Iranian Journal of Materials Science & Engineering Vol. 12, Number 1, March 2015

SYNTHESIS OF NANO SIZED MESOPOROUS Γ - Al_2O_3 POWDER FROM DOMESTIC HAMEDAN KAOLIN

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Received: June 2014 Accepted: December 2014

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Abstract: *. A method for producing high surface area nano-sized mesoporous alumina from inexpensive Iranian kaolin as raw material is proposed. In this method, first, kaolin was purified; for purifying Kaolin, High Grade Magnetic Separation and leaching with HCl and chemical bleaching treatment by using sodium dithionite ($Na_2S_2O_4$) as reducing agent in acidic media (H_2SO_4) were used. Purified kaolin was calcined. After that, Al (hydr) oxide from acid - leachates of calcined kaolin was precipitated with ammonia, in presence of polyethylene glycol. Finally, a white powder of nano-sized alumina particles was obtained after calcination. BET surface area, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) were used to characterize the sample. The resulting alumina with relatively high surface area (201.53 m^2 g^{-1}) and narrow mean pore diameter (6.91 nm), consists of a particle size distribution ranging from 22 to 36 nm.*

Keyword: *Nano- alumina, kaolin, Synthesis, precipitation.*

1. INTRODUCTION

Nano Al_2O_3 has immense technological and industrial applications, and has been widely used as catalysts[1, 2], catalytic supports [3], abrasive and thermal wear coatings and adsorbents [4-7]. Various methods like sol–gel, hydrothermal process and controlled precipitation of boehmite from solutions of aluminum salts, alkoxides and metal powders have been used for synthesizing nano-alumina. Aluminum alkoxides and other raw materials for processing of alumina are high cost. In recent years, cheaper materials like urban waste[8], low cost Al and $AlCl_3 \cdot 6H_2O$ powders[9] have been used for synthesis of nano alumina. Furthermore, there are inexpensive minerals that are known as a good source of aluminium and can be used for synthesis of nano alumina. Some of these minerals are known as bauxite, kyanite, alunite, sillimanite, andalusite, kaolin, mica and fly ash. Among these minerals, Bauxite is a good source of alumina, but is very scarce. The rareness of bauxite, suggests abundant kaolin as an alternative raw material for production of alumina.

In this paper, kaolin, which is an abundant and inexpensive mineral in Iran, was used as a starting material for Synthesis of Nano alumina Powder.

Before the leaching, kaolinitic clay must be purified. In a general way, in the state of the art a number of techniques for purifying kaolin clay are known. Among these, the most common comprise: magnetic separation [10], leaching[11, 12], chemical bleaching[13], flotation[14, 15] and selective flocculation[16-18]. The studies show that the calcination of purified kaolin before the leaching is necessary for solubilizing aluminium in HCl acid solution[19]. It has been reported that, Metakaolin is more reactive than kaolin under chemical treatments. After calcination, AlO_6 octahedrals are transformed into much more reactive tetra and penta coordinated units. The best conditions for obtaining more reactive metakaolins have been discussed by different authors who reported values between 600 and 800 °C [20].

For leaching alumina from kaolin, some of the important advantages of using hydrochloric acid instead of other acids are the insolubility of titanium dioxide and the ease of filtration of slurries which is present in kaolin. Surfactants as

[DOI: 10.22068/ijmse.12.1.59]

structure-directing agents have been applied to control the pore size, shape and to direct the formation of mesophases on the bases of electrostatic and hydrogen bonding interactions[21]. In this study, the long-chain, inexpensive and non-ionic surfactant-polyethylene glycol (PEG, molar mass 4500) was used as structure-directing agent before the precipitation process. After leaching process, aluminium ions in solution can readily be precipitated as $Al(OH)_3$ by adjusting the solution to be neutral or slightly alkaline[22]. The precipitation process was conducted in an aqueous media at room temperature using ammonia. The amorphous alumina powder can be transformed to γ- alumina and δ -alumina powder at 700 °C and can be converted to α-alumina powder above 1100 °C. Researchers demonstrated that, Alumina prepared by the sol–gel method usually exhibit higher pore volumes and surface areas as compared with precipitation in aqueous solutions counterparts[22, 23].

