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Synthesis and Characterization of Potassium Silicate Fertilizer Using Fly Ashes of Bituminous and Sub-bituminous and Lignite Coal

M. Imran[1], K.Shahzad[1], S. Munir[1], M. Wasim[2], A. Hussnain[3]

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Abstract

The Present study focuses on coal fly ash, a waste acquired from coal power plants for the synthesis of potassium-based fertilizer using coal fly ash and lignite with the simple blending of KOH and adding a small amount of citric acid. Lignite and two types of fly ash bituminous and sub-bituminous were utilized for the formulation of fertilizer. X-ray diffraction (XRD) revealed the occurrence of quartz and oxides of potassium in all fly ashes. XRD pattern also exhibited the orthoclase, mullite, and zeolite as major compounds in fertilizer which should be synthesis from sub-bituminous ash. K_2O, P_2O_5, and N were determined as essential compounds in sub-bituminous through wet analysis. However, a major presence of humic acid and organic matter was observed in lignite through wet analysis. Fourier transform infrared (FTIR) spectroscopy also confirmed the occurrence of humic acid in the form of a carboxylic group in lignite and bituminous. Surface Mean Diameter measured by sieve analysis showed that particle size of sub-bituminous ash was smaller than others that most appropriate for synthesis of potassium silicate fertilizer.

***Keywords**: Fly Ash, Fertilizer, Xrd, Humic Acid, Lignite*

1. Introduction:

Coal combustion fly ash as a soil amendment in agricultural lands describing the fly ash as important waste material that had the potential to improve soil physical, chemical, and biological properties due to the presence of essential plant nutrients [1-8]. Fly ash can be used with chemical fertilizer as it reduces the cost by utilizing half percentage of chemical fertilizer, increasing soil fertility and crop yield, the best source of nutrients for acidic soil and having minimum environmental pollutants [9-10]. Fly ash contains the essential minerals in the form of different oxides, while such minerals were investigated by X-ray diffraction (XRD) technique that was used to examine those minerals [11-12].

The improvement of fertilizer produced from coal fly ash was carried out [13] to eliminate the toxic elements present in coal ash as the heavy metal load to a threshold level that was increased through repeated application of coal fly ash to soil. It also describes to overcome the research gaps of refining the ash before its utilization in agriculture as a fertilizer and also fly ash showed the immense potential to supply the phosphorus (P) in crop production as a major element. In their study chemical concentration of major elements as oxides in different ashes from different countries was analyzed using X-ray fluorescence (XRF) spectrometry and also determines the typical

[1] *Center for Coal Technology, University of the Punjab, Lahore-Pakistan.*
[2] *QA Lab, Millat Tractors Ltd, Lahore-Pakistan.*
[3] *Department of Physics, GC University, Lahore-Pakistan.*
***Corresponding Author:** (khurram.icet@pu.edu.pk)

elements required for plant growth.

Due to increased energy consumption, many countries are dependent on coal for power generation leading to unfavorable and hazardous environmental conditions as its disposal has become a serious burning issue in the world. Both India, as well as China, has numerous Coal Power Plants to fulfill the energy demands and the annual production in million tons of fly ash is 112 and 100 whereas the percentage utilization is only 38% and 45% respectively. In another end, a risk factor is also involved for the utilization of CFA to soil due to presence of small amounts of Cr, Si, Hg, Pb, and Ar as toxic metals. These heavy metals percolate to the soil and pollute the groundwater [14].

Coal ash consists of the maximum percentage of silica and crystal structure of mullite formed by combining silica to alumina, as the second-highest percentage element in fly ash. A complex chemical compound is formed by the reaction of silica with magnesia and caustic potash as Coal Fly Ash (CFA) is mainly consisted of silica and alumina. These are vitreous and cannot be directly absorbed by crops. Silicate reacts with magnesia and caustic potash to form a chemical complex (i.e., Calcium Potassium Silicate) and crops can easily absorb nutritional elements such as silicate, potash, and magnesia contained in this complex [15].

