International Journal of Civil and Structural Engineering – IJCSE
Copyright © Institute of Research Engineers and Doctors
Volume 6 : Issue 2 - [ISSN : 2372-3971] - Publication Date: 27 Dec, 2019

Sulfates and Water Hardness Treatment of Wastewater by Zeolite Synthesis from Oil Palm Ash and Coal Bottom Ash

[Rewadee Anuwattana, Pattamaphorn Phuangngamphan, Narumol Soparatana and Worapong Pattayawan]

***Abstract*— This work focus on the synthesis of a NaA zeolite from oil palm ash and coal bottom ash and the CEC assessment of synthesized products. Zeolite synthesis was carried out at three alkaline salts (NaOH, KOH, $Ca(OH)_2$) and three time levels (1, 3 and 5 hours)at the temperature of 105 ^oC and two concentration of base concentration (1 and 3 M). Consequently, Zeolite NaA was produced from coal bottom ash with a good calcium exchange capacity (CEC) was used as sulfate, hardness, ammonia and phosphate adsorbent. The coal bottom ash and aluminium hydroxide sludge were sources of starting materials for Na-A zeolite (4A zeolite) conversion using the fusion prior alkali hydrothermal process. The coal bottom ash and NaOH were mixed at the weight ratio of 1:1.2 and 1:1:3 and then fused at 700 ^oC for 1 hour prior to the hydrothermal treatment. Sodium hydroxide solution of 3 M was added to the fused material and thoroughly stirred at 105± 3 ^oC in the stainless steel reactor. The reaction time was varied from 1 to 5 hours. The results showed that the highest CEC of Na-A zeolite was approximately 380 $mgCaCO_3/g$ zeolite and was obtained from the mixtures containing 3M NaOH, stirred for 5 hours. Results indicated that wastewater treatment by zeolite synthesis from coal bottom ash, sulfate removal of 36.88% and water hardness removal of 61.13%, respectively.**

***Keywords*— Na-A zeolite, Wastewater treatment, sulfate, hardness, Coal Bottom Ash, Aluminium Hydroxide Sludge, Fusion Method, Waste Utilization**

I. Introduction

The amount of coal usage in Mae Moh power plant, Thailand, has been increasing every year. It has increased proportionate to the increase in coal usage. Coal ash has been derived into fly ash and bottom ash. The eighty percentage of fly ash was reused in concrete and cement industry. However, bottom ash has not been useful and be deposed of ponds and used as for sand in the concrete blocks production. Disposal of bottom ash has become an increasing burden for economics and environment. Bottom ash from oil palm is the one type of solid waste. The extraction at 200 kg of crude oil palm from fresh fruit bunch and based on the processing at 1000 kg of EFB and general of solid waste is 750 kg which disposed as white to environment [1]. Utilization of these bottom ash have still been centralized at the building material product and the ratio of high additional value product is very low. However, process that turns these ashes into higher value added materials are becoming necessary to reduce environment impacts.

The main chemical composition of bottom ash from Power Plant and Oil palm ash have SiO_2, Al_2O_3 and the mineral composition is mainly glass phase such as quartz and mullite. Most of bottom ash could be synthesized high quality zeolite. Among the ashes and zeolite there are similarties on their composition, many researchers report that the coal bottom ash have in the amorphous phase aluminum silicate in mass composition, and there are precursor of synthetic zeolite. However, the bottom ash includes in the composition elements that by their nature make zeolite difficult to form (iron case), because of the high aluminum silicates content, these ashes become attractive soujrces in the synthesis of zeolite. [2]. Zeolite is a type of inorganic porous material which is framework structure hydrous aluminosilicate with special channel structure. It has a-three-dimensional framework of SiO_4 and AlO_4 tetrahedra of a high selectivity and high ion exchange capacity. It is widely used to dispose environment pollutant from water and air as adsorbent because its special adsorption, ion exchange and catalytic property. Zeolite have been used the sulfate and hardness adsorbent. [3] Therefore zeolite material are used as adsorbents for NH_4^+ removal [4].