2. EXPERIMENTAL

2. 1. Materials

All chemicals used are analytical reagents. The kaolin used came from Hamedan province, west of Iran. The iron and calcium content of this kaolin were high.

2. 2. Purification of Kaolin

After leaching with water, high energy magnetic separation was done for removing the impurities having magnetic susceptibility such as hematite, titanium, rutile, mica and pyrite. About 47% of iron was removed in this step. For reducing CaO in the sample, the kaolin was leached with hydrochloric acid (7%) at room temperature under 0.5 h stirring. To remove remained iron and other impurities, the kaolin is directed to a chemical bleaching treatment carried out by using sodium dithionite ($Na_2S_2O_4$) as reducing agent in acidic media (pH was adjusted to 3 with sulfuric acid) at 80 °C for 0.5 h[12]. Schematic for the preparation of pure kaolin has been shown in fig. 1.

2. 3. Synthesis

First, the purified kaolin was calcined into metakaolin at heating rate of 10 °C/min and the sample was kept for 2.5 h at the required temperatures to loosen the alumina component. Chemical composition of Kaolin, purified Kaolin and metakaolin (calcined at 700°C) are shown in table 1. Then, the metakaolin was leached with concentrated hydrochloric acid (6 M) at 90 °C under 3 h stirring, then; suspensions were filtered and the filtrate was collected for producing of aluminum hydroxide. After that, following addition of polyethylene glycol (PEG, molar mass 4500), ammonia (.75 M) was added. The precipitated Al (hydr) oxide was filtrated, washed with de-ionized water and dried. Finally, Subsequent calcination yielded nano-sized Al_2O_3. Schematic for the preparation of alumina nano-particles from purified kaolin has been shown in Fig. 2.

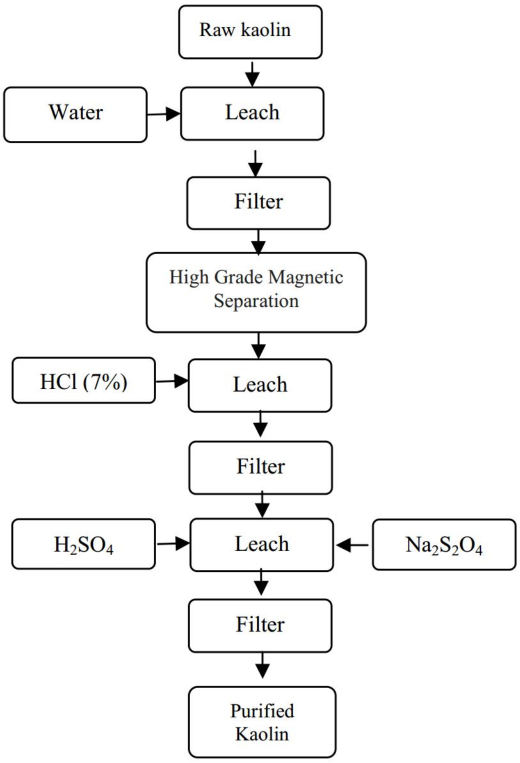

Fig.1. Schematic for the preparation of pure kaolin

[DOI: 10.22068/ijmse.12.1.59]