Many researchers contributed to CFA to determine the elements in fly ash and also treat this ash with KOH by varying concentrations which will be helpful for soil fertility and further suitable for plant growth. There is still a research gap between the development of potassium silicate fertilizer by CFA and its utilization in agriculture. Pakistan coal power plants dumped the CFA in the landfill. This study aims to determine the valuable minerals in CFA and their effective use to synthesize the fertilizer locally. Future researchers can lead this research study with the help of biological sciences and apply this potassium silicate fertilizer to plant growth.

2. Materials and Methods:

There are following three samples which were collected from three different sources:

Table 1: Sources of Samples

Sample Identification	*Source*	*Details*
A1 (Lignite Coal)	*Patala Formation, Khewra, District Jhelum-Pakistan*	*N/A*
A2 (Bituminous)	*Nishat Dying & Fishing Pvt. Ltd. Lahore-Pakistan*	*Plant Capacity=6MW/h* *Steam Temperature=485 °C* *Air Pressure = 5.3 Mpa*
A3 (Sub-bituminous)	*ICI Pakistan Limited Soda Ash Khewra District Jhelum-Pakistan*	*Plant Capacity=18MW/h* *Steam Temperature=485 °C* *Air Pressure = 7 Mpa*

After the collection of samples, 16% w/v solution of KOH was prepared and then slowly mixed with the citric acid solution. It was an exothermic reaction evolving a lot of heat which was measured as 280 °C by a thermometer. All samples were treated with Potash-Citric acid solution in ratios i.e. 62: 30: 08 (CFA: KOH: Citric acid) as Potassium is known as a quality nutrient and it is needed to sustain the plant growth so the fertilizer with more concentration of Potassium was selected for further processing [10, 16]. Finally, the mixture of fertilizer (Potassium-silicate fertilizer) was placed in sunlight (15 to 26 °C) for two days to remove moisture. The flow sheet of the complete process is presented in Figure 1.

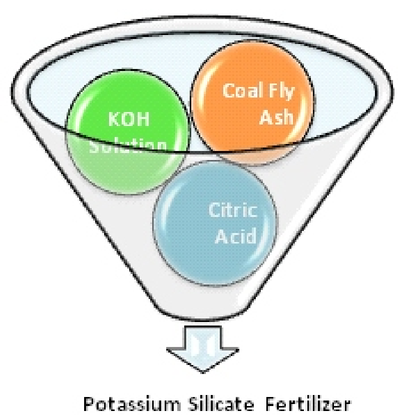


Figure 1: The Flow Sheet process of Fertilizer.

Three Samples of coal after treatment with KOH were designated as B1, B2 and, B3. Both KOH treated (B series) and untreated samples (A series) were qualitatively analyzed using the XRD technique (Figs 2 & 3).

Percentages of N, K_2O, P_2O_5, organic matter, and humic acid were measured in all treated samples using wet analysis whereas functional groups in humic acid were detected through Fourier Transform Infrared Spectroscopy (FTIR).

Sieve analysis has also been performed to find out the surface mean diameter (SMD) of untreated samples. Coal fly ash produced from different power plants contained variable particle size as it depends upon the parameters i.e. temperature, slit size, etc.

3. Results & Discussion:

3.1 X-rays Diffraction Results:

The XRD pattern of untreated coal fly ash samples (A1, A2, A3) is shown between intensity and angle 2è in Figure 2. The sharp peak of Aluminum Silicate Oxide (Al_2SiO_5) was observed at an angle of 26.64° in sample A1. In this ash sample, the compounds tetra potassium pyrophosphate ($K_4P_2O_7$) and potassium phosphate (KPO_3) were also detected at 2è position 30.57° and 26.40° respectively. A sharp peak of quartz (SiO_2) was observed in both samples A2 and A3 at 2è position 26.64°. Calcium oxide (lime) was also observed at an angle of 37.09 in sample A2. Pengthamkeerati et al. [17] also reported the silicon and calcium oxides at the same 2è position observed in untreated fly ash (Fig. 2). Ward et al. [18] & Jeong et al. [19] also mentioned the quartz phase in untreated coal fly ash. Sample A3 contained the all necessary oxides that helped to develop the potassium silicate fertilizer. At an angle of 25.43 & 23.580 potassium oxide (KO_2) & Potassium nitrate

