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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF GAMMA-ALUMINA AS ADSORBENT MATERIAL TO ENHANCE IRON REMOVAL FROM PRODUCED WATER

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In this work, gamma-alumina (γ-Al_2O_3) was synthesized from polyoxohydroxide aluminum (POHA) precursor. The POAH was formed after ethanolic treatment and then calcined at a temperature of 500 °C. The result is gamma-alumina which characterized using X-ray diffracting (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), laser granularity instrument (LGI) and atomic force microscopy (AFM). It is found from the experimental results that synthesized gamma Al_2O_3 was successfully formed due to calcination at 500 °C. The results also showed that the synthesized γ-Al_2O_3 was effective in reducing iron content in the produced water to 0.0014 ppm with removal efficiency of 99.9%.

Keywords: calcination, gamma-alumina, adsorption process, produced water.

1. Introduction

The produced water is one of the largest sources of pollution related to oil production activities, as it contains many contaminants, including hydrocarbons and heavy metals in addition to chemical additives. The treatment of these substances is extremely difficult due to the toxicity they possess. Usually, the amount of produced water is low with oil at the start of oil production, but the volume of produced water due to the decrease in oil and gas production may exceed several times the volume of oil produced. Therefore, to address the environmental risks resulting from the discharge of the produced waters and the lack of similarity between them, this requires specific studies at the regional level [1,2].

In Iraqi oilfields, the produced waters are discharged into rivers, soils or reinjected during crude oil production which have a major impact on the efficiency of oil field excavation [3,4]. The index of water reinjection quality depends greatly on iron content. If the total content of iron is greater than the suggested levels for the oilfield produced water (0.5 mg/l), results in formation plugging, instability of water reinjecting value, pipeline corrosion and blockage,

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as well as increments in effluent turbidity will be established. Consequently, it is important to reduce iron contents to be less than 0.5 mg/l [5].

Adsorption technique is a phase transfer process that used widely to remove substances from liquid phases. It depends upon the concept that a solid surface of adsorbent that comes into contact with liquids, due to the imbalance of existing surface forces, has a tendency of accumulation with a surface layer of solute molecules, because adsorbents could be simply overloaded with substance. Adsorption was utilized to remove iron, manganese, total organic carbon (TOC), oil, BTEX and greater than 80% of heavy metals exist within the produced water [6]. Assortments of adsorbents are currently used such as alumina, organoclays, activated carbon and zeolites [7,8].

Alumina represents a well-known metal oxide material used as adsorbents in environmental engineering. The alumina's asset includes low costing, comparatively high surface area and well chemical as well as thermal stableness [9]. It has numerous structural phases, namely α, β, γ, η, θ, λ, K, and X [10]. Among the alumina phases, gamma-alumina is the most employed one for applications such as industrial catalyst and adsorbent, because of its high surface area and good porosity parameters [11]. Morphology and crystallinity of material are considered so significant because of the relation amid function and microstructure. Therefore, the methods of synthesizing or modifying to obtain the chosen material with the desired features have significantly attracted researchers recently [12,13].

In the present study, synthesis and characterization of gamma-Al_2O_3 obtained from POHA were achieved via d-glucose addition and calcination at 500 °C. The characterization was performed to evaluate the synthesized γ-Al_2O_3 as iron adsorbent material to enhance the treatment of produced water.

2. Experimental

2.1. Synthesis of Adsorbent Material and Characterization Methods

The synthesis of γ-Al_2O_3 being used as adsorbent material was achieved via using 400 mg of aluminum powder, 1.5 g of KOH in 40 ml of ethanol: water with volume ratio 3:1 (V: v) and additive of 50.0 mg d-glucose. These materials were mixed in flask and sonicated in bath of ultrasonic (output 125 W/20 KHz). When the aluminum was dissolved completely, the formation of two-stages demonstrated the gel at the bottom of the vial. Decantation is a method for separating a mixture, the gel of powder remains as sediment at the bottom. After that, it was washed and dried in an oven at 70 °C, where 1g of polyoxohydroxide aluminum (POHA) was obtained. The POHA was calcined for two hours at 500 °C in the furnace.