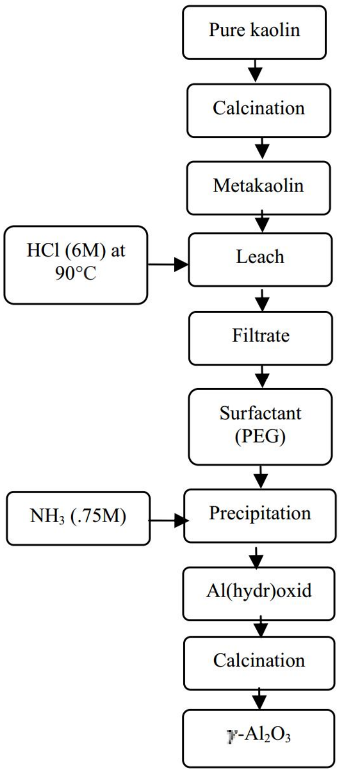

Fig.2. Schematic for the preparation of nano γ- alumina from kaolin

Table 1. Chemical composition of Kaolin and Metakaolin (calcined at 700°C)

Substance	Raw Kaolin	Purified Kaolin	Metakaolin
Na_2O	1.292	0.117	0.131
MgO	1.212	0.113	0.119
Al_2O_3	29.77	35.366	44.958
SiO_2	42.89	46.216	50.598
P_2O_5	0.297	0.166	0.148
Cl	0.189	-	-
SO_3	0.389	0.078	0.051
TiO_2	1.83	0.471	0.527
Fe_2O_3	1.79	0.366	0.371
CaO	0.841	0.058	0.055
LOI	19.5	17.01	3.04

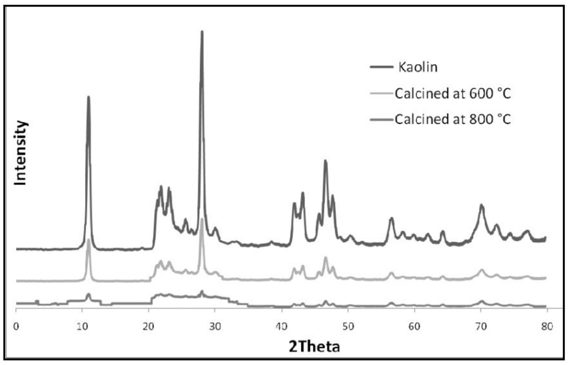

Fig. 3. XRD patterns of purified and calcined kaolin at 600 and 800°C.

2. 4. Characterization

A BET surface area was used to determine the surface area of the sample, and scanning electron microscopy (SEM) was used to determine the particle size and morphology. Sample phases were identified using X-ray diffractometry (XRD) with nickel-filtered Cu K radiation.

3. RESULTS AND DISCUSSION

3.1. Activation and Subsequent Leaching of Raw Kaolin

The XRD patterns of purified kaolin and calcined kaolin in 600 and 800 °C are shown in Fig. 3. With increasing temperature of calcinations, gradual disappearance of the kaolinite reflections has been seen and kaolin almost transformed into metakaolin. The studies showed that the calcination of kaolin prior to the leaching is necessary to solubilize aluminium in HCl acid solution. It was reported that the calcination should be realized at 750 °C for at least 2 h[19]. It was also claimed that after the calcination process and converting kaolinite ($Al_2Si_2O_5$ (OH)4) to metakaoline ($Al_2Si_2O_7$), aluminium can be extracted much more rapidly and easily [24]. Pure kaolin contains 35.36% Al_2O_3. After calcination, this ratio increases to 44.96% since all water in the structure is removed. A known amount of sample was digested with 6 M HCl acid solution at 90 °C for 3 h under a reflux condenser. The leaching rate of Al^{3+} ions from raw kaolin and metakaolin is shown in Tab. 2. Only a few amounts of Al^{3+} ions (about 6.4%) were leached from purified kaolin. With acid treatment, Fe^{3+}, Ti^{4+} (lower than others) as rutile and Si^{4+} as SiO_2 were leached and these materials can improve the thermal stability of the alumina to some degree.

