

# Synthesis and Characterisation of Zeolites From Coal Fly Ash (CFA)

M. Chigondo, U.Guyo\*, M. Shumba, F. Chigondo, B. Nyamunda, M. Moyo, T. Nharingo

Department of Chemical Technology  
Midlands State University  
Gweru, Zimbabwe  
Email: guyou@msu.ac.zw

**Abstract**— In this study, disposed coal fly ash samples from Zimbabwe were used in synthesis of zeolites. The method of direct hydrothermal treatment with sodium hydroxide at different concentrations (2, 2.5, 3.5 and 4.5 moldm<sup>-3</sup>) at a constant temperature of 100°C and activation time of 24 h was applied. Characterisation of coal fly ash and confirmation of occurrence of the zeolite material was done using XRF, XRD, FTIR, and BET techniques. The zeolite materials formed were a mixture of zeolite Na-X (NaAlSi<sub>1.1</sub>O<sub>4.22</sub>25H<sub>2</sub>O), zeolite Na-A (Na<sub>2</sub>Al<sub>2</sub>Si<sub>3.3</sub>O<sub>8.86</sub>7H<sub>2</sub>O), zeolite NaP1 (Na<sub>6</sub>Al<sub>6</sub>Si<sub>10</sub>O<sub>32</sub>H<sub>2</sub>O) and zeolite hydroxysodalite (Na<sub>1.08</sub>Al<sub>2</sub>Si<sub>1.68</sub>O<sub>7.441</sub>8H<sub>2</sub>O). The variety and yield of zeolites formed depend on the concentration of sodium hydroxide used.

**Keywords**-coal fly ash; zeolites; characterisation

## I. INTRODUCTION

Coal fly ash (CFA) is a micro spherical particulate by-product of combustion of coal. It is primarily composed of amorphous aluminosilicate and other crystalline minerals like mullite, quartz, haematite and magnetite [1]. Combustion of coal in thermal power stations produces over 800 million tonnes of fly ash worldwide annually [2,3]. The disposal of such huge quantities of ash has become a problem [4,5]. The production of zeolites is one of the potential applications of CFA. The aluminosilicate glass in CFA is a readily available source of Si and Al for zeolite synthesis so as to obtain high value industrial products with environmental technological utilisation [5,6]. The chemical composition of fly ash is determined by the source of coal used during combustion, combustion conditions and variation in composition with particle size [7].

Several approaches have been done for proper utilisation of fly ash, for reduction of cost of disposal or for minimising environmental impact. Another approach is the conversion of coal fly ash to zeolites which have wider applications in ion exchange, molecular sieves, catalysts and adsorbents [8]. Zeolites are natural or synthetic aluminosilicates comprising of ordered arrangement of silicate and alumina tetrahedra. The substitution of Si by Al ions create an overall negative charge that is compensated by cations such as Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, providing zeolites with cation exchange ability [3,9]. The high percentage of aluminosilicate in fly ash (60-80%) makes them a cheap and readily available source of Si and Al for zeolite synthesis

[2](Scott *et al.*, 2001). Low cost fly ash based zeolites can be used for environmental mitigation where the use of commercial zeolites is restricted due to procurement and prohibitive costs [10].

The use of zeolites in environmental applications is gaining new research interests because of their unique properties. Numerous studies have been done on use of zeolites to remove heavy metals [2,6,11-20]. Heavy metals in waste water have emerged as the focus of environmental remedial efforts due to their toxicity and threat to human life [8,9]. Due to rapid growth of industrialisation and urbanisation with technological advancement, the existing water resources are becoming increasingly contaminated by discharge of effluent containing organics, colour, heavy metals and other contaminants. One such heavy metal is copper which, though it is an essential micronutrient for human life, is detrimental in large quantities. Copper at high levels causes stomach intestinal distress, kidney damage, anaemia, and even death [21]. It is discharged into water bodies from mining operations, metal plating and tanneries

The conditions of hydrothermal synthesis of zeolite, the type and source of coal fly ash determine the type of zeolite produced [3,15,20,22,23]. Several studies focussing on the conversion of CFA into zeolite by hydrothermal treatment have been done but these have not exhausted all the types of CFA in different parts of the world [2-4,8,9,14,15,22-28].