Ammonia is toxic to giant fresh water prawn farm or fish if allowed to accumulate in giant fresh water prawn and fish production systems. If the ammonia concentration gets high enough (1-2 mg N/dm^3), the aquatic animal will become lethargic and eventually fall and die. The relative proportion of the two forms present in water is mainly affected by pH and temperature following the equation (1). Unionized ammonia is the toxic form and predominates when pH is high. [5-6]

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad (1)$$

Various technology treatment such as chemical precipitation, biological treatment, ion exchange, adsorption, electrochemical technology, and membrane process have been used for the removal of ammonium ions from wastewater. [7]

This is further aggravated by dumpling of mine waters into natural water reservoirs. In addition, underground water and surface water have increased levels of mineralization cause of hardness and sulfate to natural factor.

Rewadee Anuwattana, Pattamaphorn Phuangngamphan,
Naurmol Soparatana and Worapong Pattayawan

Expert Centre of Innovative Clean Energy and Environment,
Thailand Institute of Scientific and Technological Research
Thailand.

Hardness is the one point for water improvement. The two main cations that cause water hardness are calcium and magnesium. Because groundwater and mining are in contact with geologic formation for a longer period of time. The lignite coal cause serious problem from SO_4^{2-}. The data for the toxicology of sulfate shows that the high content of sulfate (>5,000 mg/L) can be inhibited the activity of microorganism and corrosion. Sulfate and hardness are the serious problem for reuse wastewater. The existing methods of sulfate removal from the wastewater using the compounds of calcium [8], barium [9], lime and aluminum coagulant [10-14]. Improvement in the wastewater reuse is required. One point for bottom ash useful subjected to the zeolite synthesis for water purification.

In this study, the fusion prior to the hydrothermal in zeolite synthesis from bottom ash and empty fruit bunches (EFB) ashes as a raw material to prepared Na-A zeolite were investigated is type of alkali solution. The optimum condition for high cation capacity of zeolite product was used for an adsorbent of hardness, sulfate, NH_4^+ and phosphate in wastewater reuse.

II. Experimental

Materials and Methods

The bottom ash sample was obtained from the Mae Moh Power Plant in Thailand and Nam Hong Palm Industry. They were ground below 150 µm before wet digestion by acid solution. The pretreatment of coal bottom ash is required to synthesize high quality zeolite. It was digested by acid digestion (3 M HCl activated at 60 °C for 30 minute) for removing organic matter and impurities. The obtained product was filter, washed and calcined at 700 °C for 3 hours. The obtained product was fused with alkaline salts (NaOH, KOH and $Ca(OH)_2$ in the ratio of 1:1.2 and 1:3 at 550°C for 1 hour. After that, the fused product slurry was prepared with DI water, Alkaline Solution, NaOH and $Al(OH)_3$ solution in the ratio (1:20:70:7) at 60 °C for 1 hour. The slurry precursor having the oxide molar composition: $13.75\ Na_2O \bullet Al_2O_3 \bullet 2.46\ SiO_2 \bullet 1433.2\ H_2O$ following by aging with stiring for 1, 3 and 5 hours at 105± 3 °C into the vessel. Finally, the product was washed to pH value of 7 and drying for 24 hours in a drying oven at 105 °C. The standard 4A was purchased from Thai Silicate Co, Ltd (Thailand).

Finally, the zeolite from bottom ash (ZBA) and NaA zeolite standard were was characterized the pattern of zeolite by X-ray Diffraction (SHIMADZULab X (XRD 6000)). The chemical composition was identified by XRFS, Model PW 2400, Philips and SEM, Model JSM 6400, Hitachi was used to investigate the morphology of the product. The cation exchange capacity (CEC) value of product were analyzed using calcium exchange capacity

