

## Synthesis of Zeolite A from Aloji Kaolin to Investigate Its Performance in Hard Water Softening

Elizabeth OKPONG<sup>1</sup>, Patience Oshuare SEDEMOGUN<sup>2</sup> and Abdulsalami Sanni KOVO<sup>3</sup>

<sup>1,2,3</sup>Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria

[elizabeth.okpong@st.futminna.edu.ng](mailto:elizabeth.okpong@st.futminna.edu.ng) / [pilalokhoin@futminna.edu.ng](mailto:pilalokhoin@futminna.edu.ng) / [kovo@futminna.edu.ng](mailto:kovo@futminna.edu.ng)

Corresponding Author: [pilalokhoin@futminna.edu.ng](mailto:pilalokhoin@futminna.edu.ng)

Date Submitted: 07/11/2019

Date Accepted: 21/03/2020

Date Published: 30/06/2020

**Abstract:** Aloji Kaolin was used as a combined sourced of silica and alumina to synthesize Zeolite A in this study. The raw Aloji kaolin was purified via sedimentation process to get rid of the underlying impurities such as quartz and this was then followed by metakaolinization at 800 °C for 2 h to incur reactive metakaolin phase. The purified and calcined kaolin were used to synthesize Zeolite A through conventional hydrothermal crystallization method. The synthesized Zeolite A was characterised by Scanning Electron Microscopy and X-ray diffraction methods. The synthesis parameters of Zeolite A synthesized through conventional hydrothermal route was 1 M NaOH, crystallization temperature of 100 °C and crystallization time of 6 h after aging for 6 h at room temperature. The synthesized Zeolite A was used for softening of hard water containing 76ppm of calcium ions for Gidan Kwano water sample and 178 ppm of calcium ions for Maitumbi water sample, the synthesized zeolite A was able to reduce the hardness to 4ppm and 6ppm respectively for both water samples within 40 minutes of treatment. Zeolite A was successfully synthesized from Aloji kaolin and can be used for water softening.

**Keywords:** Zeolite, Kaolin, hard water, softening, Maitumbi water.

### 1. INTRODUCTION

Zeolites are hydrated, aluminosilicate substance made from completely linked tetrahedral of alumina (AlO<sub>4</sub>) and silica (SiO<sub>4</sub>). Zeolites are termed molecular sieves, because they have pore structures that are of uniform sizes and have the ability to adsorb molecules that fit closely into their pores and also selectively discharge molecules that do not fit into their pore spaces [1]. They can be utilized or employed extensively in catalysis, separation techniques, ion-exchange and these have given rise to various types of zeolites to be used in many process industries such as the petrochemical, nuclear, agricultural, construction, refrigerating and biogas industries [2, 3, 4]. The high reactivity of zeolites in various reactions is based on their well-defined pore structure and adjustable acidity [5].

Kaolin is a whitish, amorphous clay substance composed mainly of kaolinite, Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>.2H<sub>2</sub>O. It is normally used to refer to both the raw clay and the refined commercial clay. Kaolin can be utilized extensively in paint, rubber and plastic industries as filler and flattening agent. It has been used as a starting material in the production of zeolite [6]. Kaolin is also a significant ingredient in the production of ink, organic plastics, cosmetics and many other products. Notwithstanding, it is originally valued in the production of white ware ceramics, the most important use of kaolin is now in the filling and coating of paper. The uniqueness of kaolin as compared to other clays is their whitish nature, fine and controllable particle size, chemical inertness, and adsorption properties [7]. The use of kaolin to produce zeolite is led by the fact that it provides a cheaper and easy means of silica and alumina source [8].

The unique properties of zeolites that makes them captivating, such as ion-exchange, adsorption, shape selectivity, and catalytic properties are controlled by their structural properties such as pore size, pore volume, ion-exchange capacity, channel system, etc [9].