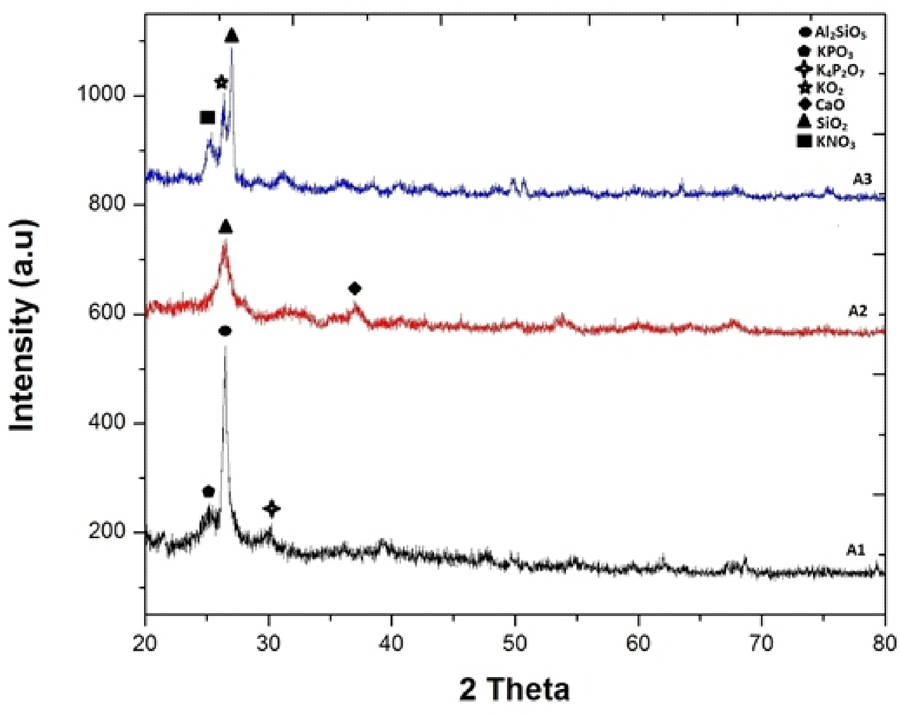


Figure 2: XRD Pattern for untreated Coal Fly Ash.

Figure 3 shows the XRD pattern between intensity and 2θ of KOH treated fly ash i.e. potassium silicate fertilizer. The sharp peak of quartz (SiO_2) was observed in both samples B1 and B2 at 2è position 50.21°, 68.19 and, 26.64° respectively which shows the silica haven't react to form new compounds but the presence of silica in B1 react with Zr to form $ZrSiO_4$ at 2θ position 26.78°. Fly ash sample A1 contained a small amount of Hg as toxic metal. This heavy element Hg reacted with the sulfur present in this sample to form HgS thus confirmed by XRD patterns at 2θ position 31.15. XRD pattern of B1 confirmed the presence of potassium hydrogen phosphate K (H_2PO_4) at 2è position 73.57°.