Batch sorption experiment

The batch adsorption of sulfate (SO_4^{2-}), hardness and ammonium were also conducted in batch experiments. The 0.1g of standard NaA (Z4A) and zeolite A from bottom ash (ZBA) and zeolite A from EFB were left in contact with 100 ml of synthetic wastewater (mixed sulfate and hardness ion solutions by using sulphuric acid and calcium chloride (400 and 700 mg/l, respectively), Total Ammonia Nitrogen: TAN in synthetic = 10 mgN/dm^3 and equal to unionized ammonia = 1.95 mgN/dm^3 at the initial pH valves 8 at 26 °C for 1 hour. Aliquots of supernant were filtered with 0.45µ m filter. The residue sulfate content was analyzed by spectrophotometer and hardness content was analyzed by titration method. The initial and final NH_4^+ concentration remaining solution were analyze by the standard Nesslerization method by UV spectrophotometer at 425 nm. The removal efficiency of sulfate and hardness and NH_4^+ ions by the adsorbent is considered in percentage as:

$$\%\ Removal\ Efficiency = \frac{C_0 - C_e}{C_0} \times 100$$

Where Co is the initial concentrate of sulfate, hardness and NH_4^+ ions (mg/L)

Ce is the final concentrate of sulfate, hardness and NH_4^+ ions (mg/L)

III. Results and Discussion

Characterisation of Adsorbents

The results of chemical analysis by X-Ray Fluorescence spectrometry of the raw bottom ash from power plant and oil palm ash industry are presented in Table1. The composition of bottom ash presents as SiO_2 (37.71 %w/w) and Al_2O_3 (19.61 %w/w) as main oxides. The SiO_2/Al_2O_3 ratio of coal bottom ash is 3.276.

TABLE I. CHEMICAL COMPOSITION ANALYSIS OF RAW COAL BOTTOM ASH

Composition	coal bottom ash		oil palm ash	
	%wt	%mol	%wt	%mol
MgO	2.53	0.063	401	10.025
Al_2O_3	19.61	0.192	0.89	0.009
SiO_2	37.71	0.629	54.5	0.908
P_2O_5	0.22	0.001	3.47	0.022
CaO	2.54	0.045	6.37	0.114
MnO	0.43	0.005	0.141	0.002
Fe_2O_3	0.16	0.001	1.13	0.007
Na_2O	0.88	0.014	636 ppm	0.001
SrO	13.89	0.134	177 ppm	0.000
TiO_2	19.82	0.248	506 ppm	0.001
$SiO_2/\ Al_2O_3$	1.92	3.276	61.24	100.89

In the Figure 1, the result from XRD can confirmed that aluminum silicates and the activated oil palm ash was kaolinite (JCPDS NO. 06-0221) presents in the ashes which converted into NaA zeolite.

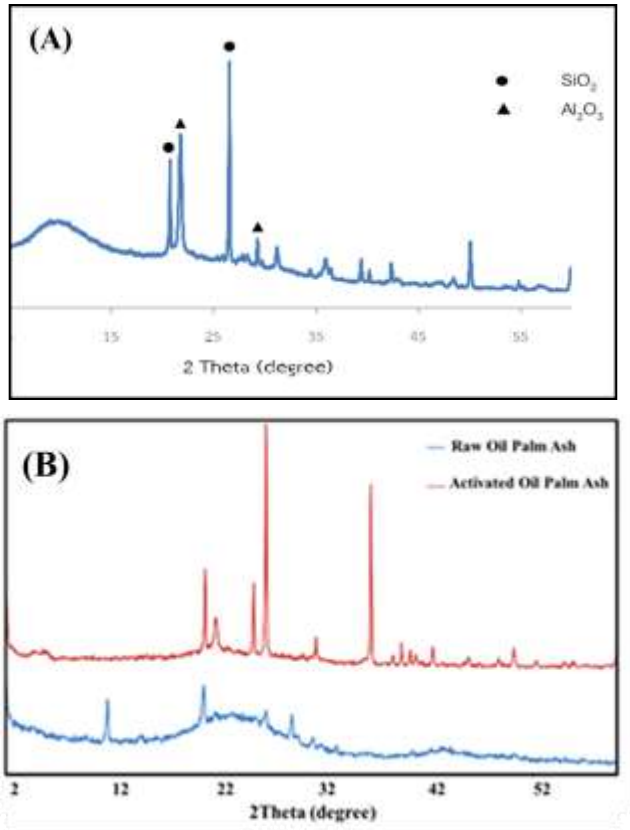

Figure 1. X-Ray Diffraction pattern of raw coal bottom ash (A) and oil palm ash (B)