XRD of the POHA and calcined POHA was performed using X-ray diffractometer type Shimadzu model AA-6800/ Japanese made, with Cu Kα (λ=1.5418 Å). Fourier transform infrared spectroscopy (FTIR) using Bomen model type MB 100 with KBr pellets in the range of 4000 to 500 cm^{-1} was used to characterize the surface of synthesized adsorbents. Evaluation of surface morphology of the synthesized POHA was performed by using scanning electron microscopy (SEM) type Hitachi 3400N instrument. The particle size of POHA and calcined POHA was measured by laser granularity instrument using Brookhaven 90 Plus model. To confirm the results, the particle size was determined three times for each sample. Atomic force microscope (AFM) type Shimadzu model AA-6800/ Japanese made was used to examine the surface roughness of the synthesized adsorbents.

2.2. Adsorption Experiments

The oilfield produced water was supplied from Petroleum Research and Development Center related to Middle Oil Company (East Baghdad). The iron content of the produced water was 39000 µg/l (equivalent to 39 ppm) determined using inductively coupled plasma optical emission spectrometry (ICP-OES) type Thermo Fisher iCAP 6500/USA with detection limit $\leq$ 0.01 µg/l. The pH of produced water was determined at 6.6 using pH meter model Hanna Bench pH 211 Meter /UK. The optimal conditions of adsorption process were determined using certain experiments taking the contact time influence (30, 60, 90, 120, 150, and 180 min) at pH 7, and the effect of the contact time 30 min at pH 4, 7, and 10, and adsorbent dose (0.2 and 0.4 mg/l). All experiments were conducted at room temperature (25 $^{\circ}$C).

During adsorption experiments, 0.2 mg of adsorbent was added into 1litter of the aqueous adsorbate solution using magnetic stirring at 50 rpm. The initial pH of the solution was adjusted by adding 0.1 *M* HCl and 0.1 *M* NaOH to reach the required value. After the predetermined time period has elapsed, the mixture of adsorbent and adsorbate was directly separated using a 0.42 µm filter. Sample of the filtered solution was collected for iron analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). The removal efficiency (R %) of iron was calculated by the following equation [10].

$$R\ \% = \frac{Ci - Cf}{Ci} \times 100\ \% \qquad (1)$$

where *Ci* and *Cf* are initial and final concentrations of iron (ppm), respectively.

3. Results and Discussion

3.1. X-Ray Diffraction

The XRD patterns of the synthesized adsorbents are presented in Fig. 1 which shows intensity in counts per second (c.p.s) and 2 theta in degree. The results are inconsistent due to aggregates and/ or agglomerates of POHA due to calcination at 500 °C. The XRD of POHA (Fig.1a) shows sharp peaks at 2θ of 29.44° and 30° which indicate hydrated potassium aluminum oxide while the peaks at 2θ of 21.4° and 27.8° indicate the bayerite phase. The XRD of calcined POHA (Fig.1b) shows sharp peaks at 2θ of 44.7°, 38.5°, and 65.1°, and this definitely indicates the formation of γ-Al_2O_3 phase. From this, it appears that the most intense peaks recorded in the XRD pattern of calcined POHA are related to the γ-Al_2O_3.