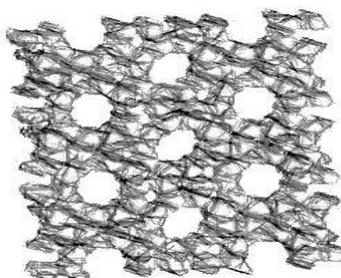


Figure 1: Structure of Zeolite silicates showing its pores [10]

Hydrothermal synthesis of zeolite was pioneered by Barrer in 1948 and Milton in 1949 and it has become the fundamental method in the synthesis of zeolites. It is a heterogeneous reaction that is required to dissolve and recrystallize substances that are partially insoluble under normal conditions [11].

Water is said to be "hard" when it has a high concentration of dissolved minerals, specifically calcium and magnesium and these minerals dissolve in it as they move through soils and rocks and are carried along, eventually ending up in water supply [12]. Hard water leads to reduced efficiency, reduced capacity and scaling in appliances where it is used. It also requires high cost of treatment to avoid large scale down time in industry.

The need for softening of water is required to reduce cost and increase efficiency in water-using appliance. This article investigates the use of hydrothermal synthesis for the production of Zeolite A as a softening agent of treatment of hard water.

## 2. MATERIALS AND METHODS

### 2.1 Materials preparation

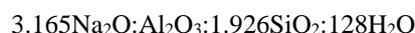
The raw Aloi kaolin was sourced from Aloi in Ofu Local Government in Kogi State, Nigeria. Analytical grade sodium hydroxide pellets (NaOH 99% purity) was provided by Sigma-Aldrich.

50 g of raw Aloi kaolin was measured with the aid of a digital weighing balance into a measuring cylinder which served as a settling tank containing 150 ml of deionised water. The mixture was thoroughly mixed and was allowed to settle for 20 minutes. At the end of the settling time (20 minutes), the heavier component (quartz) of the clay sample settled at the base of the settling tank while the lighter component (kaolin sample) remains at the surface (supernatant). The supernatant was carefully decanted into another measuring cylinder and was allowed to settle for 24 hours. After 24 hours, a settled fine clay sample was obtained after decanting; the settled fine clay sample was dried in an oven for 24 hours at a temperature of 60 °C. The procedures were repeated severally to obtain enough samples of the refined kaolin clay.

Metakaolin was produced by calcining the refined kaolin in a muffle furnace which was heated to a temperature of 800 °C. A crucible containing 20 g of the refined Aloi kaolin was placed in the furnace and allowed to heat for 2 hours. At the end of the heating process, the crucible was brought out of the furnace and allowed to dry.

### 2.2 Hydrothermal Synthesis of Zeolite A from Refined Aloi Kaolin

The synthesis was carried out using the metakaolin produced at 800 °C and exposure time of 2 hours. The gel composition used to synthesize Zeolite A was produced based on the following molecular ratio [5].



Sodium hydroxide pellet were used as a source of Na<sub>2</sub>O and the refined Aloi kaolin was used as a source of alumina and silica.

9.84 g of Sodium hydroxide pellets (1M) was measured and mixed carefully with 90 ml of deionised water and stirred for 5 minutes until the Sodium hydroxide pellets were completely dissolved.

8.5 g of the metakaolin was then added to the mixture to obtain a homogeneous gel mixture. The aluminosilicate gel was aged for 6 hours at room temperature. The hydrothermal treatment of the aged mixture was performed in a Teflon lined autoclave at crystallization temperature of 100 °C for 6 hours. At the end of the hydrothermal treatment, the autoclave was then placed in a water bath to cool. The reaction mixture was filtered and washed with deionised water to remove excess alkali until the pH fell to 7. The sample was dried in an oven at a temperature of 100 °C for 6 hours.

### 2.3 Application of Zeolite A in Water Purification

Hard water was obtained from two local wells in Gidan Kwano and Maitumbi areas of Minna, Niger State. The collected water samples were analysed to obtain their pH, turbidity, hardness, TDS, calcium hardness and magnesium hardness. 200 mg of the synthesized zeolites was added to 50 ml of the analysed water samples and stirred vigorously for 10 minutes. It was then filtered and stored in a plastic container for further investigations. The same procedure was repeated for 20, 30, 40, 50 and 60 minutes.

### 2.4 Characterisation of material and product

The prepared Zeolite A was characterised using Scanning Electron Microscope, Energy Dispersive X-ray Spectroscopy and X-ray Diffraction method.

