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Adsorption of Deltamethrin using Aluminosilicate Synthesized from Wheat straws: A Greener Approach

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ABSTRACT: Aluminosilicate (zeolites) were prepared from wheat straws. Physicochemical properties of zeolites were characterized by scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDX). The examinations showed that the synthesized product was crystalline in nature and size obtain was 5µm. Adsorption characteristics of the pesticide deltamethrin was studied in aqueous solution through Ultra Fine Liquid Chromatography (UFLC). The adsorption results show that the modified zeolite was better as compare to unmodified zeolites.

KEYWORDS: Adsorption, Deltamethrin, Zeolite, CTAB.

1 INTRODUCTION

In the last few decades water pollution by organic and inorganic chemical pollutants has become a major public concern (Oketola & Fagbemigun. 2013). Pesticides are considered the most hazardous organic pollutants encountered in wastewater effluents (Koner et al., 2012) due to their high stability and toxicity, usage in huge quantities, and wide applications for many purposes, particularly the production of massive quantities of crops. Pesticides are a diverse group or concoction of chemical compounds, biological agents, antimicrobials, disinfectants that are deliberately applied for selective management and reduction of pests including insects, plant pathogens, weeds, birds, nematodes, and microbes that destructively affect the production, processing, storage, transport, marketing of food or spread of diseases (Corsini et al., 2008; Corsini et al., 2013). Pesticides belonging to Organochlorine, carbamate, pyrethroid and herbicide groups are mostly used for the control of pest and weeds due to its cost effectiveness and easy availability. Deltamethrin is a one of synthetic pyrethroid that destroys insects on contact and through digestion (Hasan et al., 2013). It is used for many agricultural crops and home pest control throughout the year, and consequently is widespread in the environment. Moreover, it is non-degradable during storage and it is stable when exposed to atmospheric oxygen and sunlight. Acute and chronic effects on the human body include convulsions leading to muscle fibrillation and paralysis, diarrhea, dermatitis, headache, peripheral vascular collapse, vomiting, hypotension, prenatal damage, shock, and death due to respiratory failure.

Different methods have been studied for the elimination of pesticides, metals, dyes and other pollutants from the aqueous solutions such as photo catalytic degradation (Aungpradit et al., 2007), biological oxidation (Dehghani et al., 2014), nano filtration (Ahmed et al., 2008), ozonation (Maldonado et al., 2006) and adsorption (Mon et al., 2009; Ayar et al., 2008). But all these techniques except adsorption require capital cost to establish exclusive instruments for the check and balance before and after installation of these high technology processes, prerequisite of power and also production of noxious sludge or by-products for disposal. Adsorption on a solid surface is most important and useful method for removal of pesticides due to its effectiveness at low contaminant concentration, selectivity, and regenerability and cost efficiency pesticides (Sergiane et al., 2010). Activated carbon is primarily used solid adsorbents because its removal efficiency is very high and used on a wide scale due to its pore size and surface area and wide range of contaminants are elimination (Salman et al., 2012). But it is considered an expensive adsorbent due to the use of raw materials which are costly and valuable natural resources such as coal. Therefore zeolite is used as adsorbent because several agricultural waste products are used as raw material for its synthesis, like sugarcane baggase (Purnomo, 2013) and rice husk (Tan et al., 2011).

The present study was designed on the green route synthesis of Si-Al Zeolites by utilizing the waste of crops towards sustainable development. Wheat straw was used as silica natural precursor. Whereas, aluminum foil (spent) is accepted as alumina source.

2 METHODOLOGY

2.1 PREPARATION OF WHEAT STRAW ASH (WSA)

The wheat straws obtain from local market was treated with 3M hydrochloric acid (HCl) for 6 hours for preliminary removing all impurities. The treated wheat straws were washed thoroughly with distilled water, dried at 100 ^{0}C and pyrolyzed at 600 ^{0}C for 6 hours in furnace. The white ash obtain was used as silica source.