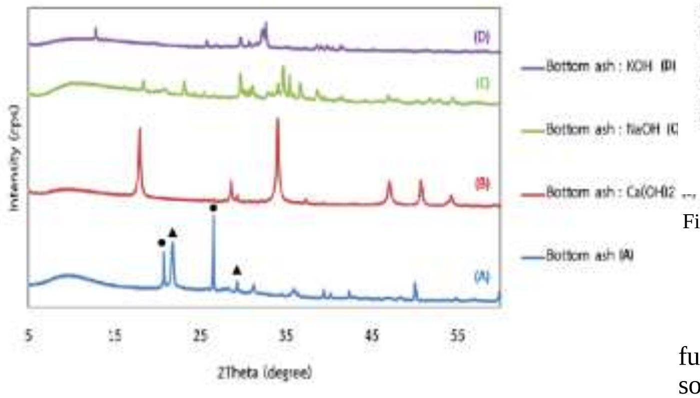

Figure 2. X-ray diffraction of the acid treated of the coal bottom ash (A), Acid treated coal bottom ash fused with $Ca(OH)_2$ (B), Acid treated coal bottom ash fused with NaOH (C) and Acid treated coal bottom ash fused with KOH (D) as the weight ratio of 1:1.2 at 550 °C for 1 hour.

(● = SiO_2 , ▲ = Al_2O_3)

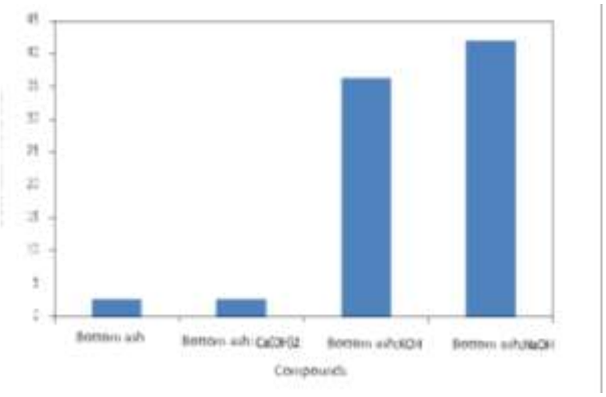

Figure 3. The dissolution rate of various fusion compounds.

From the Figure 2 shows that the disappearance of quartz and mullite peaks, that both quartz and mullite in the bottom ash have reacted with NaOH. The data of XRD shows Portlandite, ($Ca(OH)_2$), Dialuminium silicate oxide, ($Al_2(SiO_4)O$) is the main product of fused bottom ash: $Ca(OH)_2$. The main product of fused bottom ash with KOH is Dipotassium carbonate sesquihydrate, ($K_2(CO_3)(H_2O)$) and the main product of the fused bottom ash with NaOH is Sodium Aluminum Oxide, ($NaAlO_2$), Fukalite, ($Ca_4(SiO_2O_6(OH)_2(CO_3)$)), Sodium Iron Oxide, ($Na_4FeO_3$), Silicon dioide, ($(SiO_2)_{64}$), Cacium Carbonate, ($CaCO_3$) which is the good solubility. This results show that the suitable starting raw material is the fused bottom ash with NaOH in the weight ratio of 1:1.2 and 1:3. Figure 3 show that dissolution ratio of fusion NaOH compound is higher than fusion KOH compound and fusion $Ca(OH)_2$ compound.

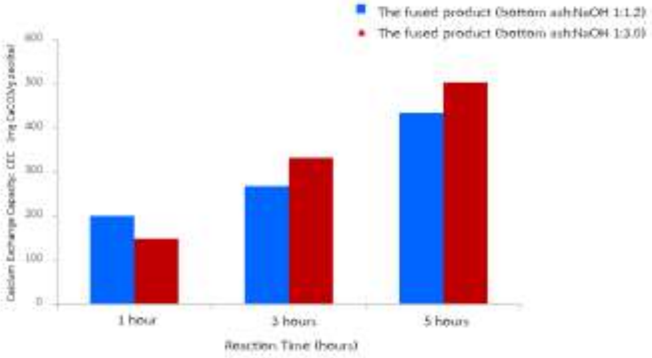

Figure 4. The calcium exchange capacity value of the fusion obtained product between treated bottom ash: NaOH as 1:1.2 and 1:3.