It is therefore important to study synthesis of zeolites coal fly ash from Zimbabwe to determine the utilisation of various types of coal fly ash. Various conditions such as temperature, incubation time and concentration of alkaline produce different types of zeolites worth studying in that particular respect. The obvious environmental benefit is the utilisation of a waste material as an adsorbent in removing metal contaminants from water. This will contribute towards good water quality and waste management in the country [10].

Traditional methods for the removal of heavy metals from aqueous environment are expensive, not effective and always give rise to chemical and sludge handling problems hence sorption methods may be an alternative.

## II. MATERIALS AND METHODS

### A. Sampling and Sample Pretreatment

The coal fly ash samples were collected from Hwange dumping sites, a local power company in Zimbabwe. The samples were sealed and transported in polythene bags and then air dried for 24 h. Before use, they were screened by 180 micron sieve followed by removal of magnetic materials mainly iron fillings using a magnet which interfere with zeolite formation [2,8].

### B. Zeolite Synthesis

The direct hydrothermal method was used for the synthesis of zeolites since it is fast, economic and less involving than the other the fusion and the microwave methods [5,24]. Triplicate 25 g masses of fly ash was weighed and added each to polypropylene beakers containing 200 cm<sup>3</sup> of NaOH of varying concentrations (2.0, 2.5, 3.5 and 4.5 moldm<sup>-3</sup>) to produce triplicate samples of four different groups of zeolite material coded ZM 2, ZM 2.5, ZM 3.5 and ZM 4.5 respectively [29]. The resulting solutions were heated at 100°C for 24 h [30]. The resulting zeolite cakes were recovered by filtration and washed several times with distilled water until the pH a of 10 was attained. The resulting zeolite material was dried to constant mass at 100°C. and stored in a desiccator before use [2,8].

### C. Characterisation of Coal Fly Ash and Zeolites

Raw and treated CFA crystalline phases were characterised by XRF (Axios<sup>max</sup>-Cement XRF), XRD (Burker D8 Advanced Diffractometer), FTIR (Merlin DigiLab) and BET (Micromeritics ASAP 2020).

## III. RESULTS AND DISCUSSION

### A. X-ray Fluorescence

The chemical compositions of CFA and the synthesised zeolite material ZM 2 are shown in Fig. 1. The type of CFA used in this study can be classified as class F since it contains a total percentage of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> of more than 70% and CaO of less than 20% [14,26]. The CFA contains mainly SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> with a SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> ratio of 1.28. This is consistent with other CFA samples analysed and used in literature to synthesise zeolites [3,29] hence the CFA is suitable for use as a low cost raw material for zeolite synthesis.

There was a marked increase in the percentage of Na<sub>2</sub>O in the zeolite material compared to CFA (from 0.40 to 5.36 %) due to the capture of sodium ions needed to neutralise the negative charges on the aluminate in the zeolite during hydrothermal treatment to form zeolites. This correlates well with observations made by Jha *et al.*, (2009) [5].

TABLE 1. XRF CHEMICAL COMPOSITION OF CFA AND ZEOLITE ZM 2

Components	% Composition	
	Coal Fly Ash	ZM 2 zeolite material
SiO <sub>2</sub>	40.92	34.79
Al <sub>2</sub> O <sub>3</sub>	31.91	26.59
Fe <sub>2</sub> O <sub>3</sub>	11.02	10.96
CaO	6.10	5.80
MgO	0.34	0.32
SO <sub>3</sub>	2.06	2.01
Na <sub>2</sub> O	0.40	5.36
K <sub>2</sub> O	1.08	0.98
TiO <sub>2</sub>	2.04	1.98
P <sub>2</sub> O <sub>5</sub>	1.18	1.10
MnO	0.06	0.03
Loss of Ignition	2.89	10.08

### B. X-ray Diffraction

XRD characterisation revealed the occurrence of the characteristic reflection peaks of CFA and the generated zeolite materials (Figs. 1-5). As shown in Fig. 1 the XRD pattern of CFA mainly shows the presence of crystalline quartz and mullite phases. Besides some crystalline phases (quartz, mullite, hematite etc), ash is primarily composed of amorphous material. The partial hump seen in the background at lower diffraction angles in CFA is attributed to the amorphous phases. After CFA treatment several sharp diffraction peaks of great intensity emerge confirming formation of zeolites (Figs. 2-5). Upon treatment of CFA there was disappearance of some mullite and quartz peaks as well as emergence of new peaks. The phases were identified using the Bruker DIFFRAC plus evaluation software (EVA), in combination with the ICDD powder diffraction database (International Centre for Diffraction Data). To compliment the technique, zeolitic phases present in the treated fly ashes were also identified by comparing with other diffractograms from literature obtained by using inorganic index to the powder diffraction of JCPDS (Joint Committee of Powder Diffraction Standards) for inorganic compounds and data files compiled in the book by Szostak, (1976) [31].