2.2 PREPARATION SEED GEL AND FEED STOCK GEL

The procedure for the synthesis of Zeolites follows the layout of (Tan et al., 2011), and is briefly described below:

A Teflon beaker containing a magnetic stirrer was used for the seed gel preparation. Sodium hydroxide pellets was dissolved in distill water to make clear solution, add WSA as silica source and heated under vigorous stirring to obtain a homogenous mixture represented as mixture A. In another beaker made sodium hydroxide solution and add spent aluminum foil and stir to made sodium aluminate solution as mixture B. Both mixture A and B were mixed together and aged for 24hours at room temperature in the teflon bottle and used as seed gel. The silicate (mixture A) and aluminate (mixture B) solutions were mixed together in the Teflon beaker, subsequently stirred for 2hrs with the purpose of making it completely homogenized. This combined solution

was used as the feed stock gel. Both the gels were mixed together and stir for 5hrs and aged for one day for the crystallization. After this the obtain crystals were decanted and thoroughly washed with distill water for several times and obtain the zeolite coded as WSZ. The whole process was represented in Figure 1. The obtain zeolite was modified by using cationic surfactant, cetyltrimethylammonium bromide (CTAB), to enhance the surface characteristics of the materials. A known mass of the zeolite was vigorously stirred with 0.5 molar aqueous solution of CTAB filtered and oven dried. The dried modified zeolite was coded WSZ_m.

2.3 CHARACTERIZATION

The energy dispersive X-ray spectroscopy (EDS) analyser (Hitachi X-650 scanning electron microanalyser) that was coupled to the SEM was used to identify the chemical composition of a specific area of a sample and to observe the size and shape of crystals in the zeolitic material synthesised.. Before analysis, the samples were dried, ground to a fine powder, spread on a carbon tape mounted on an aluminium stub and coated with graphite to make them conductive.

