmaceuticals, absorbents, electrical and thermal insulators, pneumatic manufacturing, and many other applications [2, 5, 8].

For different applications, the sodium silicate modulus varies depending upon needs. The kinetic dissolution of diatomite in alkaline solution represents the principle approach for the process optimization of alkaline reaction, as well as applications. In this connection, the

kinetic behaviour between sodium hydroxide (NaOH) and quartz material in aqueous solutions under different conditions has been reported [6].

Sodium silicate is usually prepared by reaction of quartz (SiO₂) and sodium carbonates or sodium sulphates (Na₂CO₃ or Na₂SO₄) under high temperatures (above 1000 °C) [10]. This technique requires very high energy consumption, which, together with the environment pollution effects, is the main drawback of this conventional technology. In recent years, numerous new methods have been developed, facing the challenge of avoiding the environmental and energy related issues. [7].

The aim of the present work is to develop an efficient route to extract a simple, cheap, and low-energy method, high purity; nanostructured amorphous silica production. The final product is characterized thereafter, in order to effectively remove organic and metallic impurity compounds.

2. Experimental

a- Materials: we collected natural diatomite from sig region in north-west of Algeria (35° 17' 1, 32" North, 0° 30' 39, 24" West) according to sexagesimal coordinates in the WGS84 system GeoHack. Figure 1 represents scanning electron microscope (SEM) images of the Algerian diatomite at different scales. We used sodium hydroxide (NaOH 99% 2N, RANCHET), sulphuric acid

(H₂SO₄, 98% 10N, Biochem Chemopharma), and hydrochloric acid (HCl, 36.5%-38% 1N, Sigma Aldrich), and pure water with resistivity of 18 MΩ·cm in order to ensure low level of contamination. We crushed natural diatomite using an automatic grinder to make diatomite powder.

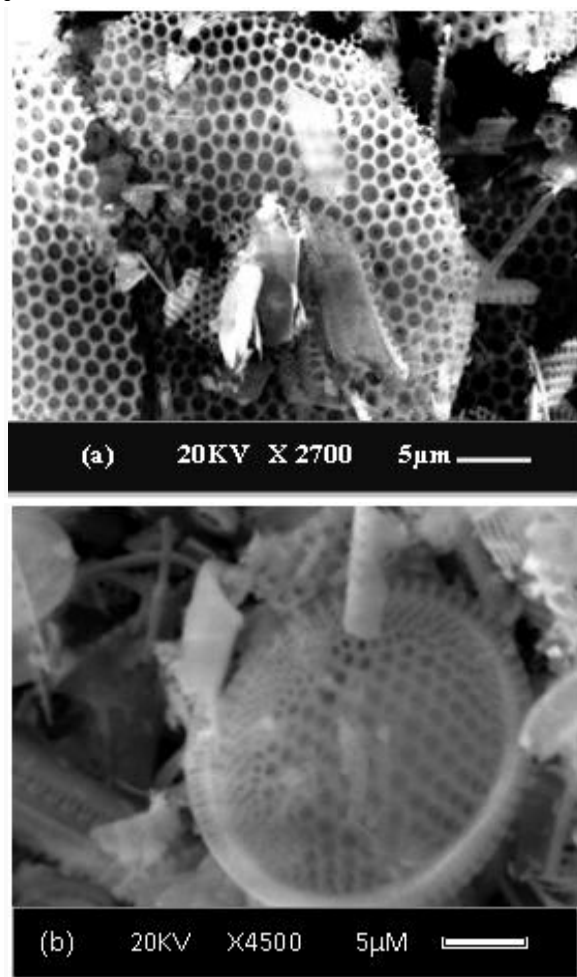
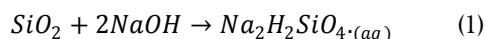


Figure 1. Scanning electron microscope (SEM) images of raw diatomite at different scales.

b- Synthesis of silica gel: we used a mixture of 2N of NaOH and 15 g of raw diatomite, the mixture was diluted in pure water, heated in perfluoroalkoxy teflon (PFA) at two value of temperature 80 and 100°C, and stirred continuously. Subsequently, liquid sodium silicate (Na₂H₂SiO₄) was obtained according to the following chemical reaction:



Afterwards, the mixture was centrifuged to separate the resulting liquid sodium silicate (Na₂H₂SiO₄) from the slurry. Thereafter ; sulphuric acid (H₂SO₄, 50% v/v) was added slowly to the Na₂H₂SiO₄, the mixture was kept under stirring at room temperature for 2 hours. In

the aim to study the effect of pH on the diatomite purification process, we monitored and varied the pH at values of 1, 7, 8 and 9. The obtained sodium silicate gel was first neutralized with HCl at diluted concentration of 1N. Subsequently leaching operation was conducted with more concentrated HCl acids (2N, 4N and 6N), and then cleaned with ultra-pure water. Finally, the resulting material was dried at temperature of 150°C.