[DOI: 10.22068/ijmse.12.1.59]

Table 2. Leaching rate of Al^{3+} ions from purified kaolin and metakaolins

Temperature (°C)	purified kaolin	500	600	800
Leaching rate(%)	6.4	58.3	82.7	89.2

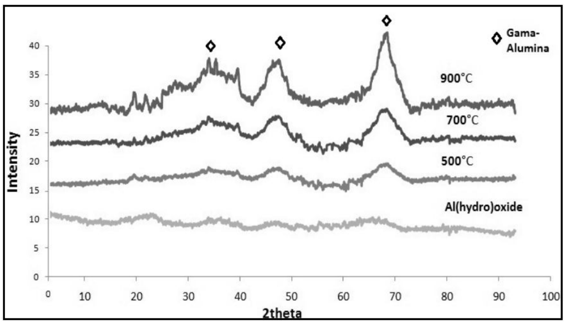

Fig. 4. XRD patterns of the Al (hydr) oxide and calcined samples at different temperatures.

The sample calcined at 900 °C showed an Al^{3+} ions leaching rate of about 82.9%. The lower reactivity after calcination at still higher temperatures may be related to the sintering of kaolin particles at 900 °C and to the gradual transformation of metakaolin into mullite[20].

3. 2. Formation of Nano Alumina

By removal of the adsorbed water, small mass loss beneath 114 °C was seen. Due to the removal of water during the formation of the oxide phases, The mass loss of the Al Between 500 and 900 °C, the three main reflections of nano γ - Al_2O_3 phase are obviously observed as broad peaks at 2 angles around 38.0◦, 46.0◦, and 66.0◦ which correspond to the [3 1 1], [4 0 0], and [4 4 0] planes, respectively. The peaks in all patterns are meaningfully broad indicating the formation of nano sized γ - Al_2O_3 crystallites. XRD patterns of the Al (hydr) oxide and calcined samples at different temperatures are shown in Fig. 4. The crystallite sizes were calculated by using Scherrer equation:

(1)

Where γ is the wavelength of the X-rays, is the full width of diffraction peak at half maximum intensity and is the Bragg angle. The calculated crystallite sizes were found to be in the range of 22–36 nm.

As can be seen from Fig. 4, the precursor Al (hydr) oxide show amorphous structure and with increasing temperature of calcination, the crystal phase increased and the amorphous Al (hydr) oxide have almost transformed into γ-Al_2O_3. The addition of the surfactants resulted in the formation of an amorphous Al (hydr) oxide phase coupled with some hydrates of surfactant. This may be the result of the adsorption of surfactant layer on the surface of the initial Al (hydr) oxide nuclei, which prevented the aggregation and grain growth of Al (hydr) oxide in the absence of surfactants that would allow the formation of crystalline phase. Fig. 5 shows the SEM micrograph for γ-Al_2O_3 powders. The γ-Al_2O_3 indicated low agglomeration of particles with uniform sizes and spherical in shape.

According to FTIR spectra (Fig. 6) the bands in the region of 400–1000 cm^{-1} are generally associated with the stretching vibration of Al–O bonds[25] and broad bands around 3500 cm^{-1} and 1630 cm^{-1} are assigned to stretching and bending modes of adsorbed water. The bands at 500–750 cm^{-1} are assigned to ν-AlO_6, whereas

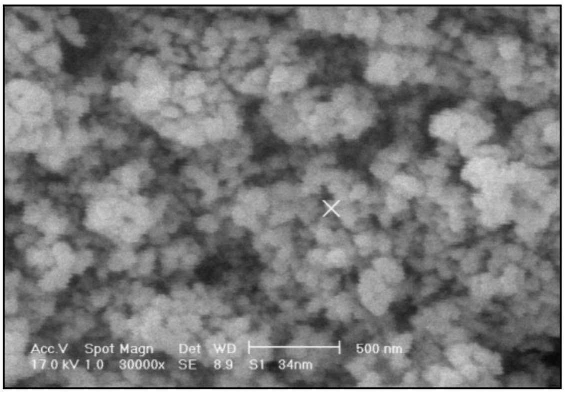

Fig.5. SEM graph of nano γ -alumina

[DOI: 10.22068/ijmse.12.1.59]