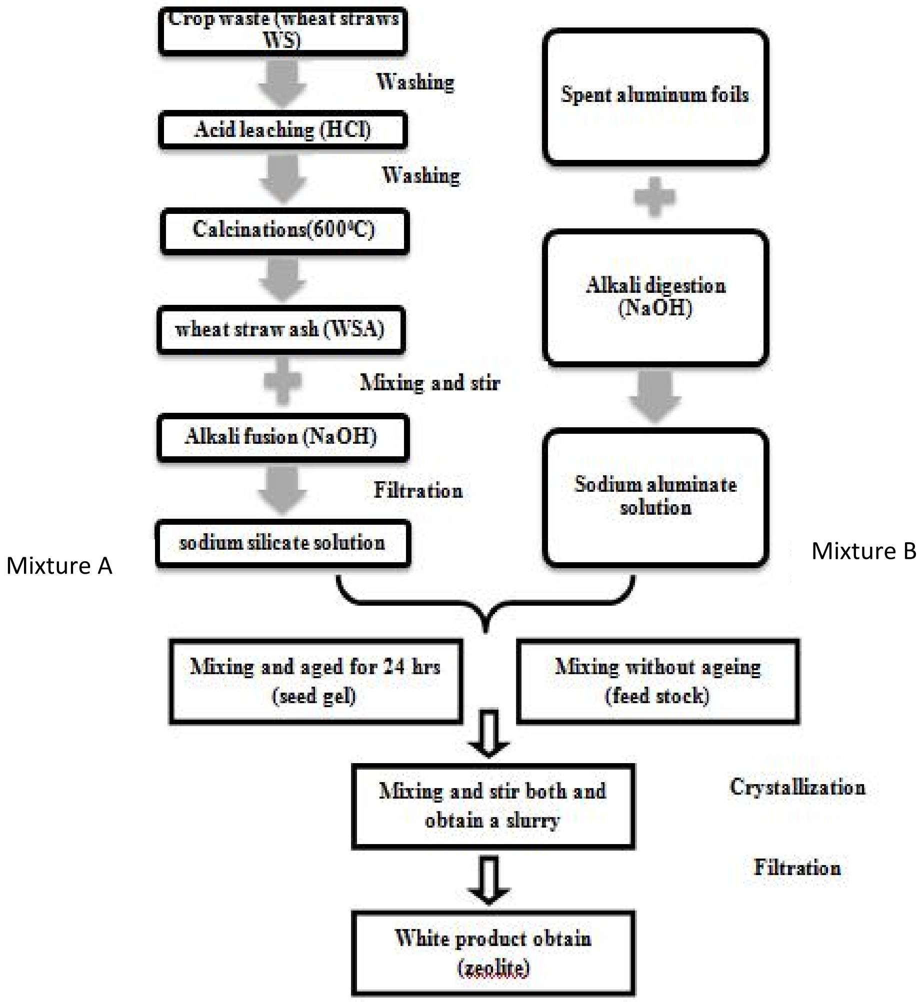


Figure.1. Flow diagram of zeolite synthesis

2.4 ULTRA FINE LIQUID CHROMATOGRAPHY (UFLC) ANALYSIS

The synthesized zeolites were subjected to analyze the pesticide adsorption by Ultra Fine Liquid Chromatography (UFLC). The adsorption process follows the layout of (Uddin et al., 2013). The pesticide were determined on Ultra Fine Liquid Chromatography (LC-2010, Schimadzu) equipped with UV detector and Reverse phase HS-C18 column (250mm 4.6mm).

2.4.1 STANDARD SOLUTION AND MOBILE PHASE

Standard solution (1 mg/L) of pesticide (deltamethrin) was injected (10-µL) using micro syringe into the column, followed by elution with a solvent mixture of acetonitrile (ACN) and water (H_2O) in 65:35 ratios at 0.5mL/minute. The calibration curve was constructed with three working standards of known strengths. UV wavelength selected for deltamethrin was 254nm.

2.4.2 EXTRACTION

Pesticide was extracted from water by liquid-liquid extraction. If pesticide was not present in the water than was spiked with desire pesticide concentration. To remove the pesticide from the water we have to use the solvent whose polarity is close to the target compound so, n-hexane along with water was taken into separatory funnel and shaking for 5 minutes. Two distinct layers were formed. The hexane extract was separated and collected in evaporating flasks. Same process was repeated two times and combines all the extracted hexane in flask. Water present in the extract was removed by treating it with anhydrous sodium sulfate and the organic solvent from water free extract was evaporated in a rotary evaporator to a small volume (Approx. 1 mL) and appends acetonitrile to make 10mL of the aliquot and transferred to a glass-Stoppard test tube for UFLC analysis.

3 RESULT AND DISCUSSION

The present investigation is centered on the green route synthesis of Zeolites (aluminosilicates) and further enhancement of surface area of the synthesized materials through modification with cationic surfactant. The application is also envisaged for the adsorptive removal of pesticide.

3.1 EDX AND SEM ANALYSIS

The zeolites synthesized using green approach was characterized for its physio-chemical properties. Figure 2 shows the elemental composition of raw and synthesized zeoites determined on Energy dispersive X-ray Spectrometer. It can be seen that aluminium, oxygen, silica and sodium are the major elements identified in the zeolites while carbon was present in the modified product which confirm the successful incorporation of surfactant. Figure 3 represents the micrographs of the zeoites. The addition of surfactant to zeolites significantly impacts the morphological characteristics. It is evident (see Figure 3 (b)) that more uniform distribution of particles with crystalline geometry appears on addition of CTAB.

