Impact of lignite coal extracted humic acids on vertical movement of ammonical nitrogen through alluvial soil of the middle Gangetic plain, Varanasi, Uttar Pradesh

Akhila Nand Dubey & Priyankar Raha

Abstract

Nitrogen leaching is major problem resulted to low fertilizer use efficiency. Humic acids (HAs) are proposed as a chelating / complexing agent to minimize these losses. The aim of the work was to evaluate the effect of different type of humic acids on ammonical nitrogen vertical movement from the Gangetic alluvial soil. A vertical soil column leaching experiment was carried out in the laboratory with seven different treatments of three different layers (yellow, brown and black) of lignite coal originated and purified humic / fluvic acid [i.e. 0.0 (H0), 10 (HY1), 20 (Hy2), 10 (HB1), 20 (HB2), 10 (HK1) and 20 (HK2) mg HA 500g⁻¹ soil] in soil. The vertical soil column studies were carried by spiking the ammonium chloride solution through (2000 mg NH₄⁺) on the top of the saturated soil columns followed by constant water head flow at definite time interval (1,2,3,4,5,6,10 & 24 hours). It was observed that the amount of leachates and ammonical concentration from humic / fulvic acid treated soil was comparatively low in which addition of black humic acid (10 & 20 mg) followed by brown humic acids as compared to control. In addition, the break through curve (BTC) of NH₄⁺ leaching through different soil columns were drawn with respect to relative concentration (Cw/Ci) of NH₄⁺ leachate against the pore volume (PV) of the soil columns within the period (1 to 24 hours) of leaching. The chelation / complexation of nitrogen in the form of NH₄⁺ by humic substances (containing –carboxyl & phenolic hydroxyl group on surface) originated from lignite coal was the basic cause of the diminishing ammonical nitrogen vertical movement through soil column.

Keywords: Lignite coal, humic acid, ammonical vertical movement, alluvial soil

Introduction

Nitrogen leaching from arable land is complex phenomena, and the direction and intensity of these processes depend on soil properties, climate and weather conditions, and agro-technical factors. Nitrogen losses due to leaching from soil within conventional agricultural production systems usually are in a range from <10 to 30% (Meisinger and Delgado, 2002) [9], although they may exceed 30% in coarse-textured soils (Sapek, 2004) [10]. The studies on nitrogen fertilization of cultivated crops must consider nitrogen losses, not only in economic terms, but also in relation to the aforementioned environmental threats. This refers in particular to coarse textured (sandy) soils that are characterized by limited retention capacity and a poor sorption complex. Humic substances (HS) have been shown as an amalgamation of manifold molecular & functional groups i.e. polysaccharides, fatty acids, polypeptides, lignins, esters, phenols, ethers, carbonyls, quinones, lipids, peroxides; various combination of benzene, acetals, ketals, and lactol, and furan ringed compounds; and aliphatic (carbon chains) compounds venture on to structure humic substances (Stevenson, 1982) that chelating and complexing the NH₄⁺ and NO₃⁻. Lignite popularly known as brown coal is a lower rank premature stage coal and an important precursor of humic acid. Lignite coal may remain in soil due to low decomposition rate (Robertson & Morgan, 1995) [11] and have impact on the quantity and composition of the soil organic matter. In aqueous solution of humic and fulvic acid (HA & FA) act as a weak-acid polyelectrolyte and have buffering capacity over wide range of pH (Stevenson 1982). HA, the component of HSs plays an important role in reducing loss of nitrogen. The effect on increasing soil organic matter could be approved to improvement in physical properties, soil fertility, and soil moisture condition (Ahmed et al., 2006) [12]. Application of lignite coal in agriculture is very desirable worldwide as humic acid is most often used to improve soil structure and content of soil organic matter. However, the effects of humic acids addition to soil on the fate of mineral N are scarcely studied. For example, there is lack of information on improving NH₄⁺ release from urea using lignite coal.
Thus, the objective of this study was to determine the effects of humic acids (originated from lignite coal) on vertical movement of NH₄⁺ from nitrogenous fertilizers.

Methods and Materials

Lignite coal originated humic acids

The different types of lignite coal were collected from Kasanau - Matasukh Coal Mines, Nagaur, Rajasthan, India. The lignite coals were air dried, crushed and sieved in 2 mm sieve. The humic acid was extracted by 0.5 N KOH (Stevenson, 1994 & Yuan et al., 2015) from three different layers (yellow, brown & black) of lignite coal according to colour and geochemical processes. The extracted humic acid salt was precipitated by 1 N HCl. The precipitated humic acid was dialysed and purified. The material was dried through lyophilizer.