Therefore the amount of sodium hydroxide employed in fusion affects not only the converts of treated bottom ash into sodium aluminosilicate but the alkalinity of the solution in hydrothermal treatment can adjust the molar ratio of starting raw material. Figure 4 indicated that the fusion obtained product between treated bottom ash: NaOH as 1:3 activated in 3M NaOH at 105 °C for 5 hours.is the good calcium exchange capacity.

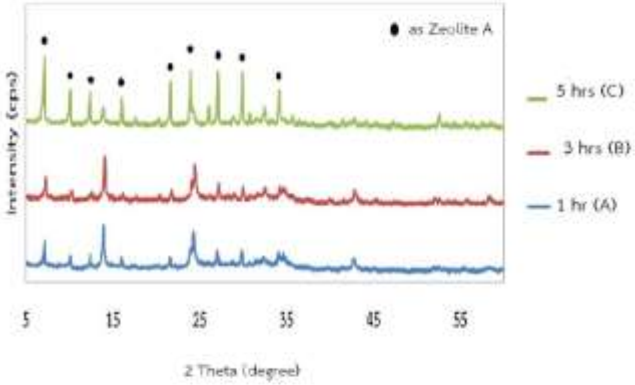

Figure 5. X-ray diffraction of the obtained productsby using the treated bottom ash fused with NaOH as 1:3 at 105 C for 1 hour (A), 3 hours (B) and 5 hours (C), respectively.

The XRD pattern of zeolite A from bottom ash, standard 4A zeolite and zeolite from oil palm ash show in Figure 6 and 7. It confirmed that the major crystalline phases of synthesized zeolite from oil palm ash were sodium aluminum silicate hydrate, as SCPDS NO. 11-0590. The XRD pattern of the zeolite A (ICDD No. 00-038-0241) from treated bottom ash fused with NaOH as 1:3 activated in 3M NaOH at 105 °C for 1,3 and 5 hours show the optimum condition is the treated bottom ash fused with NaOH as 1:3 activated in 3M NaOH at 105 °C for 5 hours. The XRD intensity of zeolite A will increase in longer reaction time. The result of CEC corresponds to the results of XRD pattern.

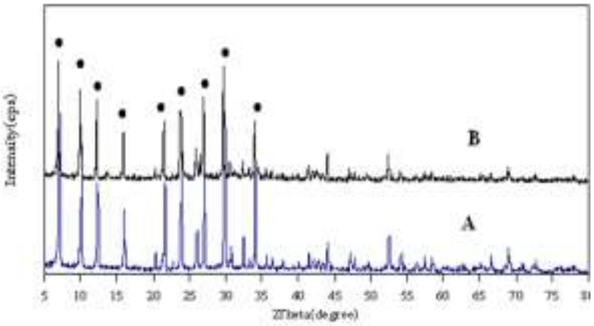

Figure 6. X-ray diffraction of the commercial NaN standard zeolite or standard 4A zeolite (Z4A) (A) and zeolite A from acid treated bottom ash (B).

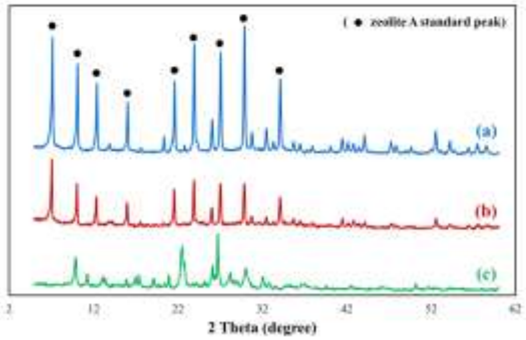

Figure 7. XRD pattern of the synthesized Na-A zeolite product from oil palm ash, (a) zeolite A standard, (b) zeolite from oil palm ash and (c) commercial zeolite