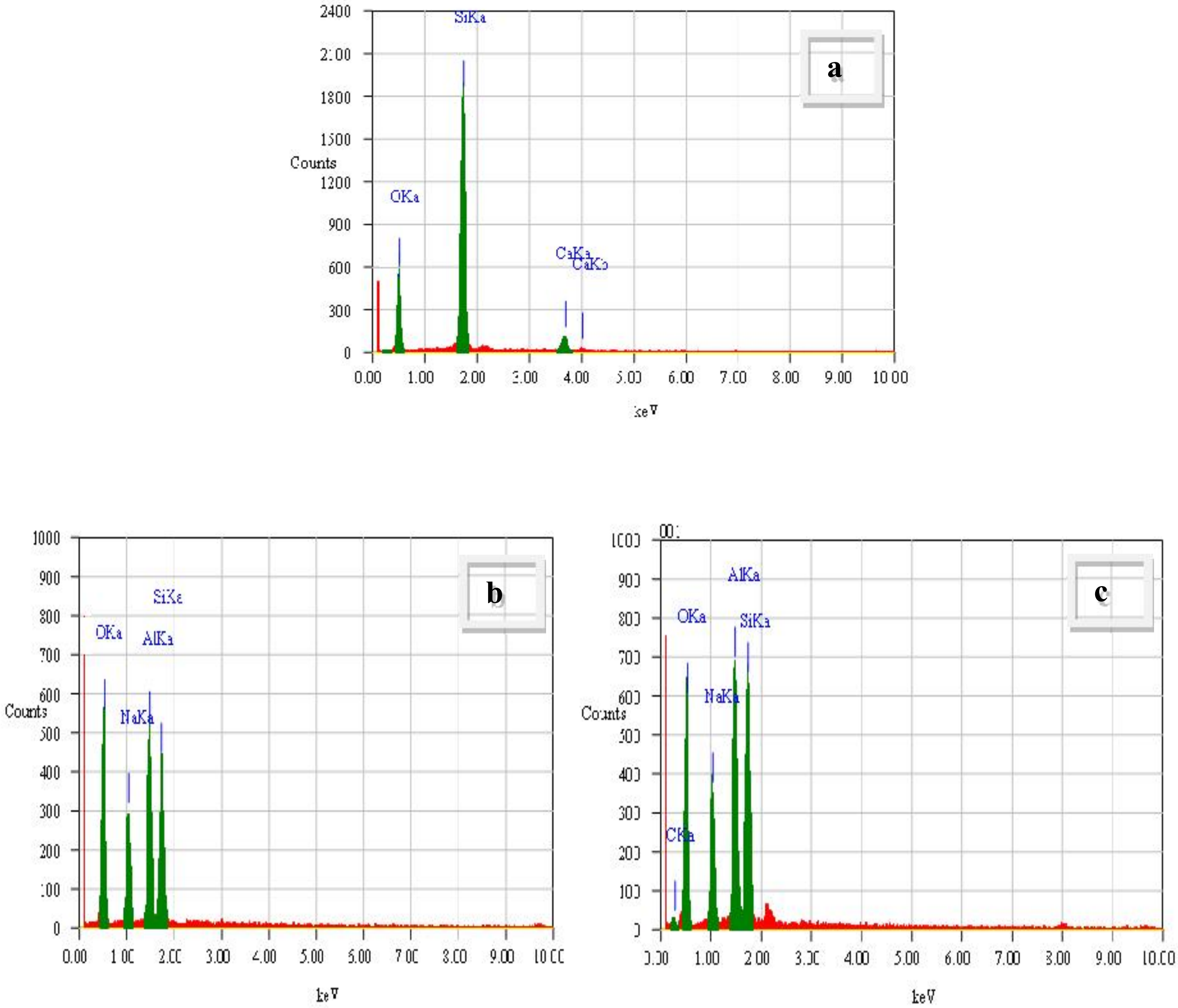
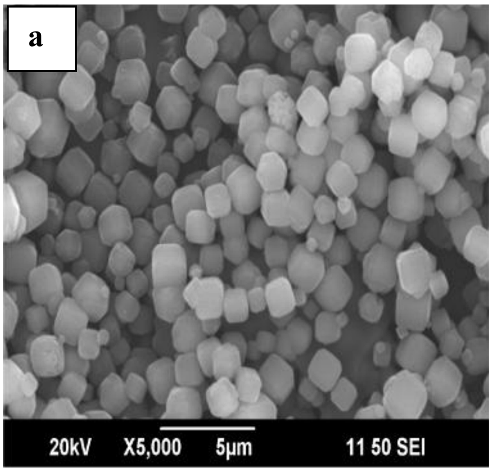