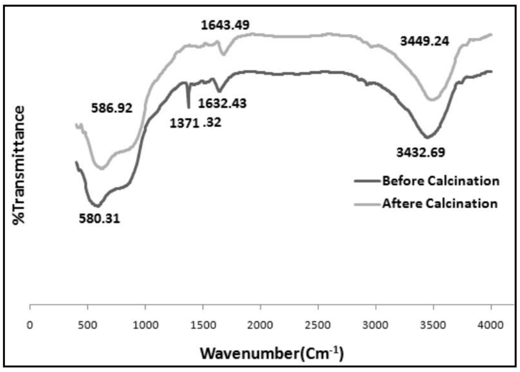

Fig. 6. FT- IR spectra of the nano γ -alumina before and after calcination at 700 °C.

the band around 900 cm^{-1}corresponded to ν-AlO_4[23]. The bands from 1400 cm^{-1} to 1600 cm^{-1} indicated the formation of alumina[26]. The composition of synthesised Nano γ - Al_2O_3 is shown in Tab. 3. The absence of band around 1371 cm^{-1} due to C–H implied that the alumina was without PEG after calcination.

N_2 adsorption/desorption experiments for synthesised Nano γ- Al_2O_3 were carried out using a Belsorp mini II (BelJapan), and pore size distributions were calculated using the Barret-Joyner-Halenda (BJH) model on the desorption branch.

Synthesised Nano γ- Al_2O_3 showed a narrow pore size distribution with a high surface area (201.53 m^2 g^{-1}), a mean pore diameter of 6.91 nm and a high pore volume (0.33 cm^2 g^{-1}). The location of the hysteresis loop in the N2 isotherm obtained nano γ- Al_2O_3 sample (Fig. 7) displays type IV hysteresis pointing out the presence of mesoporosity and can be used to determine whether the material possessed a regular framework pore or interparticle voids, such as a textural pore. The framework porosity at 0.4-0.75 P/Po in the N_2 isotherm shows that the porosity was framework, while the textural porosity at 0.8-1 P/Po indicates porosity arising from the noncrystalline intra-aggregate voids and spaces formed by interparticle contacts. The large surface areas (201.53) and narrow pore size distributions (around 7 nm) integrated with excellent thermal stability promised potential applications of these mesoporous nano Al_2O_3 in catalysis [1, 27] and water treatment applications[5, 28, 29].

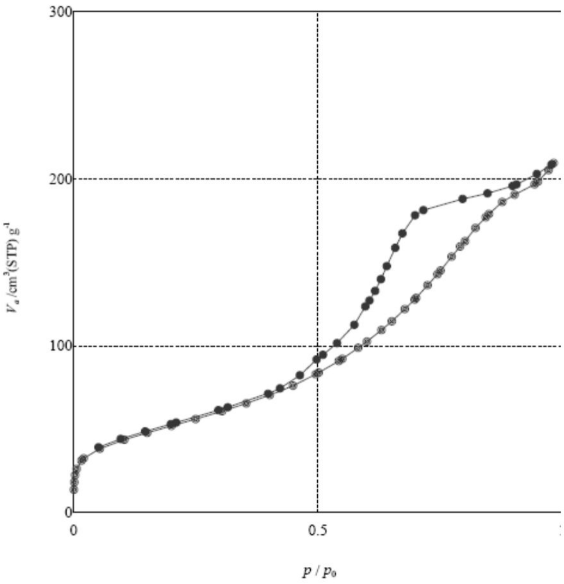

Fig. 7. N_2 adsorption/desorption isotherm for synthesised Nano γ - Al_2O_3.