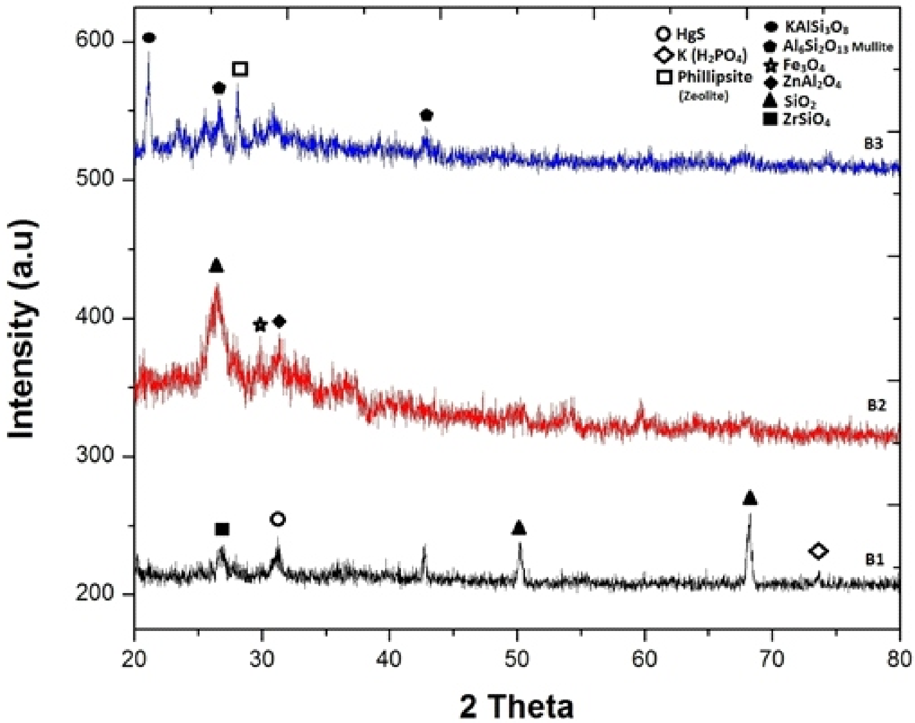


Figure 3: XRD Pattern for KOH-treated Coal Fly Ash (Fertilizer)

In sample B2, magnetite (Fe_3O_4) & gahnite ($ZnAl_2O_4$) at 2è positions 29.78 ° & 33.31° were detected respectively. In sample B3, orthoclase ($KAlSi_3O_8$) mullite ($Al_6Si_2O_{13}$), phillipsite-K (Zeolite $(K_2)_{0.48}Ca_{0.52}Al_2Si_4O_{12} \cdot xH_2O$), 2$\theta$ positions 21.01°, 26.03°, 27.86° were observed respectively. Pengthamkeerati et al. [17] and Jeong et al. [19] demonstrated the mullite ($Al_6Si_2O_{13}$) phases in both treated and untreated fly ash respectively. In [17] study NaOH treatment was given to ash particles, magnetite, and zeolite were formed whereas in [19] research 6N KOH treatment was given to ash particles at different sintering temperatures, after XRD analysis the compounds of mullite and potassium aluminum silicate were observed in ash samples.

The main purpose of this research was to develop the potassium silicate fertilizer using coal fly ash. Figure 3 clearly shows the formation of new compounds of potassium silicate as indicated in sample B3. Mullite, zeolite, and orthoclase are compounds of potassium aluminum silicates and were laid under the umbrella of fertilizer. Such new compounds are suitable for soil health as well as crop production and B3 was suggested well than two treated ash samples for fertilizer manufacturing. Yasuko et al. [20] also identified the major ingredients in fused potassium silicate fertilizer using XRD technique. Although such a study was conducted on the formation of potassium silicate fertilizer, but new compounds e.g. $K_2Ca_2Si_2O_7$ were also observed in fused potassium silicate fertilizer by using steel slag. Better plant growth, reduction of nutrients loss in soil, long-term improvement in soil quality, retention of nutrients in plants, yield improvement, improvement of water retention and filtration are the application of zeolite, moreover many consumers around the globe are using zeolite as fertilizer.

3.2 Surface Mean Diameter:

The relationship between Surface Mean Diameter (SMD) of untreated samples and Mesh number of different particles was observed through sieve analysis indicating that as the mesh size increased, the surface mean diameter of the particles was decreased. It was inferred from the graph that the A3 sample had the lowest value of Surface Mean Diameter (about 203.081micron) that indicated its homogeneous mixing and readily available mineral particles to the plants whereas the value of SMD for sample A1 and A2 was 221.9962 and 221.7846 respectively.