Figure.2. EDX analysis of (a) Wheat ash (b) WSZ and (c) WSZ$_m$



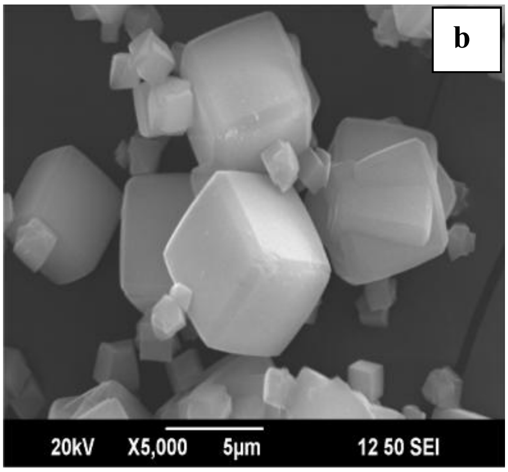


Figure.3. SEM images of (a) WSZ and (b) WSZ_m

3.2 UFLC ANALYSIS

The synthesized zeolites were applied as adsorbents to determine efficiency for the removal of pesticides and estimated on Ultra Fine Liquid Chromatography (UFLC).

The stock solution of the standard pesticides was 1 mg/L. From this we prepared three working standard solutions for the calibration with 0.03, 0.06 and 0.09 mg/L concentrations by adding the proper amount of stock standard solution and making dilutions with solvent. Calibration curves of the pesticides are shown in Figure 4.

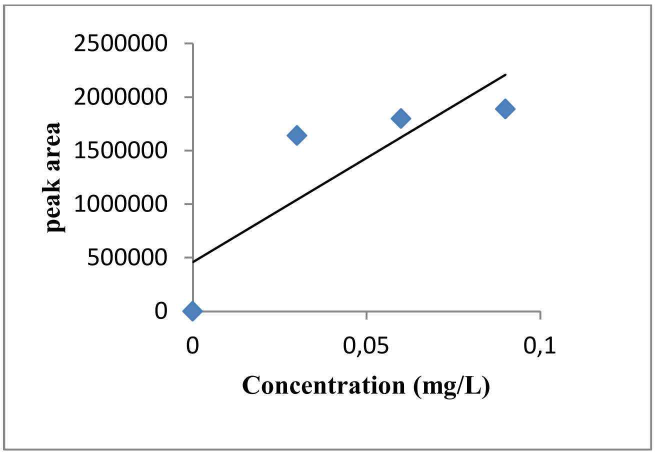


Figure.4. Calibration curve for Deltamethrin

The constant concentration of pesticide was adsorbed on a known mass of synthesized adsorbent (zeolite). The mixture was stirred for 30 minutes, filtered and an aliquot (10 µL) of filtrate was injected on UFLC. The retention time of pesticide was determined from standard calibration curve which was 4.8 minutes for deltamethrin.

Quantitative analysis was done by Limit of quantification (LOQ) and Limit of detection (LOD). LOQ was defined as the lowest concentration of the analyte that could be compute with adequate exactitude and accuracy. The Limit of detection (LOD) was defined as the lowest concentration of the analyte in a sample that could be detected but not necessarily measured. The LOQ and LOD were assessed as signal-noise ratios (S/N) of 10: 1 and 3 : 1, correspondingly, and were attained by evaluating un-spiked samples (Falqui-Cao et al., 2001). In the present investigation, LOD and LOQ results are summarized in Table 1.

