

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Effect of Fly Ash Addition on Characteristics of Peat Soil.

Rini Masril<sup>1</sup>, Edison Munaf<sup>1\*</sup>, Hazli Nurdin<sup>1</sup>, Hamzar Suyani<sup>1</sup> and Teguh B. Prasetyo<sup>2</sup>.

<sup>1</sup>Department of Chemistry, Faculty of Mathematics and Natural Science, Andalas University, Padang, 25163, Indonesia.

<sup>2</sup>Laboratorium of Soil Science, Faculty of Agriculture, Andalas University, Padang 25163, Indonesia.

### ABSTRACT

The effect of fly ash addition on physico-chemical characteristics of peat soil has been investigated. Peat soil was taken from Rimbo Panjang village of Riau Province, Indonesia. The Scanning Electron Microscope for viewing the morphology structure of the initial peat soil and Gas Chromatography–Mass Spectrophometry analysis of sample was shown that the addition of 0.2 g of fly ash to 10 grams of peat soil can reduce humic acid from 0.23 g/g to 0.12 g/g, acetic acid from 1470 mg/kg to 708 mg/kg and benzoic acid from 189 mg/kg to 119 mg/kg. On the other hand the pH of the peat soil was increase from 3.5 to 6.6 and increase pH of the soil from 3.5 to 6.6 and decreased the concentration of toxic elements such as Al and Fe.

**Keywords:** fly ash, peat soil humic acid, scning electron microscop, gas chromatography-mass spectrometry, acetic acid, benzoic acid

*\*Corresponding author*

## INTRODUCTION

Riau is one of the Province in Indonesia having rich in peat soil. Approximately 56% of Riau Province consists of peat soil which is poor of nutrients. For agricultural development, the main problem of peat soil is the high content of organic acids which affects its physical properties such as irreversible drying, low content of macro and micro nutrients and low pH.

The presence of high organic acids in peat soil gives the negative effect for agriculture. Its characteristics such as low pH (acidic), poor nutrient, irreversible drying that lead to low productivity for agriculture. Therefore special treatment is needed to control the organic acids for instance, by adding ameliorant of fly ash (ash from pulp mill boiler). Fly ash is a pulp mill waste, it is alkaline (pH 10-13) and it contains essential cations for plants (Ca, Mg, Zn, K and P). It does not contain heavy metals that are harmful to plants. The addition of fly ash can increase pH and reduce organic acid content in the soil. Peat soil has a high Exchange Cation Capacity caused by the negative charge from carboxyl groups and a little bit phenolate groups and enol (Moore and Jukka, 2004)

Peat soil contains simple aliphatic acids, heterocyclic acids and aromatic acids due to plant residue accumulation. Destruction of organic substance in the soil can be carried out both in aerobic and anaerobic condition. In aerobic condition, those compounds will be decomposed quickly, but in anaerobic condition, which has less oxygen, those compounds will be partially decomposed and produce organic acids. The produced acids include humic acids, methane, ethylene, acetic acids, lactic acids and phenolic acids. Phenolic acids include benzoic acids, P- hydroxy benzoic acids and ferulat acids (Moore and Jukka, 2004, Dombrowski et al, 2010).

Humic acid is the main acids component in peat soil. Humic acid has a high acidity which can be dissolved in base condition and precipitated acids condition. In a high content, humic acid can inhibit the plant growth.

Phenolic acids are more dangerous than carboxylic acids, based on their content and toxicity. Hertkorn et.al (2005), reported that the acid concentration of phenolic such as benzoic acids, P-hydroxy benzoic influence the growth of root in rice plant 0,73  $\mu\text{m}/\text{l}$ . Carboxylic acid has smaller level of concentration or in other words it less dangerous than phenolic acids. Carboxylic acid only will affect the growth of root in rice plant in 0, 25  $\mu\text{m}/\text{l}$  of concentration.

Fly ash can decrease organic acids concentration in peat soil. Such as humic acids, phenolic acids and carboxylic acids. The treatment will change those elements in peat soil for productive agricultural land. Rai *et.al* (2010) expressed that reaction of functional groups pair of organic acids in peat soil can be discharged by adding base and hydroxyl groups so that peat soil function became more reactive. This study aims to determine the concentration of major organics acids in peat soil such as; ascetic and benzoic acid. Those characteristics are identified by GC-MS equipment to evaluate the changes in physico-chemical properties and how fly ash addition changes the chemical reactions in peat soil.