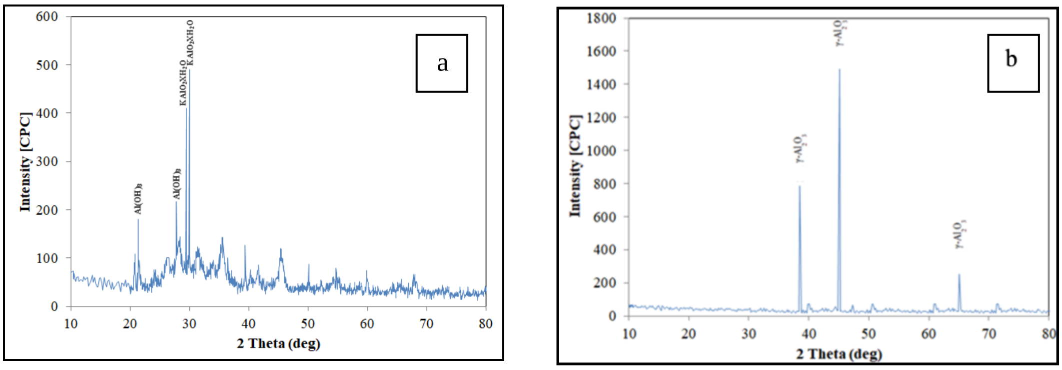


Fig. 1. X-ray diffraction of POHA: a. without calcination, b. calcined at 500 °C.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 2 and Fig. 3 illustrate the FTIR spectra of POHA before and after calcination, respectively. Fig. 2 shows the presence of typical vibrations of hydroxyl groups positioned at 3401.78 cm^{-1} and 1636.73 cm^{-1}. The AlO_6 stretch peaks can be found at positions of 661.94 cm^{-1} and 601.02. The AlO_4 stretch peaks are appeared at positions of 734.69 cm^{-1} and 662 cm^{-1}. The d-glucose peaks are demonstrated at positions of 989.31 cm^{-1} and 1409.06 cm^{-1}.

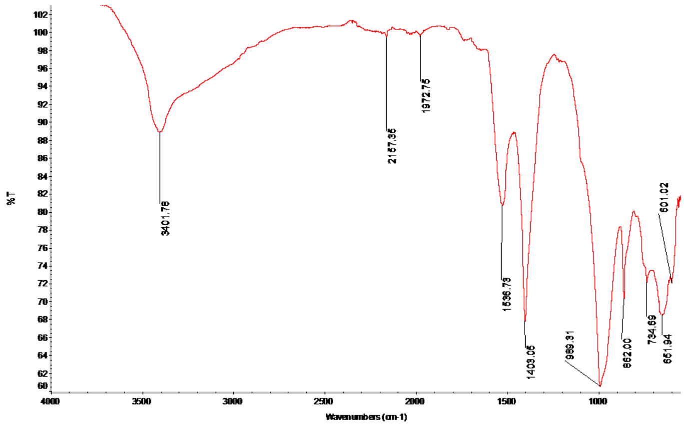


Fig. 2. FTIR spectrum of POHA.

Fig. 3 shows FTIR spectrum of calcined POHA at 500 ˚C. The adsorbed water vibration peaks are positioned at 3404.96 and 1639.91 cm^{-1}. The AlO_4 peak is positioned at 690.13 cm^{-1} and AlO_6 peak positioned at 667.85 cm^{-1} assigned to the coordinates of γ-Al_2O_3. The peaks that disappeared are related to d-glucose due to its decomposition that occurred with POHA calcination.

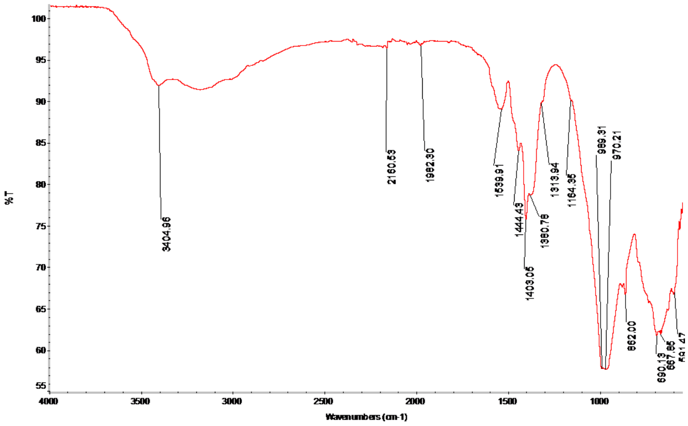


Fig. 3. FTIR spectrum of calcined POHA at 500 ˚C.

