



ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(5):151-165

Comparative study on agro-potentiality of Paper mill effluent and synthetic nutrient (DAP) on *Vigna unguiculata* L. (Walp) Cowpea

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ABSTRACT

A comparative study was conducted to assess the agro-potentiality of Paper mill effluent (PME) concentrations such as 10%, 25%, 50%, 75% and 100% along with control (Bore well water) and Di-ammonium phosphate (DAP) separately for the cultivation of *Vigna unguiculata*. The results revealed that PME concentrations had significant ($P < 0.01$) effect on WHC, EC, Cl^- , Mg^{2+} , OC, HCO_3^- , exchangeable Na^+ , available K^+ , Ca^{2+} , TKN, PO_4^{3-} , SO_4^{2-} , Zn, Cu, Fe, Cd, Ni and Cr while insignificant ($P > 0.05$) effect on pH, bulk density and moisture content. Irrigation with 100% concentration of effluent, decreased WHC (14.48%), moisture content (3.10%), bulk density (6.45%) and pH (9.33%) and increased EC (42.46%), Cl^- (88.84%), Mg^{2+} (1209.77%), OC (1807.76%), exchangeable Na^+ (60.47%), available K^+ (37.57%), Ca^{2+} (708.39%), TKN (798.28%), PO_4^{3-} (118.86%) and SO_4^{2-} (39.15%), Zn (158.87%), Cu (215.16%), Fe (94.57%), Cd (125.00%), Ni (3840.00%) and Cr (650.00%) in effluent irrigated soil. The performance of the *V. unguiculata* was increased from control to 25% concentration of the PME and decreased from 25% to 100% effluent in comparison to control and DAP. It was noted maximum with 25% effluent treatment in comparison to control and DAP. Based on the crop yield of and its cultivation cost of the various treatments, the 25% concentration of PME was found more economical than that of the other effluent concentrations and synthetic nutrient DAP.

Key words: *Vigna unguiculata*, Agronomical characteristics, Effluent irrigation, Heavy metals.

ABBREVIATIONS

| | |
|-------|--|
| ANOVA | Analysis of variance |
| BD | Bulk density |
| BIS | Bureau of Indian standards |
| BWW | Bore well water |
| CD | Critical difference |
| DAP | Di- ammonium phosphate $(NH_4)_2HPO_4$ |
| EC | Electrical conductivity |
| PME | Paper mill effluent |
| WHC | Water holding capacity |

INTRODUCTION

The recycling process of effluent for irrigation can make a significant contribution to the management of our water resources. It plays outstanding role to maintain the crop yield and also minimizes the water pollution for better development of agriculture production and health status. Irrigation with wastewater had both beneficial and damaging effects on various crops including vegetables [35]. The wastewater may act as a resource that can be applied for productive uses. It contains nutrients that have potential value for its use in agriculture, aquaculture and other activities [17]. The disposal of wastewater is a major problem in urban and peri-urban areas. Hence applying these industrial effluents to agricultural field instead of disposing off in lakes and rivers can make better growth of crops due to presence of various nutrients like N, P, K, Ca, and Mg etc., if used in permissible limits. Most crops give higher potential yield with wastewater irrigation and reduce the need of chemical fertilizers, resulting in net cost savings to farmers [20; 35; 36]. Thus it is important to understand the specificity of crop-effluent liaison for their appropriate application in irrigation practices [36]. Cowpea (*Vigna unguiculata* L. Walp.) is a nutritive vegetable and pulse rich in protein. It grows in tropical, subtropical and temperate regions of Asia, Africa, and Latin America parts of southern Europe and USA [31]. Beans and seeds of *V. unguiculata* are eaten fresh as a green vegetable, dried, fried, roasted, boiled and also in the form of snack. Its flour could be used in soup and dhal and to make bread also. Animal feed is another use of these beans in many developing countries like India and makes the soil more fertile when it is grown. It also has medicinal values. The leaves and seeds are applied as a poultice to treat swellings and infections. Leaves are chewed to treat tooth ailments. Powdered and carbonized seeds are applied on insect stings. The root is used as an antidote for snakebites and to treat epilepsy, chest pain, constipation and dysmenorrhea. The unspecified plant parts are used as a sedative in tachycardia and against various pains [8]. The seed is diuretic and used to strengthen the stomach. When boiled and eaten as a food it is considered to destroyed worms in the stomach [9].

In recent past various studies have been made on the characteristics of effluent of industries, agronomical properties of various crop plants [6; 16; 19; 26; 28; 30; 35; 36; 37, 38; 39]. But much attention has not been paid so far on the use of industrial waste effluent on the seed germination, growth and productivity of agricultural crops like *V. unguiculata*. Keeping in view, the reuse of industrial effluent, the present investigation was undertaken to assess the comparative agro-potentiality of paper mill effluent and additive fertilizer Di-ammonium phosphate (DAP) on *V. unguiculata*.