After hydrothermal zeolite synthesis, the XRD pattern of the commercial standard 4A zeolite (Z4A) and zeolite A from acid treated bottom ash is similar as shown in figure 6, indicating that the crystalline zeolite phase called zeolite 4A has been formed. It shape of the obtain product is look like cubic shape as shown in figure of 4. The calcium exchange capacity of the zeolite A standard, zeolite from oil palm and zeolite from bottom ash were 420, 386 and 380 mgCaCO$_3$/g zeolite.

Figure 8 shows the morphology of zeolite A standard, zeolite from oil palm and zeolite product from bottom ash with NaOH in the weight ratio of 1:3 and activated with 3M NaOH at 105 °C for 1,3 and 5 hours. The obtained product shows the cubic shape and similar with standard zeolite A.

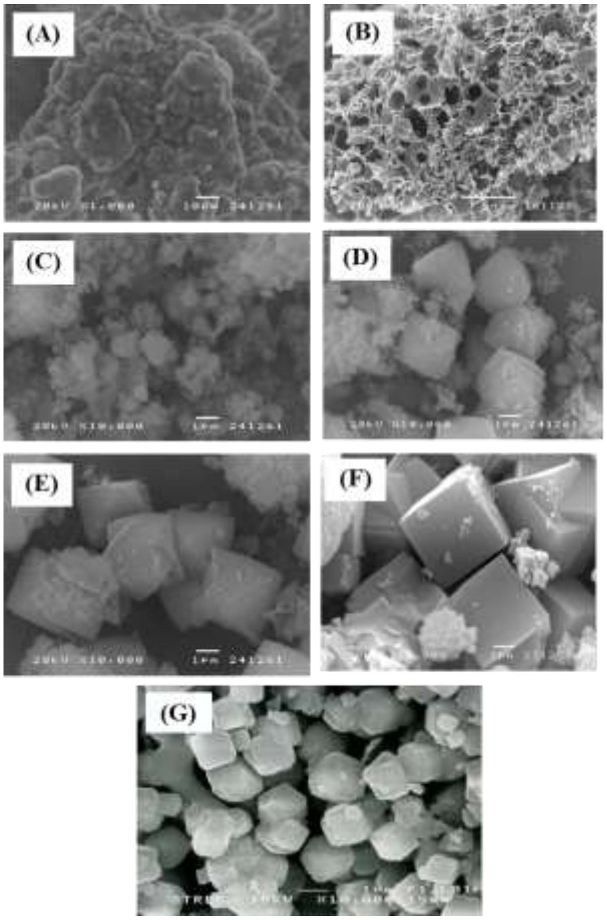

Figure 8. SEM pictures of the raw bottom ash (A), raw oil palm ash (B), zeolite A from treated bottom ash activated with 3M NaOH at 105 °C for 1 hour (C), 3 hour (D), 5 hour (E), and zeolite A from treated oil palm ash activated with 3M NaOH at 105 °C for 5 hour (F) and commercial 4A (G)

TABLE 3. THE RESIDUAL SULFATE, HARDNESS, AMMONIA AND PHOSPHATE BY USING VARIOUS ADSORBENTS

Sample	Sulfate mg/dm^3	Hardness mg/dm^3	Ammonia mgN/L	Phosphate mgP/L
Synthetic Waste water	488	710	2,700	210
Treated bottom ash 1:3 3M 5 hr	308	276	1,680	150
Treated oil palm bottom ash 1:3 3M 5hr	300	240	1,700	150
Raw bottom ash	447	468	2,100	200
Raw oil palm bottom	430	400	1,900	198

Table 3. displays the variation of sulfate and hardness ions value by using various adsorbents. The zeolite from acid treated bottom ash fused with NaOH as 1:3 and activated with 3M NaOH at 105 °C for 5 hrs is the good adsorbent for sulfate and hardness. The percentage of sulfate and hardness removal of zeolite form bottom ash were 16.3% and 61.13%, respectively.