Table.1. Quantitative analysis (Limit of detection and Limit of quantification) of pesticide

Compounds	Deltamethrin
LOD	1.16655E-07
LOQ	3.535E-07

The synthesized adsorbents were applied to determine their efficiency for the removal of the pesticide. The known concentration of pesticides along with the constant mass of the adsorbent was taken in a flask and shaken for 30 minutes. After that the solution was filtered and analyze by UFLC.

Figure 5 shows the pesticide peak area before and after the application of adsorption process and it illustrates that after adsorption there was a definite reduction in the peak area which explain that zeolite were good adsorption capacity towards the deltamethrin. And it is concluded that modified zeolite from crop waste (WSZ_m) was more efficient than unmodified zeolite (WSZ). The adsorption trends of synthesized adsorbents were as follow:

WSZ_m>WSZ

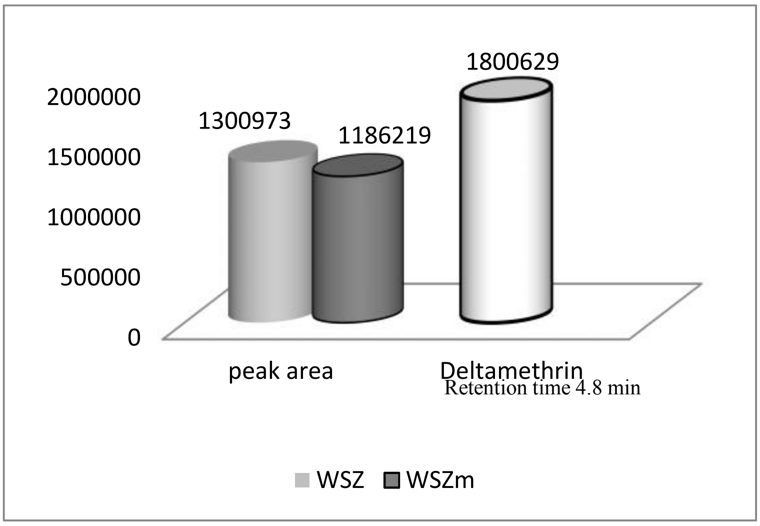


Figure.5. Peak area of Deltamethrin with and without use of adsorbents

4 CONCLUSION

Zeolites were synthesized using greener approach by utilizing the waste of wheat straws and spent aluminum foil as silica and alumina source respectively towards sustainable development. Zeolite was synthesized by hydrothermal process and later on modified by cationic surfactant cetyltrimethyl ammonium bromide (CTAB). The synthesized zeolites were characterized to study the physio-chemical properties using different standardized techniques of SEM along with EDX for identification of surface morphology and elemental composition of the obtain product. All these confirm the synthesis of the Zeolite from waste. The synthesized materials are also subjected as adsorbents for the removal of pesticide (deltamethrin) and it was concluded that zeolites has better adsorption capacity for deltamethrin. While modified Zeolite from crop waste (WSZ_m) was more efficient than unmodified Zeolite (WSZ).

REFERENCES

[1] Ahmad, S., Zia-Ul-Haq, M., Imran, M., Iqbal, S., Iqbal, J., & Ahmad, M. (2008). Determination of residual contents of pesticides in rice (Oryza sativa L.) crop from different regions of Pakistan. *Pakistan Journal of Botany*, 40(3), 1253-1257.

[2] Aungpradit, T., Sutthivaiyakit, P., Martens, D., Sutthivaiyakit, S., & Kettrup, A.A.F. (2007). Photocatalytic degradation of triazophos in aqueous titanium dioxide suspension: identification of intermediates and degradation pathways. *Journal of Hazardous Material,* 146, 204-213.

[3] Ayar, N., Bilgin, B., & Atun, G. (2008). Kinetics and equilibrium studies of the herbicide 2, 4-dichlorophenoxyacetic acid adsorption on bituminous shale. *Journal of Chemical Engineering*, 138(239), 48-26.