Geographical situation of the experimental site

Geographically, Varanasi district of Uttar Pradesh is situated at 25°18' of Northern latitude, 83° 36' of eastern longitude and at an altitude of 80.71 m above the mean sea level (MSL) in the middle Gangatic plain of eastern Uttar Pradesh, India.

Climatic conditions

The Varanasi district of Uttar Pradesh comes under in a semi-arid to sub-humid climate with moisture deficit index of 20-40%. It is often subjected to extreme of weather condition. The mean annual precipitation is 1100 mm. The mean relative humidity (RH) of this area is about 68% with maximum 82% per cent and minimum 30 per cent during July to September and April to early June, respectively. The minimum and maximum average temperature of the area range from 4.4 to 28.20 °C, respectively.

Collection of soil sample

The soil sample was collected from 0-15 cm depth from cultivated areas with high intensity cropping (rice – wheat) systems of research farm, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi Uttar Pradesh during pre-monsoon season period. The physico-chemical properties of the alluvial soil (Inceptisol) under study are given in Table 1.

Table 1: Physical and chemical properties of initial soil under study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (Mg m⁻³)</td>
<td>1.32</td>
</tr>
<tr>
<td>Particle density (Mg m⁻³)</td>
<td>2.51</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>48.21</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>61.53</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>14.05</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>24.42</td>
</tr>
<tr>
<td>Textural Class (USDA)</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Water Holding Capacity (%)</td>
<td>45.57</td>
</tr>
<tr>
<td>pH₄ (1:2.5)</td>
<td>7.91</td>
</tr>
<tr>
<td>EC (1:2.5) (dSm⁻¹)</td>
<td>0.30</td>
</tr>
<tr>
<td>Organic carbon (g kg⁻¹)</td>
<td>4.97</td>
</tr>
<tr>
<td>Cation exchange capacity (C mol (p⁺)kg⁻¹)</td>
<td>13.48</td>
</tr>
<tr>
<td>Ammonial (NH₄⁺) nitrogen (mg kg⁻¹)</td>
<td>67.34</td>
</tr>
</tbody>
</table>

Soil vertical column study

A vertical soil column leaching experiment was carried out in the laboratory of the Department of Soil Science & Agricultural Chemistry, Banaras Hindu University, Varanasi, Uttar Pradesh with seven levels different types of lignite coal originated [yellow (HY), brown (HB) and black (HK)] humic / fluvic acid [i.e. 0.0 (H₀), 10 (HY₁), 20 (HY₂), 10 (HB₁), 20 (HB₂), 10 (HK₁) and 20 (HK₂) mg HA 500g⁻¹ soil], Laboratory vertical column experiment (Mani and Sanyal, 1966) was conducted at room temperature (25°C) in a PVC column (PVC column length: 30 cm & 2.5 cm) packed with selected soil. To simulate the top depth of the soil, each experimental soil column was kept at 30 cm depth with approximate 500g processed soil maintaining the bulk density of soil. Each type of humic acids treated soil was loaded into the column with a 5 cm water level maintained on the top of the column in order to approximate the same rainfall intensity experimentally. The NH₄Cl solution was spiked according to survey report of N- fertilizer application rate (2000 mg L⁻¹ NH₄⁺) of Varanasi district. The leachates were collected at different time intervals (1, 2, 3, 4, 5, 6, 10 and 24 hours) and the experiment was continued 24 hours for each soil. The volumes of leachates, at different time intervals were recorded, while the corresponding ammonium concentration was determined by colourimetrically (Dorich and Nelson, 1983). The data were used to obtain the hydraulic conductivity (K) of the given soil for the electrolyte (NH₄⁺) used. The K values were obtained by employing the Darcy’s law (eq. 1) to the given soil-flow system.

\[ q = K \cdot \Delta H \] ............................. (1)

Thus, where q is the volume flux density (e L. cm⁻¹) through the soil column, \( \Delta H \) is the hydraulic head difference (cm) causing the flow of the electrolyte and L is the length of the column (cm).

The solute (NH₄⁺) accumulation parameter ‘r’ (eq. 2), was developed by Johnson et al. (1966) by the soil column (permeated by a given solution) is given as:

\[ r = 1 - \frac{C_e}{C_0} \] ............................. (2)

Where \( C_e \) and \( C_0 \) are the solute concentrations in effluent and the feed solution, respectively. In general, higher the value of 'r', the greater is the extent of the solute accumulation in the soil leading to a higher efficiency of ‘hyperfiltration’.