## MATERIAL AND METHODS

### Preparation of Peat Soil

Peat soil was collected from Rimbo Panjang area in a composite manner. The sample was taken from 50–70 cm in dept from the earth's surface, They were collected into a container, mixed together and finally 500 g of sample were put into a plastic bag as a final sample. Then the ollected sample has been used for further analysis.

### Preparation of Fly Ash

Fly ash (ash waste from pulp plant boiler) was taken from shelters and put into sacks. If it was damp air, it would be dried up, crushed and filtered by 250  $\mu\text{m}$  sieve before mixing with peat soil for further analysis.

## The Equipment

The equipment used were Atomic Absorption Spectrophotometer (AAS), Gas Chromatography-Mass Spectrophotometer (GC-MS), Fourier Transform Infra Red Spectrometer (FTIR).

## Method

### *Effect of addition of fly ash to the properties of peat soil irreversible drying.*

10 grams of peat soil was added with 0.1, 0.2, 0.3, 0.4, and 0.5 grams of fly ash respectively and were incubated for one week and then the pH were measured.

### *Effect of temperature and heating time on irreversible drying properties of peat soil.*

100 grams of peat soil was heated on temperature 25, 30, 35, 45°C in 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 1 week, 2 weeks until 8 weeks. It was observed if the formation of peat soil flake occurred.

### *Effect of fly ash addition on irreversible drying properties of peat soil.*

10 grams of peat soil was added with 0.1, 0.2, 0.3, 0.4 and 0.5 grams of fly ash respectively and were incubated one week and then the pH were determined. It was heated in oven on optimum temperature (35°C). It was observed if the formation of peat soil slab and pseudo sand occurred.

## RESULT AND DISCUSSION

### *Chemical Analysis of Fly Ash*

Chemical analysis of fly ash can be seen in Table 1. The results of laboratory analysis shows that fly ash has a high pH and contains a variety of macro and micro nutrients which are beneficial for plants such as K, Ca, Mg, Cu and others. Another interesting thing is that besides containing the elements of macro and micro nutrients that are beneficial to plants, fly ash has no heavy metals so that it will not affect the environment.

### *Observations of Microscopic Structure Using Scanning Electron Microscope*

The SEM analysis of morphology structure of peat soil can be shown in Figure 1.

It can be seen clearly from Figure 1.a at 350 X zoom that peat covered with an organic acids pointed by black color in the picture. The organic compound causes the acidity in peat soil. In the figure 1.b. 500 X zoom, peat soil has more porous and has more white color which contain nutrients obtained from given fly ash. Nutrient is needed for plant to grow. Figure 1.c 1000 X zoom, peat soil after 8 weeks. Peat soil looks more porous and its nutrients are mixed, spread evenly on peat soil. Peat and soil has undergone reaction with peat due to the presence of fly ash (Hill and Cardaci, 2004).

### *The Effect of Heating and Duration of Warming of Peat Soil on Irreversible Drying Nature*

There are 100 grams of peat soil, with pH 4 would be heated using varieties temperature; 25, 30, 35, 40 C and 45<sup>0</sup> C, and using varieties heating duration; 1, 2, 3, 4 and 5 hours, during a week until 3 months in the oven. The aims were to analyze the effect of heating on peat soil which was showed by the slab-forming in the peat. The slab felt clayey and hard. If we pour water to the slab, it will not adsorb the water. From the testing, we can conclude that, heating at 25<sup>0</sup> C and 30<sup>0</sup> C no slab was produced even for 3 month heating. Heating on 35<sup>0</sup> C temperatures for 7 weeks had formed the slab. The longer heating, the harder the peat soil became and the amount of reserve water become less and less. Heating at 40<sup>0</sup> C for 6 weeks to make all peat soil became slab. Lastly heating on 45<sup>0</sup> C for 5 weeks to form the slab in peat soil. In other words, we can conclude that the higher the temperature, the faster the slab produced. In accordance with Noor (2009) who reported that peat soil which has long dried period will lose its ability to hold reserve water. This condition is called irreversible drying. Peat soil in irreversible drying is not productive for agricultural land since it has lost its ability to hold reserve water. The hotter and extreme the weather, then the faster the slab will be formed.