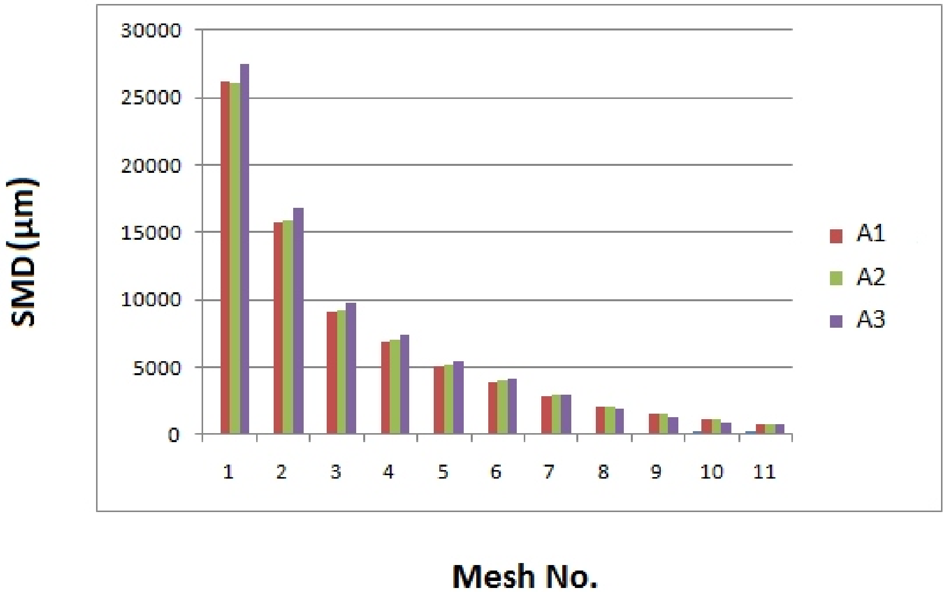


Figure 4: Relationship between Mesh Size and Surface Mean Diameter of untreated ash samples.

3.3 Effect of Organic Matter-Humic Acid on Fertilizers:

In Potash-citric acid-treated samples (B1, B2, and B3) concentration of organic mater and humic acid was measured (Fig. 5) and it was observed that the B1 coal sample contained the highest quantity of organic matter as well as humic acid whereas B2 sample had only about 30% organic matter. In sample B3, quantity of organic matter was approximately 9%. The Maximum quantity of organic matter and humic acid in B1 sample suggested that it was a very good fertilizer for plant growth[21].

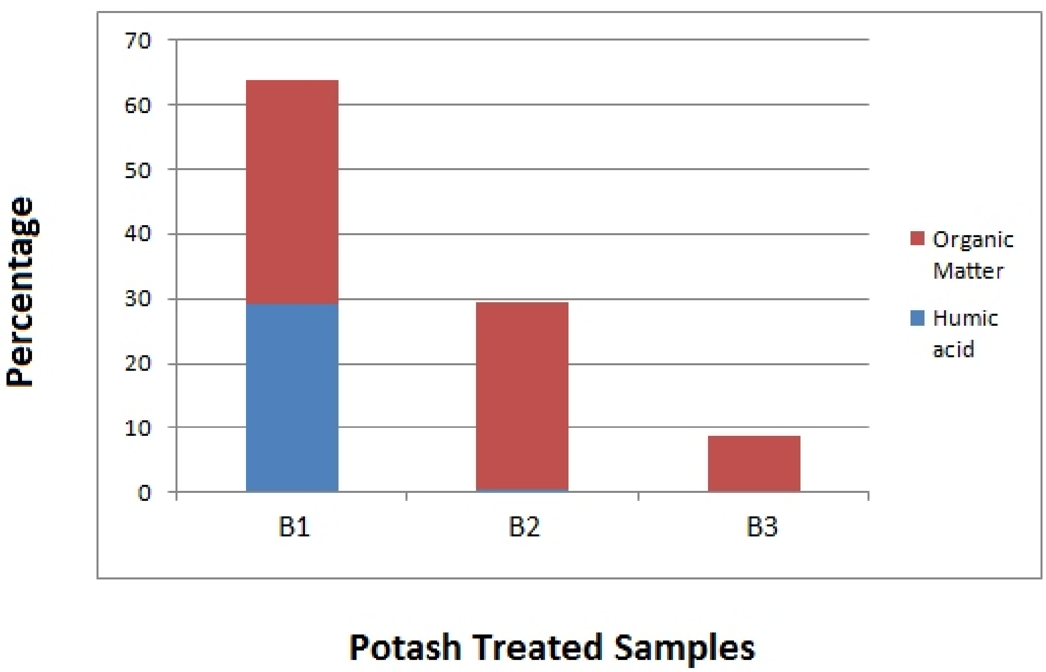


Figure 5: Organic Matter & Humic Acid in Potash treated samples.