The Phase characterization for the zeolite and metakaolin samples was carried out using the XRD machine model X'pert Pro by Philips. The beam was focused using a 1/8" and 1/4" divergence slit. Since most zeolites' features are found within the diffraction angle of  $2\theta = 50^\circ$ , all the measurements were carried out within the range of 3 to 50°. The scan step used was 65.1352s while the scan step size was 0.0170° (2 theta) and the generator setting was fixed at 30 mA and 40 kV.

The morphology was characterized by the Scanning Electron Microscope (SEM) for both the refined kaolin and zeolite samples were carried out using a FEI Quanta 200 environmental SEM.

### 3. RESULTS AND DISCUSSION

The XRD pattern of synthesized Zeolite A from conventional hydrothermal route has the characteristics intensity peak of  $2\theta$  which is in line to the XRD pattern of commercial Zeolite A [5]. The result is shown in figure 2

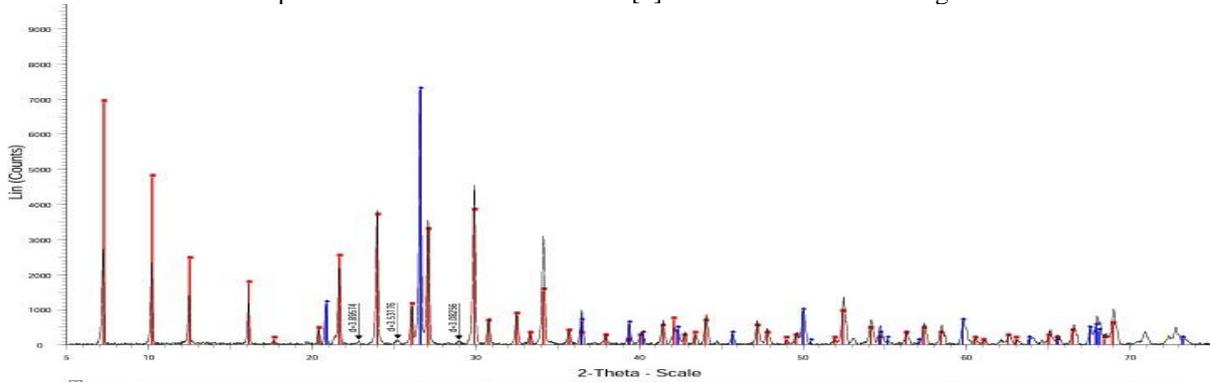


Figure 2: XRD Pattern of synthesized zeolite A (Conventional hydrothermal method)

The zeolites A obtained after the synthesis via conventional hydrothermal route were analyzed by Scanning Electron Microscopy (SEM), and are shown in Figure 3.