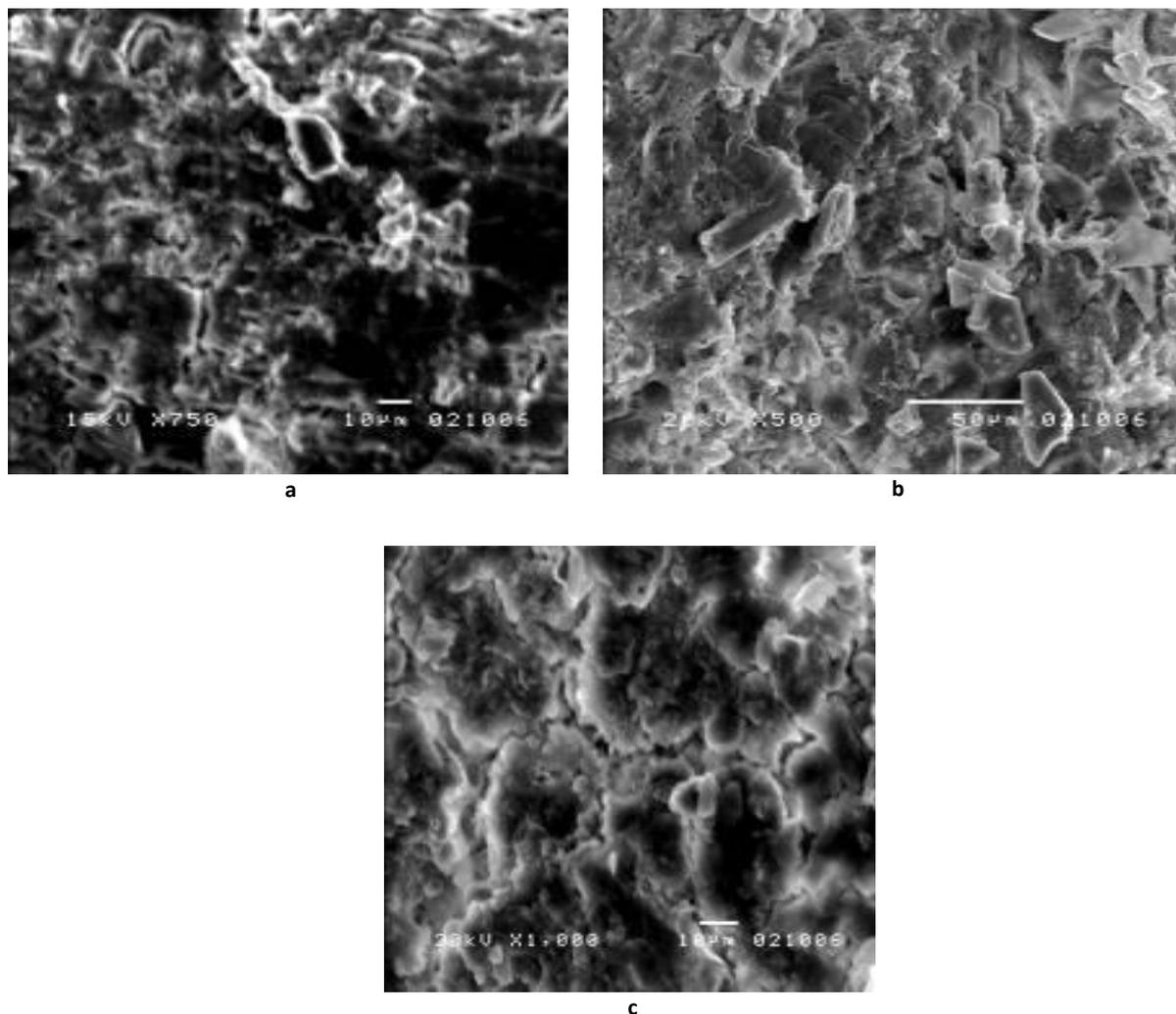


Figure 1: Scanning Electron Microscopy of peat soil sample. a. peat soil without fly ash, with magnification 350 x, b. peat with 0.2 grams fly ash/10grams peat after two week incubation (500 x magnification) and c. peat with 0.2 grams fly ash/10grams peat after eight week incubation (1.000 X magnification).

### The Effects of the Addition of Fly Ash on Irreversible Drying of Peat Soil

In the previous experiment, we had known that irreversible drying happened in the 35 °C temperature for 7 weeks heating. The increasing of temperature will make the slab-forming faster.