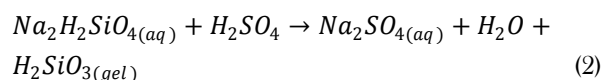
c- Characterization: We used scanning electron microscope (SEM JEOL, JSM 6610 LA) to observe the morphology of the raw diatomite and resulting nanostructured silica. X-ray diffraction (XRD) patterns were obtained in reflection mode ($\theta/2\theta$), using a PANalytical EMPYREAN diffractometer, employing CuK α radiation ($\lambda=1.5406 \text{ \AA}$). The XRD data were collected for 2θ Bragg angles between 10° and 90°.

3. Results and discussion

As shown in Figure1, the diatomite is made by disc-shaped particles that exhibit many pores. The average size of the disc-shaped particles is in the range of 80 to 200 μm, while the pores diameter are in the range of 1 to 2 μm. These pores facilitate the dissolution of the diatomite in sodium hydroxide solution [9].

Effect of pH :

Silica is extracted from diatomite by alkaline dissolution process according to the chemical reaction in Equation (1). We added H₂SO₄ dilute (50 % v/v) have been chosen, slowly added drop wise to control pH values from 1, 7, 8 and 9. Subsequently to those operations silica gel is obtained according to the equation (2). The pH variation of precipitate is studied to reveal the pH effect on the silica gel purity.



The titration is performed under permanent stirring to allow the formation of sodium sulphate and warns the large gel aggregates. As can be seen in (Fig. 2.a, Fig.2.b), the dried silica has the appearance of a fine white powder. The concentration of impurities decrease as depicted in (Fig.3). We notice that the highest purity, of 96, 21%, is obtained at a precipitate pH=1.

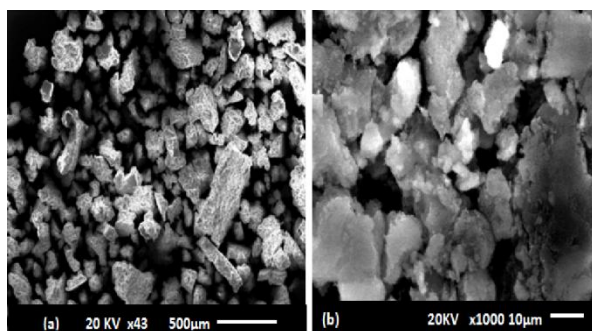


Figure 2. SEM Photographs of silica gel agglomerates elaborated in NaOH solution at 80 °C and precipitated silica at pH=1 . (a) Magnification x 43, (b) Magnification x 1000.

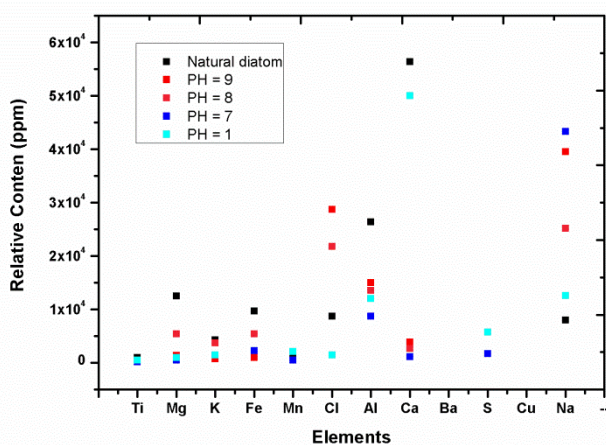


Figure 3. EDX analysis of natural diatomite and purified silica at different pH values precipitation

Temperature effect :

We reproduce the conditions of alkaline dissolution in NaOH, except the temperature of the chemical reaction, which is increased to 100°C, and the silica precipitation takes place at pH=1. After performing chemical analysis of silica powder by EDX we can notice that dissolution is promoted and the purity increases 98, 64 at% at 100 °C.

Acid leaching effect :

The SEM photographs (Fig.2) show that silica powder is composed of agglomerates with the size in the few tens of micrometer range. It shows that actual alkaline dissolution produces silica with purity around 98 at%. The HCl is used to improve the purity of silica gel and to obtain a better yield in purity which is 99.092 at% (NaOH solution, pH precipitate=1 and 6N normal concentration HCl), the impurities decrease as detailed in (Fig.4). SEM photography of precipitate silica is shown in (Fig.5). As can be ascertained from the Fig.5, silica powder exhibits nanostructure with fine particles.