[4] Corsini, E., Liesivuori, J., Vergieva, T., Van Loveren, H., & Colosio, C. (2008). Effects of pesticide exposure on the human immune system. *Human & experimental toxicology*, *27*(9), 671-680.

[5] Corsini, E., Sokooti, M., Galli, C. L., Moretto, A., & Colosio, C. (2013). Pesticide induced immunotoxicity in humans: a comprehensive review of the existing evidence. *Toxicology*, *307*, 123-135.

[6] Dehghani, M., Nasseri, S., & Karamimanesh, M. (2014). Removal of 2, 4-Dichlorophenolyxacetic acid (2, 4-D) herbicide in the aqueous phase using modified granular activated carbon. *Journal of Environmental Health Science and Engineering*, *12*(28).

[7] Dehghani, M., Nasseri, S., & Zamanian, Z. (2013). Biodegradation of alachlor in liquid and soil cultures under variable carbon and nitrogen sources by bacterial consortium isolated from corn field soil. Iran J Environ Health Sci Eng, 10(1), 21.

[8] Falqui-Cao, C., Wang, Z., Urruty, L., Pommier, J. J., & Montury, M. (2001). Focused microwave assistance for extracting some pesticide residues from strawberries into water before their determination by SPME/HPLC/DAD. Journal of agricultural and food chemistry, 49(11), 5092-5097.

[9] Hassan, A. F., Youssef, A. M., & Priecel, P. (2013). Removal of deltamethrin insecticide over highly porous activated carbon prepared from pistachio nutshells. *Carbon letters*, *14*(4), 234-242.

[10] Maldonado, M.I., Malato, S., Perez-Estrada, L.A., Gernjak, W., Oller, I., Domenech, X., & Peral, J. (2006). Partial degradation of five pesticides and an industrial pollutant by ozonation in a pilot-plant scale reactor. *Journal of Hazardous Material,* 138 (2), 363-369.

[11] Mon, E.E., Hirata, T., Kawamoto, K., Hiradate, S., Komatsu, T., Moldrup, P., 2009. Adsorption of 2,4-Dichlorophenoxyacetic Acid onto Volcanic Ash Soils: Effects of pH and Soil Organic Matter. *Matter Environment Asia,*1,1-9.

[12] Oketola, A.A., & Fagbemigun, K.T. (2013). Determination of Nonylphenol, Octylphenol and Bisphenol-A in Water and Sediments of Two Major Rivers in Lagos, Nigeria. *Journal of Environmental Protection*, 4(7A), 38-45.

[13] Purnomo, C. W. (2013). Utilization of bagasse fly ash for carbon–zeolite composite preparation. *Journal of Porous Materials*, *20*(5), 1305-1313.

[14] Salman, J. M., & Al-Saad, K. A. (2012). Adsorption of 2,4-Di- chlorophenoxyacetic Acid onto Date Seeds Activated Carbon Equilibrium, Kinetic and Thermodynamic Studies. *International Journal of Chemical Sciences*, 10(2), 677-690.

[15] Sergiane, S.C., Demoliner, A., Fabiane, P.C., Marcelo, G.M.D., Ednei, G.P. (2010). Pesticide residue determination in groundwater using solid-phase extraction and high-performance liquid chromatography with diode array detector and liquid chromatography-tandem mass spectrometry. *Journal of Brazilian Chemical Society*, 21(4), 642–650.

[16] Tan, W. C., Yap, S. Y., Matsumoto, A., Othman, R., & Yeoh, F. Y. (2011). Synthesis and characterization of zeolites NaA and NaY from rice husk ash. *Adsorption*, *17*(5), 863-868.

[17] Uddin, M. A., Saha, M., Chowdhury, M. A. Z., & Rahman, M. A. (2013). Pesticide Residues In Some Selected Pond Water Samples Of Meherpur Region Of Bangladesh. *Journal of the Asiatic Society of Bangladesh, Science*, *39*(1), 77-82.