The XRD patterns of the zeolites in Figs. 2-5 indicate that the major zeolite synthesised was Na-X type (NaAlSi<sub>1.23</sub>O<sub>4.46</sub> · 3.07H<sub>2</sub>O) and was Na-A type zeolite (NaAlSi<sub>1.1</sub>O<sub>4</sub> · 22.25H<sub>2</sub>O) [1,21,22,32]. Minor zeolite types obtained were zeolite NaP1(Na<sub>6</sub>Al<sub>6</sub>Si<sub>10</sub>O<sub>32</sub> · 12H<sub>2</sub>O) and hydroxysodalite (Na<sub>1.08</sub>Al<sub>2</sub>Si<sub>1.68</sub>O<sub>7.441</sub> · 8H<sub>2</sub>O).

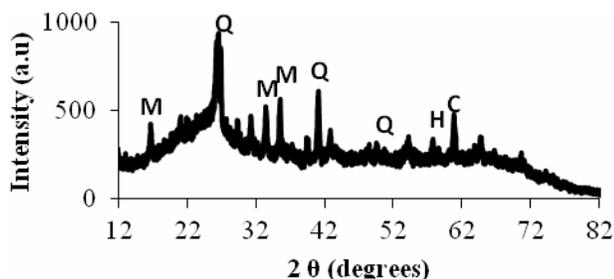


Figure 1: XRD pattern of CFA, Q-quartz, M-mullite, C-calcium oxide, H-haematite

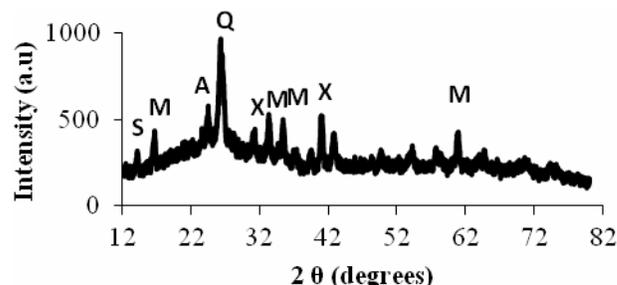


Figure 4: XRD pattern of ZM 2.5, Q-quartz, M-mullite, X-zeolite Na-X, S-zeolite hydroxysodalite, A-zeolite Na-A, P-zeolite Na-P1

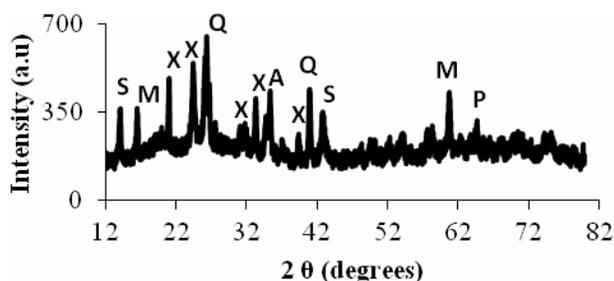


Figure 2: XRD pattern of ZM 4.5, Q-quartz, M-mullite, X-zeolite Na-X, S-zeolite hydroxysodalite, A-zeolite Na-A, P-zeolite Na-P1

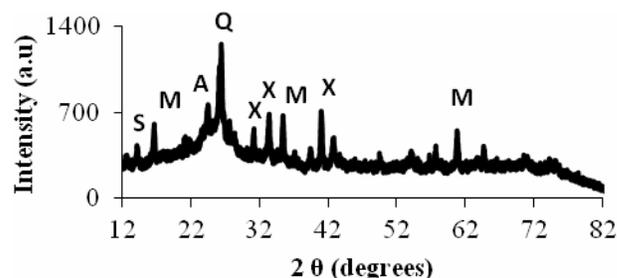


Figure 5: XRD pattern of ZM 2, Q-quartz, M-mullite, X-zeolite Na-X, S-zeolite hydroxysodalite, A-zeolite Na-A, P-zeolite Na-P1