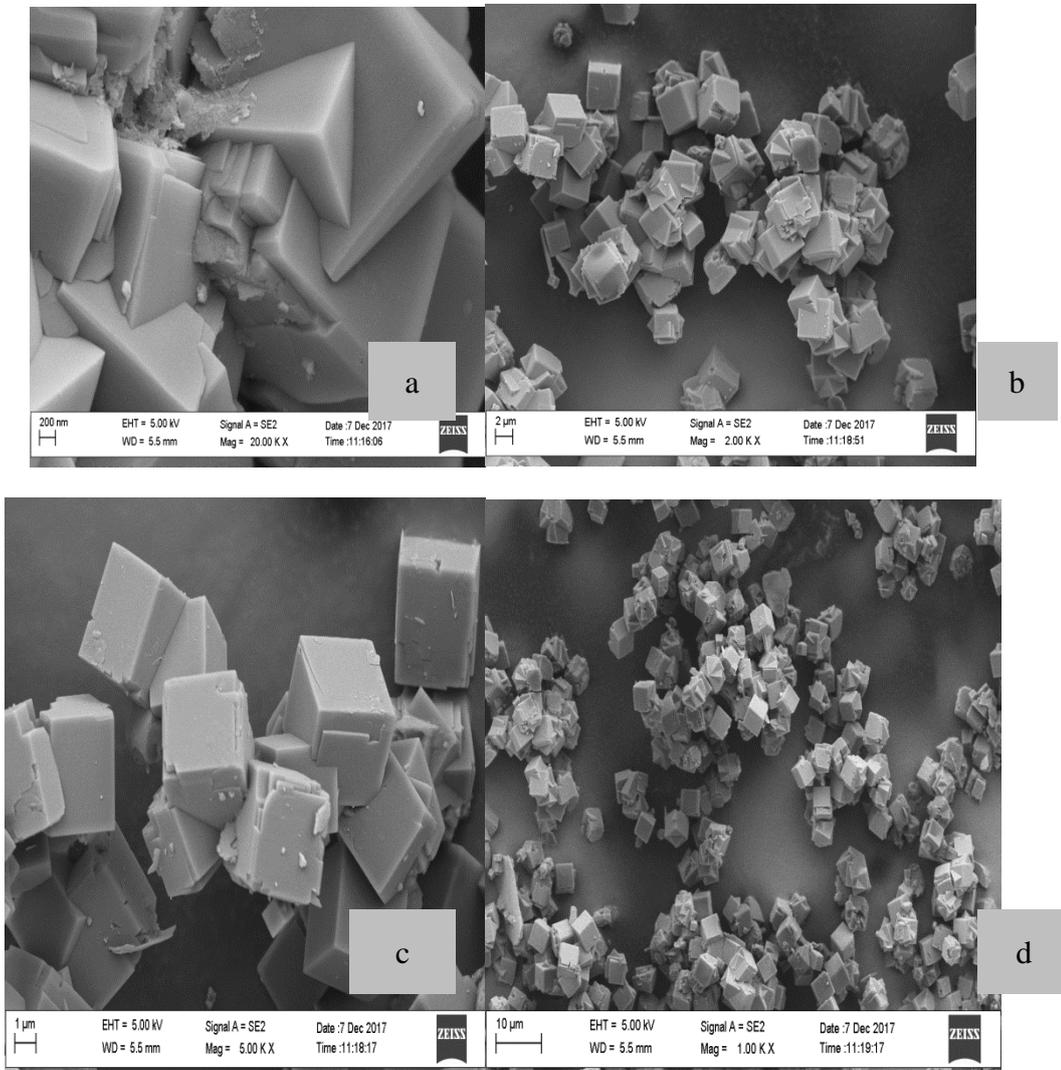


Figure 3: SEM micrographs showing the occurrence of zeolite A and associated phases obtained by hydrothermal synthesis

SEM micrographs (Fig. 3) shows the occurrence of the zeolite products obtained after hydrothermal treatment of metakaolin, the SEM images show some well-developed cubic crystals zeolite A. Fig. 3 (a-d) represents the effects of NaOH concentrations on Zeolite A formation obtained after the activation of metakaolin at 100 °C for 6 hours. According to the experimental result of this work, the observed morphologies are similar to those reported in literature [13].

The result of the EDS analysis is as shown in Table 1

Table 1: Elemental composition of synthesized zeolite A

Element	Wt %	Wt % Sigma
C	8.79	1.46
O	43.06	0.84
Na	12.01	0.32
Al	15.31	0.35
Si	19.07	0.42
Ti	0.82	0.13
Fe	0.95	0.18
<b>Total:</b>	<b>100</b>	