IV. Conclusion

The Na-A zeolite synthesis from the coal bottom ash and oil palm ash were the calcium exchange capacity (CEC) of 386.39 and 380 mg $CaCO_3$/g of product, respectively. The 86.05% of pure Na-A zeolite phase from oil palm ash and 62% from coal bottom ash were formed. The CEC of zeolite A standard was 420.8 mg $CaCO_3$/g Zeolite. The optimum condition is activated treated coal bottom ash and oil palm ash with NaOH as the weight ratio of 1:3 at 550 °C for the activated with 3M NaOH at 105 °C for 5 hours. The calcium exchange capacity was 420 mg $CaCO_3$/g zeolite. The results of residual sulfate, hardness, ammonia and phosphate by using various adsorbents indicated that zeolite synthesis from the oil palm ash and coal bottom ash has a potential to be used as adsorbent for removing sulfate, hardness, ammonia and phosphate from wastewater.

Acknowledgment

This research was financial supported by the National Research Council Thailand (NRCT) and Thailand Institute of Scientific Research (TISTR). Special thank the financial supported from Electricity Generating Authority of Thailand (EGAT) and Agricultural Research Development Agency (Public Organization) are greatly acknowledge.

References

[1] M. Faisal, Mahidin, “Biomass Residue from Palm Oil Mills in Aceh Province: A Potential Usage for Sustainable Energy,” Adv. Eng. Inf. Tech, vol. 3, 2013.

[2] C.A.F.R. Junior, S.C.A Santos, C. A. G. Souzal, R.S. Angelica, and R.F. Neves, “Sintese De Zeolitas A Partir De Cinza Volante De Caldeiras: Caracterizacao Fisica, ” Quimica E. Mineralogica, Ceramica 58, pp. 43-52. 2012.

[3] R. Kikuchi, “Application of coal ash to environmental improvement: transformation into zeolite, potassium fertilizer and FGD absrobent,” Resourc.Conserv, Recycling, vol. 27, pp.333-346, 1999.

[4] Y. Zhao, B. Zhang, X. Zhang, J. Wang, J. Liu, and R. Chen, “Preparation of highly ordered cubic NaA zeolite from halloysite mineral for adsorption of ammonium ions,” Journal of Hazardous Materials, vol. 178, 2010.

[5] J.A. Hargreaves, and C.S. Tucker, “Managing Ammonia in Fish Ponds,” SRAC Publication, vol. 4603, 2018.

[6] D.J. Randall, and T.K.N. Tsui, “Ammonia toxicity in fish,” Marine Pollution Bulletin,vol. 45, 2002.

[7] Y. Wimalasiri, M. Mossad, and L. Zou, “Thermodynamics andkinetics of adsorption of ammonium ions by graphene laminateelectrodes in capacitive deionization,” Desalination, vol.357, 2015.

[8] V.N. Lebedev, “Sulphates removal of chemical purification of baddeleite concentrate from Kovdor GOKA,” Enrichment of ores, vol. 3 pp. 42–44, 2007.

[9] V.L. Kubasov, “The scheme of water purification from ions of sulphates,” Color Metallurgy, vol. 3 pp. 26-27, 2010.

[10] M.G. Berengarten, “Create of systems of clearing of mine waters,” Water: chemistry and ecology, vol. 1 pp. 13-17, 2008

[11] M. F. Hamoda, and S. M. Al-Awadi, “Improvement of effluent quality for reuse in dairy farm,” Water Sci.Tech, vol. 33, pp. 79-85, 1996.

[12] L.N. Butseva, “Purification of sewage from sulphates by lime and coagulation with using oxychloride aluminium,” Purification of natural water and sewage, pp. 49–51, 2009

[13] E.O. Salnikova, “The sulphate removal from water using lime and oxysulphate aluminium ,” Chemistry and technology of water, vol. 14(2), pp. 152-157, 1992.

[14] L. Curkovic, S. Cerjan-Stefanovic and T. Filipan, “Metal Ion Exchange and Modifiied Zeolite,” Water Research, vol. 31, pp.1379-1382, 1996.