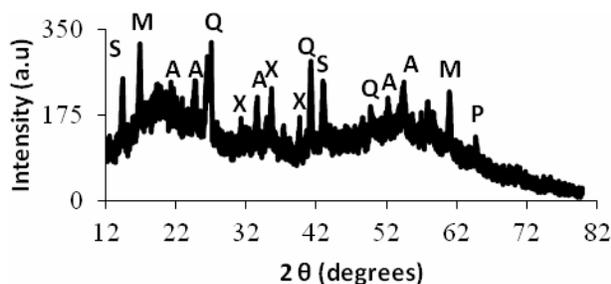


Figure 3: XRD pattern of ZM 3.5, Q-quartz, M-mullite, X-zeolite Na-X, S-zeolite hydroxysodalite, A-zeolite Na-A, P-zeolite Na-P1

The peaks pattern of Na-X and Na-A zeolite are dominant in ZM 3.5 and ZM 4.5 NaOH [1,22] with a small amounts of Na-P1 and hydroxysodalite. The use of high concentration of sodium hydroxide (3.5 and 4.5 M) results in slight decrease in peak intensities of quartz and mullite phases while the decrease in concentration of sodium hydroxide shows a progressively decreased in peak intensities of the quartz phase (Figs. 4 and 5). The mullite phase did not change much, indicating that it was a relatively stable phase during the hydrothermal reaction. These results correlate well with observations reported by Kiti, 2012 [32] and Scott *et al.*, 2001 [2].

### C. FTIR

Results for FTIR studies are summarised in Table 2. There were several band shifts as a upon zeolite formation. The band at  $1116.9\text{ cm}^{-1}$  in the FTIR spectrum of CFA became sharper and shifted to lower frequency ( $900\text{ cm}^{-1}$  range) in the FTIR spectrum of the zeolite materials. There is emergence of the double ring mode which is associated with zeolite cages and rings that is notably absent in CFA spectrum.

The types of zeolites that have been produced have IR values close to those reported in literature on zeolite A, zeolite Na-X, zeolite Na-P zeolite Na-A and zeolite hydroxysodalite. For example the in the spectral region of 750-650  $\text{cm}^{-1}$  the bands at 743.4 and 614.3 are in good agreement with reported literature values for Na-X (746 and 668  $\text{cm}^{-1}$ ) [33]. In the spectral region 650–500  $\text{cm}^{-1}$  the relatively double ring bond vibration zone there is the bond at 567.1  $\text{cm}^{-1}$  which is consistent with values known for zeolite Na-X (560  $\text{cm}^{-1}$ ).

In the region within 500-420  $\text{cm}^{-1}$ , related to the deformations of the O-T-O bond, there is evidence of one band at 460  $\text{cm}^{-1}$  characterised by a moderate intensity and good symmetry. This band is in close agreement with the one reported for zeolite Na-X (458  $\text{cm}^{-1}$ ) [33]. This strongly supports the presence of Na-X zeolite. For the zeolite Na-P1, there are bands at 450, 554, 650  $\text{cm}^{-1}$  and the asymmetric vibration at 994  $\text{cm}^{-1}$ . These values are in agreement with results obtained by Vadapilli *et al.*, (2010) [34]. Zeolite was synthesised from South coal fly ash Africa and a corresponding FTIR spectrum was obtained with bands at 434, 554, 650, 726, 1004  $\text{cm}^{-1}$ .

#### D. BET

Values of surface area for the prepared zeolite materials were found to be 52.54, 28.95, 61.48 and 67.65  $\text{m}^2/\text{g}$  for ZM 2, ZM 2.5, ZM 3.5 and ZM 4.5 respectively whereas the surface area of fly ash was only 5.22  $\text{m}^2/\text{g}$ . The increase in surface area could be attributed to the formation of zeolite structures.

#### IV. CONCLUSION

This study has shown that coal fly ash is a potential silica source for the synthesis zeolite. Na-X, Na-A, and NaP1 and hydroxysodalite type zeolites have been successfully synthesized from Zimbabwean coal fly ash.

#### ACKNOWLEDGMENT

Authors are thankful to the following organisations: Varichem Laboratories for assistance on FTIR analyses of samples; Lafarge Cement Industries for assistance on XRF analyses of samples; Tshwane University of Technology, S.A. for assistance in XRD and BET analyses of samples.