3.4 Essential Compounds For Fertilizers:

By wet analysis method, the presence of different elements and compounds like diphosphorus pentaoxide (P_2O_5), zinc (Zn), potassium oxide(K_2O), manganease (Mn), Boron (B), Nitrogen (N) and, sulpate ion (SO_4) were detected in B1, B2, and B3 samples and a graph was plotted between those compounds and their percentages. P_2O_5, K_2O, and N were recommended compounds for a good fertilizer [22]. By analyzing the graph it became evident that K_2O compound was maximum in samples B1, B2, and B3. (Fig. 6) Sample B3 also contained the maximum quantity of the other two essential elements (N and P_2O_5) which categorized it as good fertilizer but the presence of sulphuric in the form of SO_4 was unfavorable.

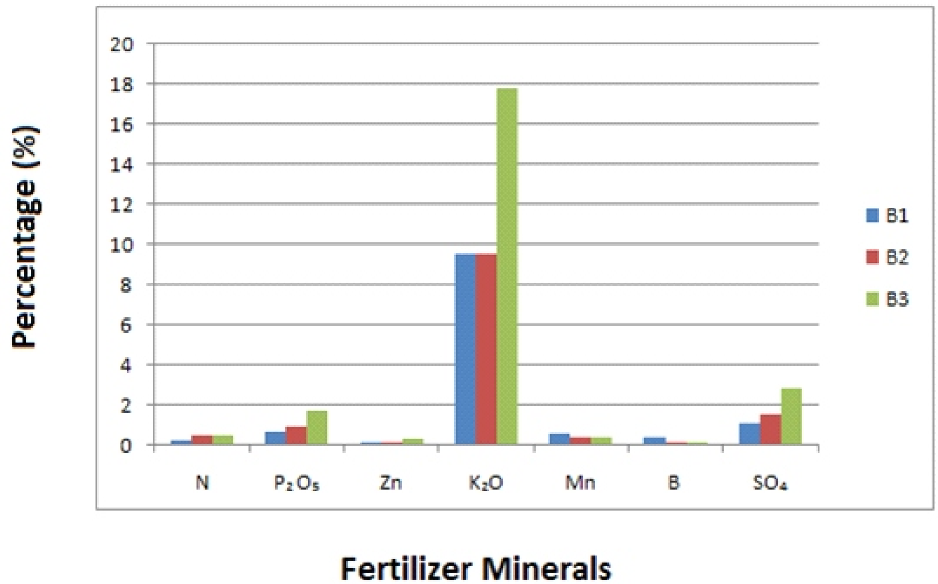
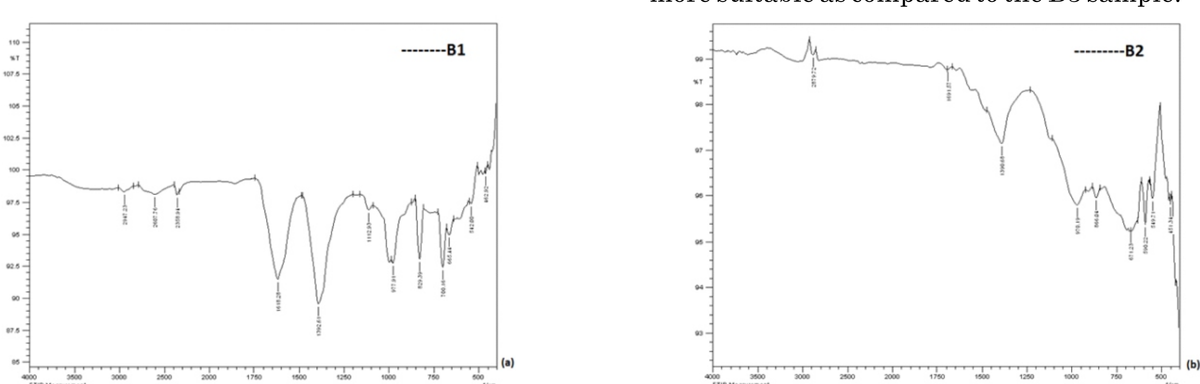


Figure 6: Relationship between percentages and essential minerals in fertilizers.