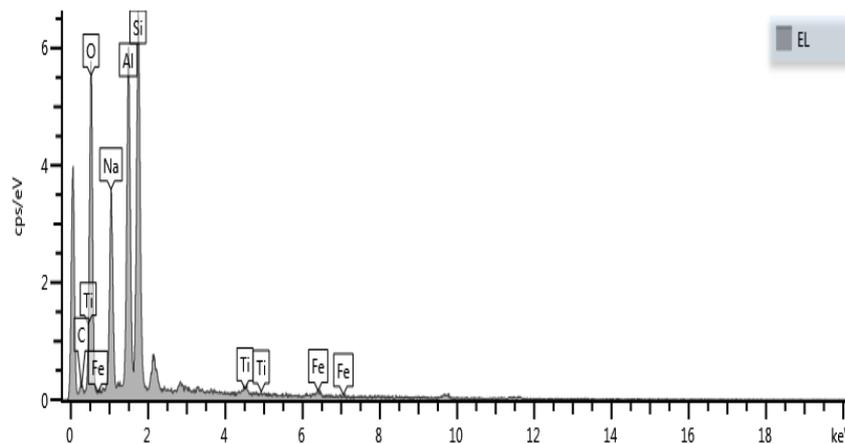


Figure 4: EDS pattern of synthesized zeolite

The EDS patterns show the elemental composition of Oxygen, Silica, Alumina and Sodium peaks

The normal range for pH in surface water systems is 6.5 to 8.5 and for ground water systems is 6.0 to 8.5. According to the Nigerian Industrial Standard for Water Quality, the maximum permitted limit of pH in water is ranges between of 6.5 to 8.5; the synthesized zeolite A has been able to reduce the pH of the hard water (Gidan Kwano) from 8.40 to 8.20 and it was also able to reduce the hard water sample from Maitumbi from 9.20 to 8.10 and this is in line with the permissible limit of pH in water.

According to WHO (World Health Organisation, 2003), the turbidity of water should not be more than 5 NTU and should ideally be below 1 NTU but the application of the synthesized zeolite A in the hard water was not able to reduce the turbidity but increased it from 2.22 NTU to 8.20 NTU and this is because high turbidity water cannot be soften efficiently by zeolite process.

The analysis carried out to test for total dissolved solids only provides information about the amount of dissolved ion but does not tell us the nature or ion relationship. In addition, the test does not provide insight into the water quality issues, such as elevated hardness, salty taste or corrosiveness. Therefore, the total dissolved solids test is used as an indicator test to determine the general quality of the water. An elevated total dissolved solid is not a health hazard but because the concentration is a water quality standard, it is therefore regulated because it is more of an aesthetic rather than a health hazard. In a study by the World Health Organization, a panel of tasters came up the following conclusions about the preferable level of TDS in water;

Table 2: Level of Total Dissolved Solids in water

Level of TDS(milligram per litre)	Rating
Less than 300	Excellent
300-600	Good
600-900	Fair
900-1200	Poor
Above 1,200	Unacceptable

However, a very low concentration of TDS in water has been found to give water a flat taste which is undesirable to many people. According to WHO, hardness in water has no known adverse effect [14]. Water hardness is classified by the water quality association as follows:

Table 3: Classification of Water Hardness

Classification	mg/l or ppm
Soft	0-17.1
Slightly Hard	17.1-60
Moderately Hard	60-120
Hard	120-180
Very Hard	120 & over

The application of the synthesized Zeolite A has successfully been able to reduce the hardness of both water samples over time, making it slightly hard.

The results of the application of the synthesized Zeolite A in water softening on the raw and treated water is shown in table 4.

Table 4: Results of some test performed on Gidan Kwano and Maitumbi water samples.

Test Performed	Gidan Kwano		Maitumbi	
	Raw	Treated	Raw	Treated
pH	8.40	8.20	9.20	8.10
Turbidity (NTU)	2.22	8.20	1.75	18.0
Total Hardness (ppm)	143	24.0	354	20.0
Calcium Hardness(ppm)	76.0	4.00	178	6.0
Magnesium Hardness(ppm)	67.0	20.00	176	14.0
Total Dissolved Solids(ppm)	286	314	503	568

Water softening was carried out using the Zeolite A synthesized through conventional hydrothermal method. The analysis of the hard water sample from Gidan Kwano showed that the water has a calcium concentration of 76.0 ppm and that of Maitumbi has a calcium concentration of 178 ppm. The effect of time was studied using 200 mg of the synthesized Zeolite A to treat 50 ml of hard water. The effect of time over the removal of calcium ion from the hard water samples (Gidan Kwano and Maitumbi) using the synthesized Zeolite A is shown in figures 5 and 6 respectively.