#### REFERENCES

- [1] M.G. Lee, G. Yi, B.J. Ann and F. Roddick, "Conversion of coal fly ash into zeolite and heavy metal removal," Korean J. Chem. Eng, 2000: 17(3), pp. 325-331.
- [2] J. Scott, D. Guang, K. Naeramitarnasuk, Thabout and A. Rose, "Zeolite synthesis from coal fly ash from the removal of lead ions from aqueous solutions," J. Chem. Techno. And Biotechno. 2001: 77, pp 63-67
- [3] A.D. Elliot, and D. Zhang, "Controlled Release Zeolite Fertilizer: A value added product from ash," Corporate Research Centre For Fuels and Energy, Curtin University of Technology, World Coal Conference 11-15 April 2005, Lexington, and Kentucky, USA.

- [4] K. Furukui, T. Nishimoto, M. Takaguchi, and M. Yoshinda, "Effects of NaOH concentration on zeolite synthesis from coal fly ash with hydrothermal treatment method," *J. Soc. Power Techno.* 2003: pp. 40, 487-504.
- [5] V. K. Jha, M. Nagae, M. Matsuda, and M. Miyake, "Zeolite From Coal Fly Ash and Heavy metal ion removal characteristics of thus obtained zeolite X in multi-metal systems," *J. Environ. Management*, 2009: 90, pp. 2507-2514.
- [6] N. Koukouzas, I. Vasilatos, G.S. Itskos, and A. Moutsatsou, "Characterisation of CFB-coal fly ash zeolite material and their potential use in waste water treatment," Centre for Research and Technology, WOCA conference, 2009, Lexington, USA.
- [7] L.W. Daniels, B. Stewart, K. Haering, and C. Zipper, "The potential for beneficial reuse of coal fly ash in Southwest Virginia. Mining Environments," Virginia Cooperative Extension Publication. 2002
- [8] P. Solanki, V. Gupta, and R. Kulshrestha, "Synthesis of zeolite from fly ash and removal of heavy metals ions newly synthesised zeolite," *Environ. J. Chemistry*, 2010: 7 (4), pp.1200-1205).
- [9] X. Querol, X. Moreno, J.C. Uman'a, A. Alastuey, Herna'ndez, Lo'pez, E.A. Soler, and P. Plana, "Synthesis of zeolites from coal fly ash: an overview," *International J. of Coal Geology*, 2002: 50, pp. 413– 423.
- [10] S.S. Rayalu, A.K. Bansiwali, S.U. Mesharan, S. Labhsetwar and S. Devotta, "Fly ash based zeolite analysis: Versatile material for energy and environmental conservation," *Catalysis survey from Asia*, 2006: 10 (2), pp.74-88.
- [11] R. Apiratikul, and P. Pavasant, "Sorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  using modified zeolite from coal fly ash," *Chem. Eng. Journal*, 2008: 144, pp. 245–258.
- [12] W. Chunfeng, L.I. Jiansheng, W. Lianjun, and X. Xiuyun, "Evaluation of zeolites synthesized from fly ash as potential adsorbents for wastewater containing heavy metals," *J. of Environ. Sciences*, 2008: 21, pp. 127–136.
- [13] D. Georgiev, B. Bogdanov, Y. Hristov, and I. Markovska, "The Removal of Cu (II) Ions from aqueous solutions on synthetic zeolite NaA," World Academy of Science, Engineering and Technology, 2012: 64.
- [14] T.C. Hsu, C.C. Yu, C.M. Yeh, "Adsorption of  $\text{Cu}^{2+}$  from water using raw and modified coal fly ashes," *Fuel*, 2007: 87, pp. 1355–1359.
- [15] T. Mishra, S.K. Tiwari, "Studies on sorption properties of zeolite derived from Indian fly ash," *J. of Hazardous Materials*, 2006: B 137, pp. 299–303.
- [16] T. Motsi, "Remediation of acid mine drainage using natural zeolite," PhD thesis University of Birmingham, United Kingdom. 2010
- [17] M. Nascimento, P.S.M. Soares, V.P. de Souza, "Adsorption of heavy metal cations using coal fly ash modified by hydrothermal method," *Fuel*, 2009: 88, pp.1714–1719.
- [18] N. M. Pandey, S. Sambi, S. Sharma and S. Sing, "Batch adsorption studies for removal of Cu (II) by elite NaX from aqueous stream in Proceedings of The World Congress on Engineering and Computer Science," 20-22 October 2009, San Francisco, USA.
- [19] C.A.R. Reyes, "Synthesis of zeolites from geological materials and industrial wastes for potential application in environmental problems," Doctoral thesis, Graduate School of the University of Wolverhampton, UK., 2008
- [20] D. Wu, Y. Sui, S. He, X. Wang, C. Li, H. Kong, "Removal of trivalent chromium from aqueous solution by synthesised from fly ash," *J. of Hazardous material*, 2008: 155, pp. 415- 423.
- [21] N.M. Musvoka, L.F. Petrik, G. Balfour, N. Musherr., W. Gitari, and B. Mabovu, "Removal of Toxic Elements from Brine Using Zeolite NA-P1 made from a South African Coal Fly Ash," In Environmental and Nano Science Research Group, University of Western Cape. International Mine Water Conference, Pretoria 19<sup>th</sup> – 23<sup>th</sup> October 2009; Document Transformation Technologies.
- [22] K. Ojha, M.C. Pradhan, and A. Samanta, "Zeolite from fly ash: synthesis and characterization" *Bulletin of Material. Science*, 2004: 27(60), pp. 555–564.