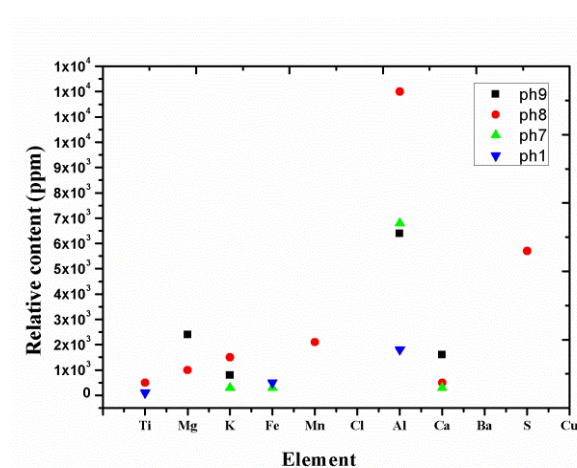


Figure 4 EDX analysis of pure silica powder (6N HCl leaching).

The samples prepared at different pH 9, 8, 7 and 1; each sample is cleaned with 6N hydrochloric acid HCl. Almost all of impurities decreases. At pH=9, there is still some impurity Mg, Al, K and Ca. At pH=8 there is Ti, Mg, K, Mn, Al, Ca and S. At pH=1 there is a small amount of Ti, Fe and Al.

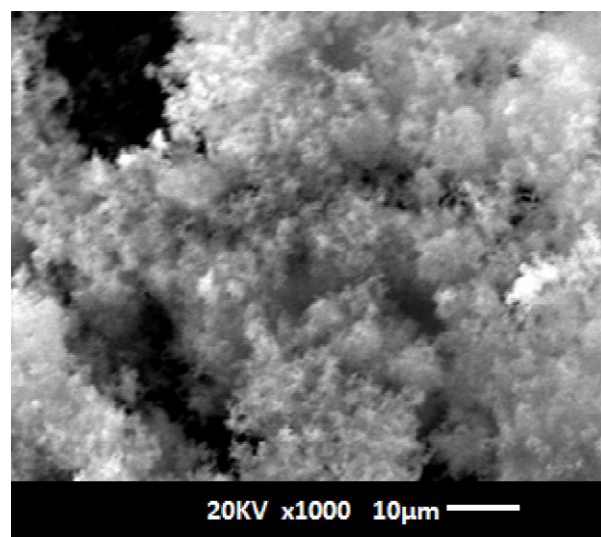


Figure 5. SEM photography of purified silica (precipitation at pH=1, 6N HCl) [99.092%].

The XRD pattern of raw diatomite is given in (Fig.6). It indicates a prevailing amorphous phase, also displaying the characteristic main peak of SiO_2 , located at $2\theta=26.00^\circ$, together with that at $2\theta=29.29^\circ$, characteristic to CaCO_3 , $2\theta=34.40^\circ$ characteristic to Al_2O_3 , and $2\theta=42.02^\circ$ characteristic to Fe_3O_4 . As can be observed in (Fig.7), the XRD pattern of silica powder exhibits fewer peaks than crude diatomite. A high intensity peak, located at $2\theta=26.01^\circ$, can be emphasized, which is characteristic to SiO_2 , $2\theta=25.39^\circ$ is characteristic to Al_2O_3 and $2\theta=18.31^\circ$ is characteristic to Fe_3O_4 .

A comparison between values of *full width at half maximum (FWHM)* of silica Physical properties of both, diatomite and sand are given in (Table 1), this comparison give us information about the size of the crystallites in each materials. FWHM for silica and diatomite with respect to that of desert sand is likely due to the micro structural features, FWHM inversely proportional with crystallites size. Raw diatomite and the obtained silica is amorphous. The mineralogy details are identified using a high score version 3.0e (3.0.5).

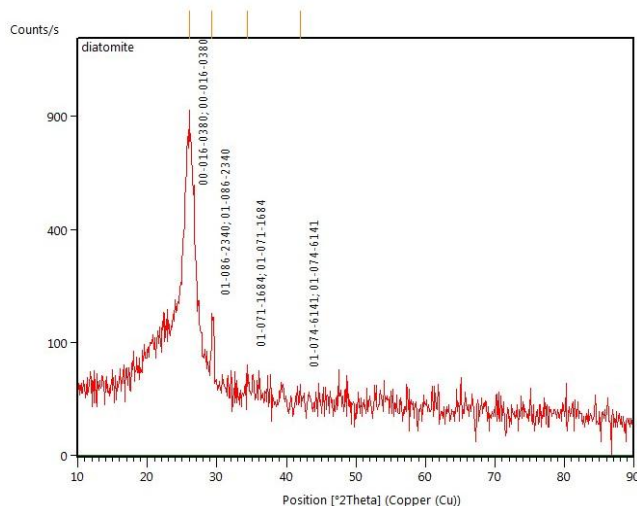


Figure 6. XRD pattern of algerian natural diatomite.