3.3. Scanning Electron Microscopy (SEM)

Fig. 4 shows the SEM images of POHA and calcined POHA. It demonstrates a high degree of agglomeration with non-uniform particles. On the other hand, the results of Fig. 5 (a and b) indicate that average diameters of 5770 nm and 1476.6 nm were obtained with a polydispersity index of 0.413 and 0.283 for the POHA and calcined POHA, respectively. Therefore, reducing particle size increases the surface area of the adsorbent material, which increases adsorption.

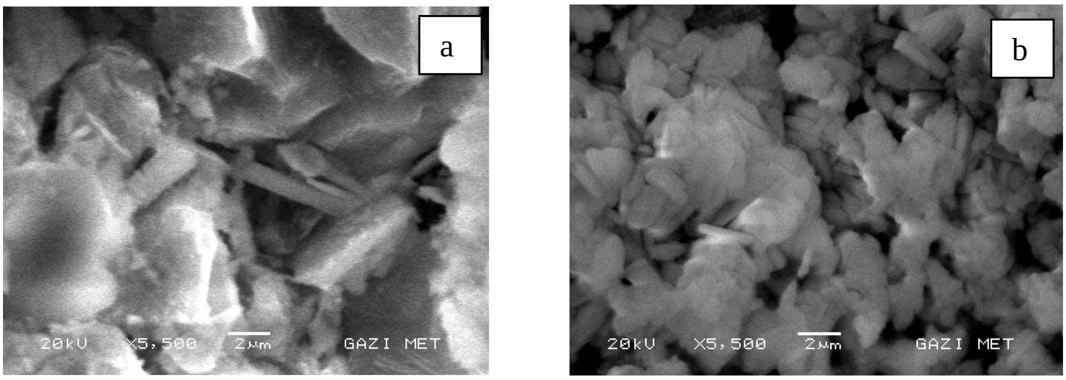
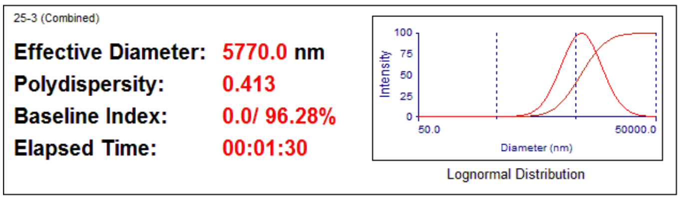
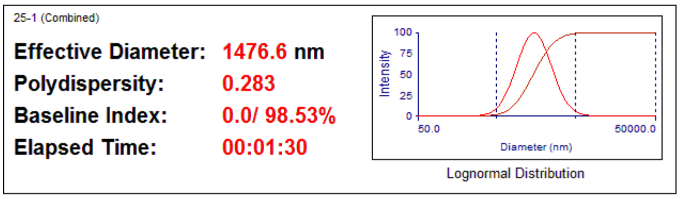


Fig. 4. The SEM image of POHA: a. without calcination, b. calcined at 500 °C.


25-3 (Combined)

Effective Diameter: 5770.0 nm
Polydispersity: 0.413
Baseline Index: 0.0/ 96.28%
Elapsed Time: 00:01:30

(a) without calcination.


25-1 (Combined)

Effective Diameter: 1476.6 nm
Polydispersity: 0.283
Baseline Index: 0.0/ 98.53%
Elapsed Time: 00:01:30

(b) calcined at 500 °C.

Fig. 5. Lognormal distribution of diameter results for POHA.