- [23] Z. Adamczk, and B. Biacka, "Hydrothermal Synthesis of zeolite from Polish coal fly ash," *Polish J. Environ. Studies*, 2005: 14 (4), pp. 713-719.
- [24] Y. P. Chauhan, and M Taliba, "Novel and green approach of synthesis and characterization of nano-adsorbents (zeolites) from coal fly ash: a review," *Science Review and Communications*, 2012: 2(1), pp.12-19.
- [25] K. S. Hui, K. N. Hui, And N. Lee, "A novel and green approach to produce nano-porous material zeolite A and MCM -41 from coal fly ash and their application in environmental protection," *World Academy of Science, Engineering and Technology*. 2009
- [26] R. Juan, S. Herná'ndez, J.M.Andre's, and C. Ruiz, "Synthesis of granular zeolitic materials with high cation exchange capacity from agglomerated coal fly ash," *Fuel*, 2007: 86, pp. 1811–1821.
- [27] N. Koukouzas, I. Vasilatos, G.S. Itskos, and A. Moutsatsou, "Characterisation of CFB -coal fly ash zeolite material and their potential use in waste water treatment," Centre for Research and Technology, WOCA conference, Lexington, USA.. 2009
- [28] N. Murayama, T. Takahashi, K. Shuku, H. Lee, J. Shibata, "Effect of reaction temperature on Hydrothermal synthesis of potassium type zeolites from coal fly ash," *International J. Mineral Processing*, 2008: 87, 129–133.
- [29] X. Querol, C.U. Juan , F. Plana, A. Alastatuely, A. Lopez-Sole, A. Madinaceli, A. Valero, M. J. Domingo, and E. G. Rojo, ".Synthesis of zeolites from fly ash in a pilot plant scale," example of environmental application, in Institute of Earth Science 1999, International Conference on Ash Utilisation, Centre for Applied Energy Research University of Kentucky, USA.
- [30] S. S. Nam, M. W. Lee, S. Kim, K. W. Lee, M.K. Ko,,"Synthesis of Various Zeolites From Coal Fly Ash," *Environmental Res. Engineering*, 2000:5 (1), pp.35-40.
- [31] R. Szoastak, "Molecular Sieves, Principle of Synthesis and Identification," New York: Reinhold. 1989
- [32] V. E. Kiti, "Synthesis of zeolites and their application to the desalination of seawater," Masters Thesis submitted to the. Kwame Nkrumah University of Science and Technology Kumasi, Ghana, 2012
- [33] M. Flanigen, "Molecular sieves zeolite technology –the first twenty five years," *Pure and applied chemistry*, 1980: 52, pp. 2191-2211.
- [34] V. R. K. Vadapalli, W. Gitari, W. A. Ellendt, P. K. Petrik, and G. Balfour, "Synthesis of zeolite-P from coal fly ash derivative and its utilisation in mine water remediation," *South African Journal of Science*, 2010: 106(5-6), pp. 0033-2353