Fly ash addition changed the physical and chemical characteristics of peat soil. It was examined on the temperature 35°C since it was the temperature when the slab of peat formed. Fly ash addition increased pH of peat soil through the neutralization reaction as clearly seen in the Figure 2. In this study 0.2 g of fly ash was mixed with 10 g of peat, this comparison considered as a leading to a neutral pH. For analyzing the properties of irreversible drying of peat soil after fly ash addition, the mixture peat and fly ash were examined at 35 °C temperature, (35 °C is the temperature when the peat form slab.

There mixture 10 g of peat and 0.2 g of fly ash was incubated for 1 week. The experiment showed that peat became more moist and crumbly texture. Although subsequently heated at 35 °C in the oven for 7 weeks, peat did not form slab. When the water was added, the dried peat soil became friable. If the water added in excess and let the peat dry, the slab was not formed.

Irreversible drying often happens in tropical peat, especially peat swamps. Irreversible drying causes decline of productivity of the peat soil. Peat soil loose its ability absorb water caused by formation of water-retaining blanket because of the carboxyl groups and phenolic acid, high humic and lignin so they prevent peat

becoming wet again. Fly ash addition can suppress even prevent this irreversible condition in peat soil. If irreversible dying can be reduced then it will intensify peat soil as a productive agricultural land (Adrianno and Weber, 2001)

According to Rai *et.al* (2010), functional groups of organic acid in peat can be removed by adding base or hydroxyl containing material so that the peat will serve again as a reactive site.

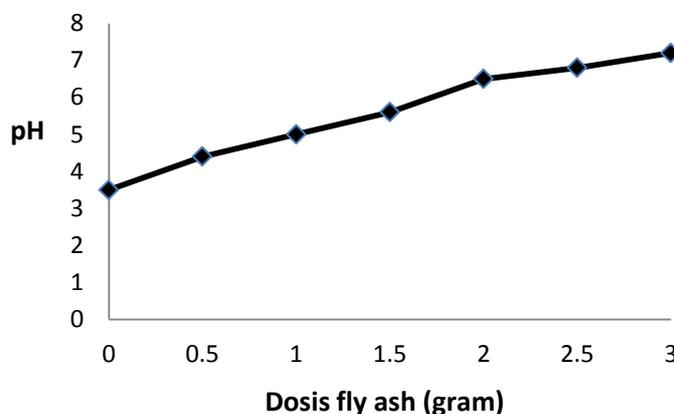


Figure 2: The effects of fly ash addition to pH of 10 g peat soil

### Analysis of Organic Acids Before and After the Addition of Fly Ash

Before prescribing the concentration, humic acid which obtained from extraction and gravimetric method developed by Tan (1998) was firstly characterized by an infrared spectrophotometer. That was to ensure that the obtained extract was true humic acid. The results of analysis of humic acid spectrophotometer by FTIR indicated that OH and N-H stretching was detected at  $3400\text{ cm}^{-1}$ , functional groups of C-H, C-O (carboxyl group), and stretching C=O aromatic was detected at wave number at  $2931, 1713$  and  $1625\text{ cm}^{-1}$ , respectively. This result indicated that the soil contain humic acid.

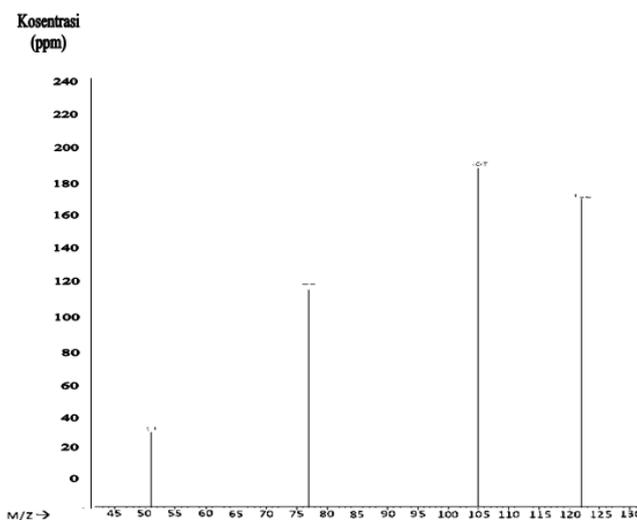


Figure 3: Mass Spectrum of peak at retention 15.8 min

More over, the experiment showed that addition of 0.2 g fly ash to 10 g of peat soil can reduce the humic acid content in peat soil from 0,23 g/g to 0,12 g/g.