3.5 Fourier Transform Infrared (FTIR):

By considering the humic acid as the main constituent of our samples, the basic functional groups were the presence of -OH functional group in the range of (3700-3780 cm^{-1}), H bonded -OH functional group in the range of (3200-3400 cm^{-1}), C-O-C (acyclic) in the range of (1170-1050 cm^{-1}) and C=O in the range of (1680-1720 cm^{-1}). Considering the fact of the H bonded -OH functional group, the broadening of a peak in sample B1 was more which evidenced more hydrogen bonding in that sample. While comparing the observed peaks in samples B1 & B3, the main constituents of the humic acid are the C-O-C and C=O functional groups which presented the sharp and high-intensity peaks [23-26]. Figure 8 indicated more amounts of such functional groups in B1 sample as compared to the B3 sample. Whereas the peak results for B2 sample showed the absence of humic acid in that sample (Fig. 9) so it is concluded that the B1 sample was more suitable as compared to the B3 sample.



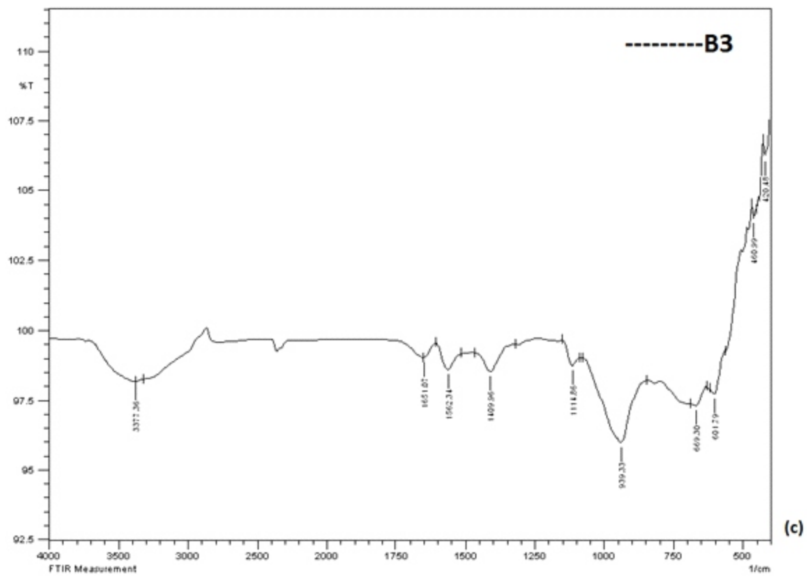


Figure 7: FTIR results for samples “B” series (a), (b)&(C)

4. Conclusions:

XRD results of untreated fly ash in A3 exhibit the presence of oxides of potassium i.e. ($K_4P_2O_7$) and (KPO_3) are significant for fertilizer synthesis. In sample B2, zinc aluminum oxide ($ZnAl_2O_4$), is formed as a small quantity of Zn which is necessary for crop yield. Fertilizer synthesis from coal ash sample A1 is not suitable due to the presence of Hg which is toxic metal as validated by the XRD in the form of HgS in sample B1. Sub-bituminous ash sample is representing a higher percentage of essential compounds including P_2O_5, K_2O and, N for fertilizer synthesis as measured through wet analysis. Lignite coal contains a higher percentage of humic acid as well organic matter as compared to fly ash of bituminous and sub-bituminous. FTIR also validates the presence of humic acid. The fly ash sample of A2 has a lesser particle size i.e.52 micron as it is appropriate for blending during the mixture of ash particles with KOH paste. XRD results of B3 samples confirm the presence of orthoclase, mullite and, zeolite, which are potassium silicate fertilizers. Zeolite is suitable for soil treatment and also provides a slow release of potassium in the soil. Instead of all, it is also used as a catalyst for several important reactions including organic molecules, used as gas separation as it behaves like a sieve due to its porous structure and as ion exchange and remove radioactive ions from contaminated water. The most significant innovation of the research was the presence of zeolite as a fertilizer type as shown by the results.

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