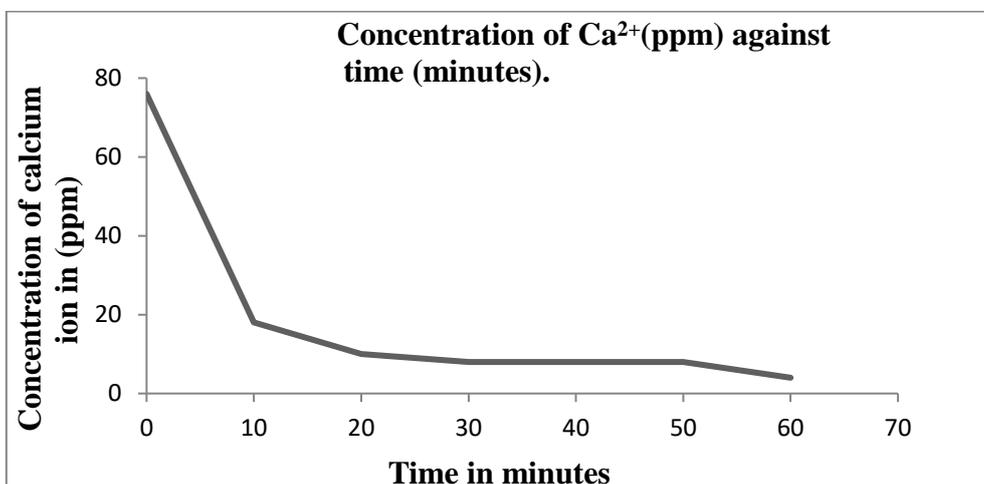


Figure 5: Graph of concentration of calcium ion (ppm) against time (min) for Gidan Kwano analysed water sample

The concentration of  $\text{Ca}^{2+}$  ions in the hard water sample from Gidan Kwano was minimized from 76 ppm to 4 ppm using the synthesized Zeolite A.

When hard water comes in contact with zeolite, the hardness causing ion i.e  $\text{Ca}^{2+}$  is retained by the zeolite as  $\text{CaZ}$ , the treated water contains  $\text{Na}^+$ ; after some time, all the cations are completely converted into  $\text{CaZ}$ .

The  $\text{Ca}^{2+}$  ion displaced the  $\text{Na}^+$  ions from the channels within the zeolite framework as demonstrated by the equation below:

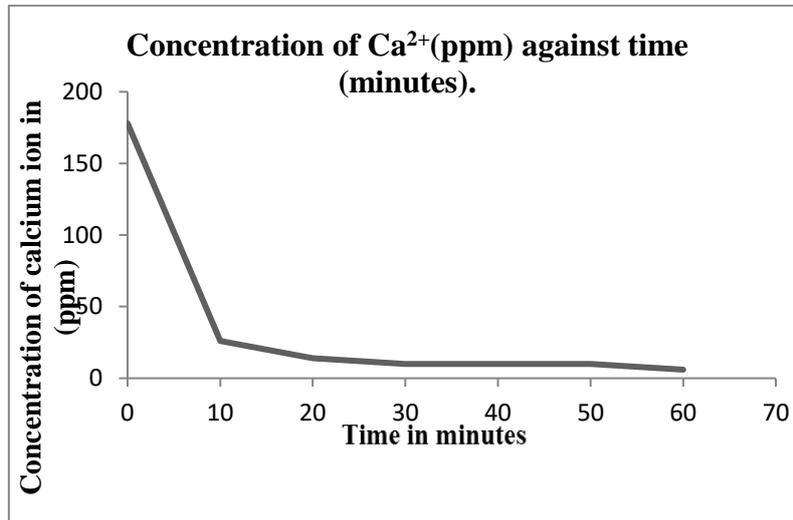
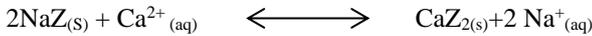


Figure 6: Graph of concentration of calcium ion (ppm) against time (min) for Maitumbi analysed water sample

The concentration of  $\text{Ca}^{2+}$  ions in the hard water sample from Maitumbi was minimized from 178 ppm to 6 ppm using the synthesized Zeolite A within 10 minutes of treatment. It was observed that the softening of the hard water assumed a steady value from 30 to 50 minutes of treatment; this may be as a result of the low crystallinity of the synthesized zeolites used.