The results of chromatogram organic acids in original peat soil. Each peak in the chromatogram was translated by MS data from the data could be concluded that the peat soil contain the main organic acids

namely acetic acid and benzoic acid as shown in Figure 3. Rimbo Panjang peat soil acidity is 3.5 due to the existence and behavior of these organic acids. No matter how much the amount of fertilizer were added to the peat, the fertilizer would remain leaching. The organic acids are poisonous to the soil and plants, especially phenolic groups.

**Determination of Organic Acid in Peat Soil After The Addition of Fly Ash by Ga Chromatography -Mass Spectrometry**

The identification of sample using GC-MS found that the retention time of peaks at 6.2, 6.7 minute, indicates the presence of water and ammonia. While the retention time 11.58 and 15.8 minute indicates the presence of acetic acid and benzoic acid, respectively. The result is shown in Figure 4. From Figure 4 show the addition of fly ash can reduce the acid organic in peat soil. The reduction of organic acid content in peat soil after fly ash addition. Peaks of acetic acid and benzoic acid appeared just a little bit as an indication of reduction of organic acids in peat soil after the addition of fly ash.

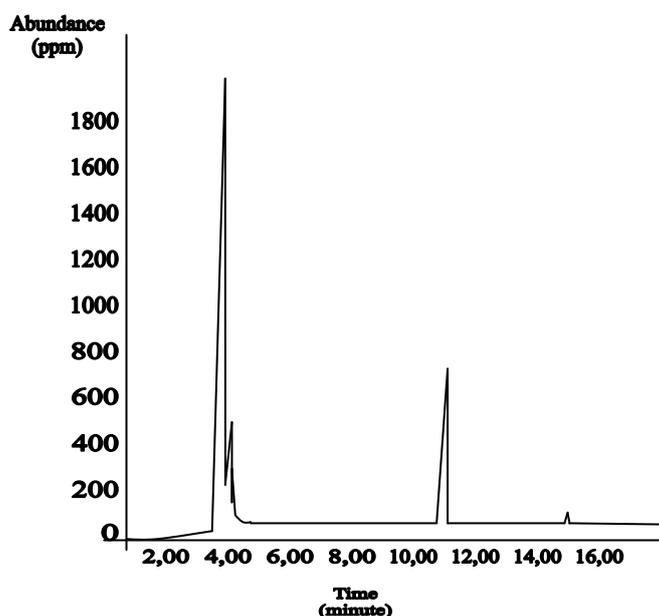


Figure 4: Chromatogram of organic acid chromatography in peat soil that has been added with fly ash and incubated for 1 month

After the addition 0.2 g of fly ash to 10 g of peat soil can reduce the acid content of acetic and benzoic in the peat soil. acetic acid from 1470 mg/kg to 708 mg/kg, benzoic acid from 189 mg/kg to 119 mg/kg. Quantitative analysis of two organic acids in peat soils shows that overall organic acids decrease and pH peat soil increases from 3.5 to 6.6.

**The Effects of Fly Ash Addition on the Content of Macro and Micro Elements in Peat Soil**

Analysis of nutrients and other micro and macro elements can be clearly seen in Table 1. Table 1 shows that peat soil has a high acidity with low pH 3.5, poor nutrients and still need a special treatment to make it productive for agricultural land. The existence and behavior of organic acids in peat soils cause low pH, poor nutrient and irreversible drying. Pathan (2004) also states that no matter how large amount of fertilizer added to peat soil, when the pH is not raised, then fertilizer would be leaching that cannot be absorbed by plants

Fly ash is a material that can distribute base cations in the form of nutrients needed for plant to grow through neutralization reaction (Adrianno and Weber, 2001), (Neuschutz and Greger, 2005).

Decreasing of organic acids because of fly ash addition on peat soil causes an increase in the number of macro nutrients calcium (Ca), Magnesium (Mg), Nitrogen (N), Phosphorus P), Potassium (K) and micro nutrients Zinc (Zn), Cupri (Cu), Molybdenum (Mo) in peat soil. At low acidity pH, the elements of macro and

micro nutrients cannot react and exchange in the peat soil so those elements will be deposited and eventually leaching in the leaching process. By increasing the pH, the nutrients will be exchangeable, react with peat soil and finally be absorbed by plants through the root hair to grow (Adrianno and Weber, 2001 and Seshadri. *et.al* , 2010 ).