3.4. Atomic Force Microscope

The evaluation of surface roughness of the synthesized adsorbents was achieved using atomic force microscope (AFM). Figs. 6 (a) and 7 (a) illustrate the surface topography of two dimensional (2D) scan areas of 3 µm x 3 µm whereas Figs. 6 (b) and 7 (b) illustrate the surface topography of three dimensional (3D) scan area of 3 µm x 3 µm with z-scale of 600 nm for the POHA and calcined POHA, respectively. The results indicated that the average surface roughness was 100.21 µm and 27.02 µm for POHA and calcined POHA, respectively. It is clear from these results that calcination reduces surface roughness, as it makes the particle surface smooth due to its responsibility to rearrange the POHA constituents to obtain the lowest free energy and minimum stress, and these results are consistent with M. Riazian [14].

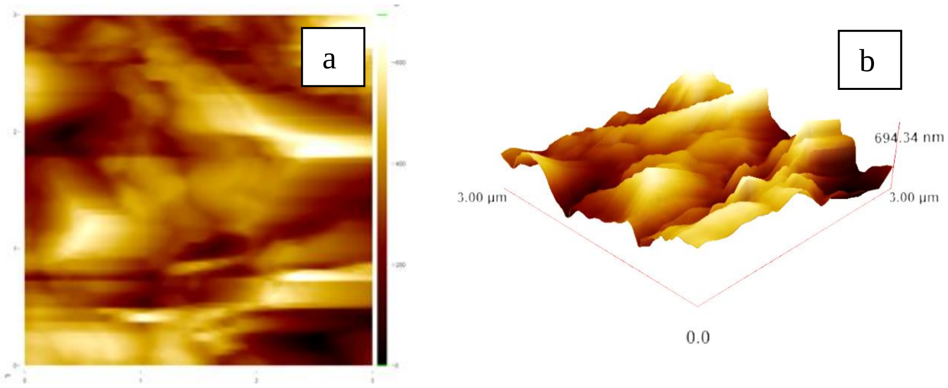


Fig. 6. AFM images of POHA: a. two – dimensional surface, b. three – dimensional surface.

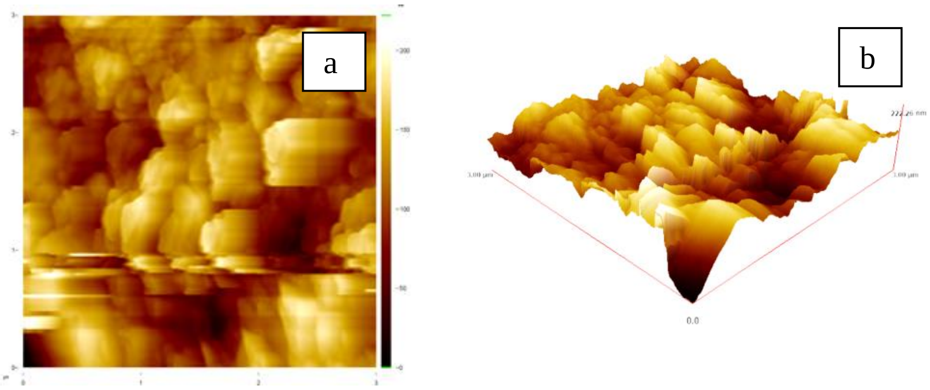


Fig. 7. AFM images of calcined POHA at 500 $^{\circ}$C: a. two – dimensional surface, b. three – dimensional surface

3.5. Adsorption Process

Fig. 8 depicts the effect of produced water pH upon the metal removal efficiency using γ -Al_2O_3 adsorbent (calcined POHA) at contact time of 30 min. It is clear that there is an increase in iron removal with an increase in the pH of the solution (pH 4-10) as it reaches the maximum at pH 7. It is observed that the lower removal efficiencies of iron were 28.8 % and 18.9 % at pH 4 for 0.4 mg and 0.2 mg of γ-Al_2O_3 dose, respectively, this could be ascribed to the competition of H^+ with metal ions to bind and occupy the active sites on the surface of γ-Al_2O_3 adsorbent. The lowest removal efficiencies of iron were 35.5 % and 20 % at pH 10 for 0.4 mg and 0.2 mg of γ -Al_2O_3 dose, respectively, this could be attributed to the excess of the competition of iron ions with hydroxyl ions for the active sites on the γ-Al_2O_3 adsorbent surface as the main reason to reduce iron adsorption.