#### 4. CONCLUSION

Zeolite A was successfully synthesized using Aloji Kaolin. The raw kaolin was refined via sedimentation process and metakaolin was achieved by the thermal treatment of refined kaolin at 800 °C for 2 hours.

The synthesis of Zeolite A through conventional hydrothermal treatment has the following optimal parameters; the concentration of NaOH of 1M, crystallization time of 6 hours and crystallization temperature of 100 °C after aging the reaction mixture for 6 hours.

It was observed that increase in the synthesis parameters (concentration of NaOH, crystallization temperature and crystallization time) resulted in an increase in zeolite A synthesis.

It was also observed that the synthesized Zeolite A causes a decrease in the concentration of calcium ion with increase in time, thereby reducing the hardness in water almost completely and required less time for softening.

#### REFERENCES

- [1] Cejka, J., Corma, A. & Zones, S. (2010). *Zeolites and Catalysis. Synthesis Reaction and Application*, 1st ed Wiley.
- [2] Ventura, G. & Risegari, L. (2008). *The Art of Cryogenics: Low-Temperature Experimental Techniques*. Elsevier, Amsterdam, Netherlands.
- [3] Jana D. (2007). *Clinoptilolite- a promising pozzolan in concrete (PDF)*. A New Look at an old Pozzolan. 29th ICMA conference. Quebec City Canada: construction material consultant Inc.
- [4] Gilson, J. (2002). *Zeolites for Cleaners Technologies. Catalytic Science Series*. Imperial College Press.
- [5] Kovo, A.S. (2011). Development of Zeolites and Zeolite membrane from Ahoko Nigerian Kaolin. PhD Thesis, University of Manchester, United Kingdom.
- [6] Querol, X., Moreno, N., Umaña, J.C., Juan, R., Hernández, S., Fernandez-Pereira, C., Ayora, C., Janssen, M., García-Martínez, J., Linares-Solano, A. & Cazorla-Amoros, D. (2002). Application of Zeolitic Material synthesized from fly ash to the decontamination of waste water and flue gas. *Journal of Chemical Technology and Biotechnology*, 292-298.

- [7] Walter, M., Olson, D.H. & Baerlocher, Ch. (2011). *Atlas of Zeolite Structure Types*, International Zeolite Association Structure Commission, Elsevier, Amsterdam.
- [8] Kovo, A.S. and Holmes, S.M. (2010). Effect of Aging on the Synthesis of Kaolin-Based Zeolite Y from Ahoko Nigeria using a Novel Metakaolinization Technique. *Journal of Dispersion Science and Tech.*, 31(4), 442-448.
- [9] Auerbach, S.M., Carrado, K.A. and Dutta, P.K. (2003). *Handbook of Zeolite Science and Technology*. CRC Press, New York.
- [10] Golomeova, M. and Zendelska, A. (2010). Application of Some Natural Porous Raw Materials for Removal of Lead and Zinc from Aqueous Solutions, In *Microporous and Mesoporous Materials*, InTech, 21-49.
- [11] Yu, J. (2007). Synthesis of Zeolites. In H. v. A.C.J. Cejka, *Introduction to Zeolite Science and Practice*, Vol. 168, pp. 39-103, Elsevier.
- [12] Kousa, A., Moltchanova, E., Viik-Kajander, M., Ryttonen, M., Tuomilehto, J., Tarvainen, T. and Karvonen, M. (2004). Geochemistry of Ground Water and the Incidence of Acute Myocardial Infraction, In Finland. *J Epidemiol Community Health*, 58, 136-139.
- [13] Heller-Kallai L.L. (2007). Reaction of Kaolin and Metakaolins with NaOH-Comparison of Different Samples. In L. L. Heller-Kallai, *Reaction of kaolin and metakaolins with NaOH-Comparison of Different Samples*, Appl. Clay Sci., 99-107.
- [14] WHO. (2003). *Hardness in Drinking Water*. World Health Organization, Switzerland.