Table 3. Composition of synthesised Nano γ - Al_2O_3

Substance	Nano γ - Al_2O_3
MgO	0.11
Al_2O_3	90.021
SiO_2	0.376
P_2O_5	0.188
Cl	0.233
SO_3	0.027
Zn	0.24
Fe_2O_3	0.648
CaO	0.087
Pb	0.029
Ga	0.011
LOI	8.03

3. 3. Formation Mechanism

After leaching of metakaolin, in presence of PEG (mass weight of 4500) as a surfactant and as dispersant for preventing the solid particles from aggregation, Al (hydr) oxide was precipitated. The reason for using PEG is that PEG can

[DOI: 10.22068/ijmse.12.1.59]

obstruct the hydrolysis and condensation of the formed Al (hydr) oxide particles, e. g. be adsorbed on the surface of the growing particles[30]. In the near neutral conditions, PEG molecules adsorbed on the surfaces of aluminum hydrate would limit its growth during the precipitation process and then lead to the formation of colloid particles.

4. CONCLUSION

A simple method for producing Nano sized mesoporous γ - Al_2O_3 from impure Hamedan kaolin with spherical shape, particle size distribution ranging from 22 to 36 nm with relatively high surface area (201.53 m^2 g^{-1}) and narrow mean pore diameter (6.91 nm), is described. In this method pre calcination of kaolin plays an important role in leaching of aluminium in solution. Besides, addition of surfactant before precipitation of nano alumina was used as dispersant for preventing the nano particles from aggregation.

5. ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support by Iran Nanotechnology Initiative Council (presidency office) and technical support provided by the Mineral Engineering Department of Tarbiat Modares University.

REFERENCES

1. Zhi-hong, W., “Preparation of nanoparticle alumina and its application in catalysis [J]”, Industrial Catalysis, 2, 2004.
2. Wang, Y., Wang, J., Shen, M., Wang, W., “Synthesis and properties of thermostable [gamma]-alumina prepared by hydrolysis of phosphide aluminum”, Journal of Alloys and Compounds, 467, 2009, 405-412.
3. Li, G., Li, W., Zhang, M., Tao, K., “Characterization and catalytic application of homogeneous nano-composite oxides ZrO_2-Al_2O_3,” Catalysis today, 93, 2004, 595-601.
4. Sharma, Y., Srivastava, V., Upadhyay, S.,Weng, C., “Alumina nanoparticles for the removal of Ni (II) from aqueous solutions”, Industrial & Engineering Chemistry Research, 47, 2008, 8095-8100.
5. Afkhami, A., Saber-Tehrani, M., Bagheri, H., “Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2”, 4-dinitrophenylhydrazine, Journal of hazardous materials, 181, 2010, 836-844.
6. Bhatnagar, A., Kumar, E., Sillanpää, M., “Nitrate removal from water by nano-alumina: Characterization and sorption studies”, Chemical Engineering Journal, 2010.
7. Rahmani, A., Mousavi, H. Z., Fazli, M., “Effect of nanostructure alumina on adsorption of heavy metals”, Desalination, 253, 2010, 94-100.
8. Martín-Ruiz, M., Pérez-Maqueda, L., Cordero, T., Balek, V., Subrt, J., Murafa, N., Pascual-Cosp, J., “High surface area [alpha]-alumina preparation by using urban waste”, Ceramics International, 35, 2009, 2111-2117.
9. Shojaie-Bahaabad, M., Taheri-Nassaj, E., “Economical synthesis of nano alumina powder using an aqueous sol-gel method”, Materials Letters, 62, 2008, 3364-3366.
10. Lofthouse, C., “The beneficiation of kaolin using a commercial high intensity magnetic separator, Magnetics”, IEEE Transactions on, 17, 1981, 3302-3304.
11. Veglio, F., Passariello, B., Toro, L., Marabini, A., “Development of a bleaching process for a kaolin of industrial interest by oxalic”, ascorbic, and sulfuric acids: preliminary study using statistical methods of experimental design, Industrial & Engineering Chemistry Research, 35, 1996, 1680-1687.
12. Ghasemi, F. S., “The removal of Iron from ROBATKHAN (TABAS) kaolinite by hydrometallurgy process”, in: Mineral processing Engineering, Tarbiat Modares University, Tehran, 2003.
13. Veglio, F., Pagliarini, A., Toro, L., “Factorial experiments for the development of a kaolin bleaching process”, International journal of mineral processing, 39, 1993, 87-99.
14. Yoon, R. H., Nagaraj, D., Wang, S., Hildebrand, T., “Benefication of kaolin clay by froth flotation using hydroxamate collectors,