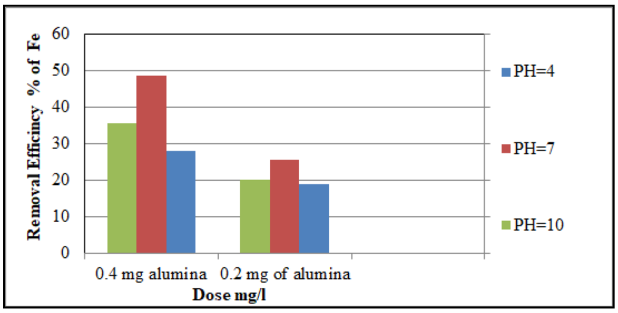


Fig. 8. Effect of pH on the removal of iron from produced water.

The effect of contact time on the removal efficiency of iron at pH 7 is illustrated in Fig. 9. It can be seen that the iron removal efficiency has been enhanced via increasing the contact time and dose concentration; this is due to the use of a more accessible energetically active site on the adsorbent surface. Therefore, the percentage of iron ions removal increased with the increase of the adsorbent dose. This result suggests that due to the presence of larger surface area in addition to greater number of active binding sites, the adsorption of iron is greater.

Iron removal efficiency was significant at the initial contact time due to the large number of vacant sites that were available on the surface of γ-Al_2O_3 adsorbent. It can be seen that at pH 7, the maximum removal efficiency of iron for 30 min of contact time was 25.6% and 48.7 % obtained using 0.2 mg and 0.4 mg of γ-Al_2O_3 dose, respectively. This result agreed with S. Homa and B. Roghiyeh (2019) [15] who explained that the increases of adsorption can be ascribed to increased adsorbent surface area and thus the availability of more adsorption sites. Fig. 9 also indicated that the iron removal efficiency using 0.2 mg and 0.4 mg of γ-Al_2O_3 dose with 90 min contact time was 99.98% and 99.99 %, respectively.

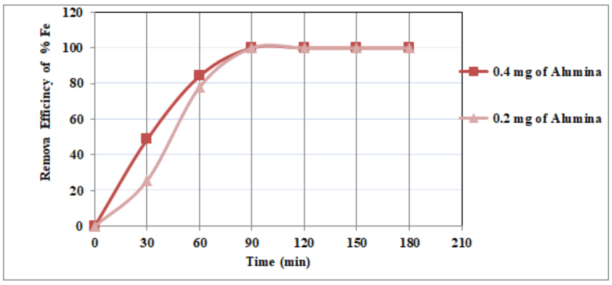


Fig. 9. The effect of contact time on iron removal.

4. Conclusions

Chemical method was successfully applied to synthesize POHA from intensive materials. Calcination at 500 °C was appropriate to attain γ-Al_2O_3 predominant phase. Calcination reduced the surface roughness of POHA to 27.02 µm compared with 100.21 µm for uncalcined one, which in turn enhanced the adsorption. The application of calcined POHA (γ-Al_2O_3) as adsorbent material to remove iron from produced water according to the use of different adsorption parameters (pH, contact time and adsorbent dose) indicates that the produced water can be greatly enhanced through reducing the iron content from 39 ppm to 0.0014 ppm with removal efficiency of 99.99%. This enhancement was acquired at pH 7, 90 min contact time and 0.4 mg γ-Al_2O_3 adsorbent dose.

REFERENCES

[1]. *N. Thyara, A. Alves, M. Sens, K. Jim, R. Dalsasso, "*Produced Water from Oil - A Review of the Main Treatment Technologies", J Environ. Chem. Toxicol., **vol. 2**, no. 1, Mar. 2018, pp. 23-27.