Breakthrough curves for the ammonical nitrogen

The above results were plotted showing (\( C_e / C_0 \)) against the pore volumes (Pv) of the effluent (leachate), obtained from (eq. 3) which reads as,

\[ \text{Pv} = \frac{V}{V_0} \] ............................. (3)

Where V is the volume of the leachate collected in given time ‘t’ and \( V_0 \), the volume of the voids,containing the displacing fluid in the soil column. The latter was obtained from eq. (4), namely,

\[ V_0 = V \cdot \eta_0 \] ............................. (4)

Where \( \eta_0 \) is the water filled porosity at the given time and V is the total volume of the soil column. The value of \( \eta_0 \) at the appropriate time intervals used in the experiments was obtained by soaking the soil (from bottom) with appropriate solution (double distilled water) over the given time periods. \( \eta_0 \) [water filled porosity (cm³ cm⁻³)] = Volume of watered by dry soil

Results and Discussions

Leaching loss of fertilizer nitrogen in soil can be minimized by controlling the releasing of NH₄⁺ in soil solution. However, this is a challenge because it requires simultaneous management of N fertilizers and water. Loss of mineral N from agricultural systems is difficult to achieve through
reduction of N fertilizer use efficiency. One of the better methods of reducing losses of mineral N is the use of humic acids derived from lignite coal.

These solution transmission characteristics curved (Figure 1) showed the trends in different levels of various humic acids (yellow, brown and black) treated soil for the spiked aqueous ammonium solution used. Cumulative volume of leachates collected after 24 hours were calculated after collecting the all leachates from different vertical soil columns. The highest amount (490.0 mL) of leachates was collected from soil column (Figure 1) prepared without humic acid addition (H0: without humic acid) and the lowest was noted in soil column with addition of black humic acid (HB2: 20 mg HB/500 g soil). The black humic acids (HK1 & HK2) was well matured humic acids followed by brown (HB1 & HB2) and yellow humic acid (HY1 & HY2) resulted to improved the water holding capacity as compared to control (H0), as well as more amount of ammonium ion (NH4+) on the cation exchange site of humic acid contributing carboxylic and phenolic hydroxyl groups.

The amounts of ammonial leached with respect to different time interval are presented in Figure 2. Results showed (Figure 2) that the effluent concentration of NH4+ was increased with time interval. But NH4+ concentration in soil was gradually decreased with application of black, brown and yellow humic acid as compared to control. Further, the order of the percent vertical movement (Figure 3) from vertical soil columns was control (H0) > yellow humic acid (HY1 & HY2) > brown humic acid (HB1 & HB2) > black humic acid (HK1 & HK2). The carboxylic and phenolic hydroxyl on the surface of humic acids are basically responsible (Stevenson, 1982) for complexation of ammonium (NH4+) ion in the vertical soil column. The matured humic acid (black humic acid) obviously has higher cation exchange capacity than others (brown and yellow).

In addition, the break through curve (BTC) of NH4+ leaching through different soil columns were drawn (Figure 4) with respect to relative concentration (C0/C1) of NH4+ leachate against the pore volume (Pv) of the soil columns in the period (1 to 24 hours) of leaching. The approximately sigmoid shape of the BTC for aqueous ammonium solution in the given soil indicated the hydrodynamic dispersion that is mixing of the permeating solution, with the soil solution originally present, leaching to displacement of the latter. The presence of ‘deadened pores’ in soils leads to no contribution from a significant fraction of the effluent measured at different time intervals. A shift of BTCs to the left (Prasad and Raha, 2016; Ghildyal and Tripathi, 1987) of the infection point was observed which were noted greater in black humic acid (HK1 & HK2) treated soil than brown humic acid (HB1 & HB2) amended soil as compared to control.
Fig 3: Percent of ammonium leaching from soils with different levels of humic acid

Fig 4: Ammonium ion breakthrough curve for the soils with different levels of humic acid

Conclusion
The application of humic acids particularly black humic (10 & 20 mg HA 500 g⁻¹ soil) in soil was significantly reduced cumulative volume of elute (329.00 & 306.00 mL), ammonium leachates (205.13 & 181.87 mg) and percent of ammonium leachate (9.92 & 8.80%), respectively as compared to without humic acids treated soil. It is valuable to note that in N-fertilized soil, humic acid amendment controls the NH₄⁺ vertical movement in soil as well as improves the nitrogen use efficiency. The experiment results also showed that application of black HA at a higher rate (20.00 mg 500 g⁻¹ soil) enhanced the retention of ammonical nitrogen as compared to without humic acid treated soil.

References