[DOI: 10.22068/ijmse.12.1.59]

Minerals Engineering", 5, 1992, 457-467.

15. Cobb, G. L., Ince, D. E., "Method for improved flotation of discoloring impurities from kaolinite", in, Google Patents, 1991.
16. Shi, J. C. S., Williams, C. L., Lowe, R. A., Basilio, C. I., "Beneficiation with selective flocculation using hydroxamates", in, Google Patents, 2000.
17. Mercade, V. V., "Purification of clay by selective flocculation, in, Google Patents", 1972.
18. Larroyd, F., Petter, C., Sampaio, C., "Purification of north Brazilian kaolin by selective flocculation", Minerals Engineering, 15, 2002, 1191-1192.
19. Ford, K., "Leaching of fine and pelletised Natal kaolin using sulphuric acid", Hydrometallurgy, 29, 1992, 109-130.
20. Belver, C., Muñoz, M. A. B., Vicente, M. A., "Chemical activation of a kaolinite under acid and alkaline conditions", Chemistry of materials, 14, 2002, 2033-2043.
21. Liu, X., Peng, T., Yao, J., Lv, H., Huang, C., "Synthesis and textural evolution of alumina particles with mesoporous structures", Journal of Solid State Chemistry, 183, 2010, 1448-1456.
22. Potdar, H., Jun, K. W., Bae, J. W., Kim, S. M., Lee, Y. J., "Synthesis of nano-sized porous [gamma]-alumina powder via a precipitation /digestion route", Applied Catalysis A: General, 321, 2007, 109-116.
23. Parida, K., Pradhan, A. C., Das, J., Sahu, N., "Synthesis and characterization of nano-sized porous gamma-alumina by control precipitation method", Materials Chemistry and Physics, 113, 2009, 244-248.
24. Phillips, C., Wills, K., "A laboratory study of the extraction of alumina of smelter grade from China clay micaceous residues by a nitric acid route", Hydrometallurgy, 9, 1982, 15-28.
25. Zhou, S., Antonietti, M., Niederberger, M., "Low-Temperature Synthesis of γ-Alumina Nanocrystals from Aluminum Acetylacetonate in Nonaqueous Media", Small, 3, 2007, 763-767.
26. Ibrahim, D., Abu-Ayana, Y., "Preparation of nano alumina via resin synthesis", Materials Chemistry and Physics, 113, 2009, 579-586.
27. De, G., Soler-Illia, A. A., Louis, A., Sanchez, C., "Synthesis and characterization of mesostructured titania-based materials through evaporation-induced self-assembly", Chemistry of materials, 14, 2002, 750-759.
28. Kim, Y., Kim, C., Choi, I., Rengaraj, S., Yi, J., "Arsenic removal using mesoporous alumina prepared via a templating method, Environmental science & technology", 38, 2004, 924-931.
29. Yan, L., Li, Y. S., Xiang, C. B., "Preparation of poly (vinylidene fluoride)(pvdf) ultrafiltration membrane modified by nano-sized alumina (Al< sub> 2</sub> O< sub> 3</sub>) and its antifouling research", Polymer, 46, 2005, 7701-7706.
30. Sun, Z. X., Zheng, T. T., Bo, Q. B., Vaughan, D., Warren, M., "Effects of alkali metal ions on the formation of mesoporous alumina", J. Mater. Chem., 18, 2008, 5941-5947.

[DOI: 10.22068/ijmse.12.1.59]