[2]. *M. Al-Furaiji, U. Karim, D. Augustijn, B. Waisi, S. Hulscher*, "Evaluation of Water Demand and Supply in The South of Iraq", Journal of Water Reuse and Desalination, **vol. 6**, no. 1, 2016, pp. 214-226.

[3]. *M. Thamer, A. Esraa, A. Thabit*, "Turbidity and Oil Removal from Oilfield Produced Water, Middle Oil Company by Electrocoagulation Technique", MATEC Web of Conferences, 2018.

[4]. *A. Al-Haleem, A. Razaq, "*Oilfield Produced Water Management: Treatment: Reuse and Disposal*",* Baghdad Science Journal.*, **vol. 9**, no. 1, 2012, pp. 1-9.*

[5]. *L. Fangwen, W. Jianfeng, X. Xiaohong, W. Xiaoai, M. Songjiang*, "Iron Removal from Oilfield Produced Water by Chemical Precipitation and Filtration" 2nd International Conference on Bioinformatics and Biomedical Engineering, 2008.

[6]. *S. Thavamanil, R. Rajkumar, "*Removal of Cr(VI), Cu(II), Pb(II) and Ni(II) from Aqueous Solutions by Adsorption on Alumina", Research Journal of Chemical Sciences, **vol. 3**, no. 8, 2012, pp. 1-9.

[7]. *T. Ebenezer, Z. George*, "Produced Water Treatment Technologies". International Journal of Low-Carbon Technologies., **vol. 9**, no. 3, Sept. 2014, pp. 157-177.

[8]. *D. Enshirah*, "Adsorption of Heavy Metals on Functionalized-Mesoporous Silica: A review", Microporous and Mesoporous Materials, **vol. 247**, no. 1, 2017, pp. 145-157.

[9]. *L. Warunee, S. Bhawan, M. Dalmo, A. Wagner, F. Sonia, P. Paolo*, "High Surface Area, Nanostructured Boehmite and Alumina Catalysts: Synthesis and Application in the Sustainable Epoxidation of Alkenes". Applied Catalysis A: General, **vol. 571**, no. 5, Feb. 2019, pp. 180-187.

[10]. *P. Thi, T. Ngoc, L. Thi, H. Thi, C. Lan, L. Hai, H. Thu, S. Thanh, D. Tien*, "Synthesis, Characterization, and Modification of Alumina Nanoparticles for Cationic Dye Removal", Materials, **vol. 12**, no. 3, Feb. 2019, pp. 1-15.

[11]. *Y. Kiran*, "Alpha, Beta and Gamma Alumina as A Catalyst - A Review", The Pharma Innovation., **vol. 6**, no. 11, Feb. 2017, pp. 236-238.

[12]. *S. Chang, H. Jeong, Y. Chan, M. Sang* "An Easy One-Pot Synthesis of Structurally Controlled Aluminum Hydroxide Particles from an Aqueous Sodium Aluminate Solution", Ceramic Processing Research, **vol. 10**, no. 6,2009, pp. 832-839.

[13]. *D. Mioara, G. Luiza, C. Constantin, V. Dan, "*Effect of Chemical Treatment of Poly (Ethylene Terephthalate) Surfaces on Mechanical and Water Sorption Properties", U.P.B. Sci. Bull., Series B., **vol. 77**, no. 3, 2015, pp. 1454-2331.

[14]. *M. Riazian*, "Nanostructural Characterization and Lattice Strain of TiO_2-Al_2O_3 SiO_2 Coating on Glass and Si (100) Substrates", Chilean Chemical Society., **vol. 61**, no. 2, 2016, pp. 2870-2877.

[15]. *S. Homa, B. Roghiyeh*, "Modification of Activated Carbon by $ZnCl_2$, $CaCl_2$, $MgCl_2$ and their Applications in Removal of Nitrate Ion from Drinking Water", Asian Journal of Green Chemistry, **vol. 3**, no. 1, 2019, pp. 1-12.