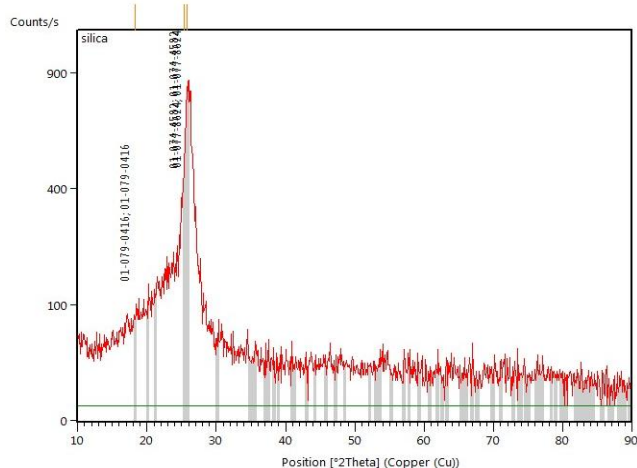


Figure 7. XRD pattern of purified silica from diatomite.

Table 1: Comparison of FWHM and D (crystallite size) for sand, natural diatomite and silica

	2 θ (°)	FWHM (°)	D (nm)
Sand	26.630	0.313	30
Diatomite	26.063	1.398	7
Silica	26.006	1.408	7

4. Conclusion

This work was undertaken in order to exploit the algerian diatomite for the preparation of nanostructured silica. The DRX analyze revealed the amorphous nature of diatom offering an easy way to dissolve it as silica gel,

unlike to quartz material. A wet dissolution of silica was proposed by using low temperature (80°- 100°C) with alkaline solution. Further, H_2SO_4 acid was used to neutralize the dissolved silica gel. The final pH of silica gel trough the neutralize protocol was studied. It was proved by EDX characterization that the best amount of low impurities was obtained when the final pH stayed in acidic interval during the neutralization process. The final material was leached under different concentration of HCl acid. The molarity of 6N was identified as the best to ensure low amount of impurities. SEM observation showed nanoparticles morphology of the final material offering an easy way To decrease further the impurities amount, a nanostructures features of material seems to be the best way to remove more impurities found in the cores of the material. We succeed, to purify the raw diatomite which contains 86% of silica to nanostructured silica with purity of 99,092%. Further wok will be carried out in the future in order to increase the yield of purified silica for industrial applications, by increasing the pressure during the dissolution. This parameter seems to be crucial.

Furthermore, it may be suitable for the preparation of high quality sodium silicate used as a precursor in the preparation of silica gel. The microporous natures of these materials facilitated their use as one of candidates for preparing silica leading to purity over 99 at%. These characteristics allowed the use of silica from algerian diatomite for many applications.

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References

- [1] P. G.Fields, Diatomaceous earth: Advantages and limitations, "proceedings of the 7th International working conference on stored-product protection, vol.1,PP.781-784,1998.
- [2] C.B. Christabel E.Fowler, Benedicte Lebeau, Joel Patarin and A.W.Cyril Delacote " An aqueous route to organically functionalized silica diatomaceous, "Applied Surface Sciences, vol.253, , (2007)5485
- [3] D.Brahim,D.Merabet,H.Belkacemi,T.A.Mostefaoui,N .Ait Ouakli,"preparation of amorpheous silica gel from

- Algerian siliceous by-product of kaolin and its physico-chemical properties", *Ceramics International* 40(2014)10499.
- [4] U.S. Geological Survey Minerals yearbook, 2009,V.III,p2-4.
- [5] A. Sdiri, "Synthesis and characterization of silica gel from siliceous sand of southern Tunisia", *Arabian journal of chemistry*,vol.7, (2010)486.
- [6] K.Jung, D.Jang, "A novel approach for improvement of purity and porosity in diatomite (diatomaceous earth) by applying an electric field", *International journal of mineral processing* 131 (2014)7.
- [7] H.Meradi,L.Atoui,A.balaska,S.Bouhouche,Contribution a la caracterisation d'une diatomite naturelle, 9^{ème} Congrès de mécanique, FS Semlalia, 21-24 April, 2009 Marrakech, Morocco
- [8] Yafei Shen, rice husk silica derived nanomaterials for sustainable applications, renewable and sustainable energy reviews 80(2017) 453.
- [9] Julien grynberg, mécanismes physiques et chimiques mis en jeu lors de la fusion du mélange $\text{SiO}_2\text{-Na}_2\text{CO}_3$, these de doctorat de l'université pierre marie curie, paris VI,2012.