Analysis of macro and micro in 10 g peat soil after the addition of 0.2 g fly ash and incubated for 1 month are shown in Table 1.

**Table 1: Peat, fly ash and 0.2 g fly ash/10g peat chemical properties.**

No	Parameter	Peat	Fly ash	Peat + fly ash
1	pH	3.5	11	6.6
2	N-total ( %)	0.15	0.02	0.8
3	P-Total (%)	0.016	0.17	0.09
4	K (mg/kg)	505.95	3063.82	1840
5	Ca (mg/kg)	212.29	7894.54	4090
6	Mg (mg/kg)	100.14	193.52	1580
7	Fe (mg/kg)	0.25	0.03	0.1
8	Al-dd me/100 gram tanah	2.25	0	0.28
9	Zn (mg/kg)	9.16	32.30	12.20
10	Cu (mg/kg)	0.04	10.60	0.30
11	Mo (mg/kg)	0.065	0.11	0.15
12	Pb (mg/kg)	0	0	0
13	Cd (mg/kg)	0	0	0

In the low pH condition, Aluminium (Al) and Iron (Fe) are in the exchangeable form. Al and Fe are toxic elements for plants. Fly ash addition can increase pH so that Al and Fe cannot be exchanged and transformed into a deposited form. As a result, the amount of Al and Fe can be reduced. In accordance with the opinion of Chabbi and Rumpel (2004). and Moore (2004) that in low pH condition, less than 5, Al and Fe numbers will rise in the soil.

**REFERENCES**

Adrianno, D.C and Weber ,J.T, 2001. Influence of fly ash on soil properties and turfgrass establishment, J. Environ. quality. 30 (2), 596-601

Chabbi ,A and Rumpell,C, 2004. Chemical composition of organic matter in extremely acid , lignite-containing lake sediments impacted by fly ash contamination. J. Environ. Quality. 33(1), 628-636.

Dombrowski,F.J., Romme,B.W., Okwadha,G.D.O and Kollokowsky, 2010, Evaluation of surface water runoff from fly ash-stabilized and non stabilized soil surface, J. Environ. Eng. 136, 939-947.

Hertkorn, N., A.Permin., I. Perminova., D.Kovalevskii., M.Yudov., V. Petrosyan and A.Kettrup. 2005. Comparative Analysis of Partial Structures of a Peat Humic and Fulvic Acid Using One- and Two-Dimensional Nuclear Magnetic Resonance Spectroscopy, J. Environ. Quality, 31(1): 375-387



- Hill,A.R and M.Cardaci.2004. Denitrification and Organic Carbon Availability in Riparian Wetland Soils and Subsurface Sediments, *J. Soil.Sci.Soc.*, 68 : 230-237
- Moore,T.R and J.Jukka Turunen, 2004. Carbon Accumulation and Storage in Mineral Subsoil beneath Peat, *Soil Sci.Soc.Am.j.* 68(1): 690-696
- Neuschutz,C and Greger, M. 2005. Stabilization of Mine Tailings Using Fly ash and sewage sludge planted with phalaris arundinaceae L, *J. of Earth and Environ. Sci*, 207 (4) , 357-367
- Pathan,S.M., L.A.G. Aylmore and T.D. Colmer, 2004. Properties of several fly ash materials in relation to use as soil amendments, *J. Environ. Quality.* 32(1), 687-693.
- Rai,U.N., Tripathi,R.D., Singh,N., Kumar,A., Ali, M.B., Pal,A and Singh,S.N, 2010, Amelioran of fly ash by selected nitrogen fixing blue green algae. *Bul. Environ. Toxicol.* 64: 294-301.
- Sharma,S.K., Kalra, N and Singh,G.R, 2010 . Fly ash characteristics and its incorporation effect on germination of maize and rice. *Journal Sci.Ind.res.* Vol 60 (1), 951-952.
- Seshadri,B., Bolan,N.S., Naido,R and Brodic,B, 2010, The role of coal combustion product in managing the bioavailability of nutrients and heavy metal in soil. *Journal of soil science and plant nutrition*, 10 (3), 378-398.