EXPERIMENTAL SECTION

Experimental design

A field study was conducted in the Experimental Garden of the Department of Zoology and Environmental Sciences, Faculty of Life Sciences, Gurukula Kangri University Haridwar, for studying the irrigation effect of paper mill effluent (PME) on *V. unguiculata*. Poly bags (dia-30cm) were used for growing the *V. unguiculata* plant. The experiment was replicated six times. Forty two poly bags were filled with soil and used for the cultivation of *V. unguiculata*. Proper distance was maintained between each replicate (30 cm) and between all treatments (60 cm) for

the maximum performance of the crop. Each poly bag was made porous for aeration and it was labelled for the various treatments viz. 10, 25, 50, 75 and 100%.

Effluent collection and analysis

Star paper mill Saharanpur (Uttar Pradesh) which produces paper as its main product from agro based residues was selected for the collection of effluent sample. The effluent was collected from outlet of the secondary settling tank situated in the campus, installed by the paper mill to reduce the BOD and solids using plastic container. The effluent brought to the laboratory was analyzed for various physico-chemical and heavy metals viz. TDS, EC, pH, DO, BOD, COD, TKN, P, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and HCO₃⁻, Fe, Zn, Cd, Cu and Cr content following standard methods [1] and further used as irrigant in different concentrations viz. 10, 25, 50, 75 and 100% for cultivation of *V. unguiculata*.

Soil preparation, filling of poly bags, sampling and analysis

The soil used for cultivation was collected at a depth of 0 – 15 cm. Each poly bag (30x30cm) was filled with 5 kg well prepared soil, earlier air-dried and sieved to remove debris and mixed with equal quantity of farmyard manure. The DAP was applied at a rate 0.7g of DAP @100Kg/ha per bag to all the six replicates for DAP treatment followed by (Ayoola and Makinde 2007) and (ILRI 2010). Five Kg of soil in each of the forty two of poly bags (the soil in each poly bag was 25 cm deep) were irrigated twice in a week/as per the requirement of crop with 500 mL of PME in five concentrations 10%, 25%, 50%, 75% and 100% along with bore well water (control) separately. The soil was analyzed before sowing and after cultivation of the crop as per effluent concentration for various physico-chemical parameters following standard methods [5] for moisture content and EC [7] for soil texture [11] for bulk density, and WHC. The soil pH was determined using glass electrode and pH meter. The other parameters such as Cl⁻, OC, HCO₃⁻, exchangeable Na⁺, available K⁺, Ca²⁺, Mg²⁺, Fe²⁺, TKN, PO₄³⁻, SO₄²⁻ and heavy metals Zn, Cd, Cu, Cr and Ni were determined using standard methods [12].

Sowing of seeds, irrigation pattern and collection of crop parameters data

The PME was applied with its dilutions of 0, 10, 25, 50, 75 and 100% concentration per 5 Kg soil and then left for 2 weeks to allow for mineralization and further irrigation of the crop plant. The seeds of *V. unguiculata* (var. Pusa-Komal) were procured from ICAR, Pusa, New Delhi and sterilized with 0.01 mercuric chloride and soaked for 12 hrs. Seven seeds were sown in each poly bag at equal distance between plant to plant (7.5 cm). Five plants were maintained in each bag by thinning out of the seven and each set was replicated six times as thirty plants were grown for each treatment group including the control group. The crops received the effluent at concentrations of 10, 25, 50, 75 and 100% of effluent as irrigant doses (500 mL) separately twice in a week/as per the requirement of crop plant and no drainage were allowed. The various agronomical parameters of *V. unguiculata* at germination and maturity stages (0-90 days) were noted following standard methods for seed germination, shoot, and root length, number of flowers, pods, and crop yield [35]; biomass [25] and chlorophyll content [29].

Heavy metals analysis

For heavy metal analysis, 5-10 mL sample of effluent, 0.5-1.0 g sample of air dried soil/plant was taken in digestion tube. After this 3 mL conc. HNO₃ was added and digested on electrically heated block for 1 h at 145° C. Then add 4 mL of HClO₄ and heated to 240° C for an additional

hour. Cool and filter through Whatman # 42 filter paper and makeup volume 50 mL and used for analysis following standard methods [12].

Table 1. Physico-chemical characteristics and heavy metal of control (Bore well water) and Star paper mill effluent

| Parameter | Effluent concentration (%) | | | | | | Values for irrigation of water as per BIS |
|--|----------------------------|-------------|--------------|---------------|--------------|---------------|---|
| | 0 (BWW) | 10 | 25 | 50 | 75 | 100 | |
| TDS(mg L ⁻¹) | 244±9.15 | 686.4±5.10 | 1006.42±4.11 | 1924.40±12.12 | 2597.60±9.71 | 2681.60±9.43 | 1900 |
| EC(dS m ⁻¹) | 0.35±0.18 | 1.01±0.45 | 1.48±0.55 | 2.83±0.20 | 3.82±0.73 | 4.19±1.25 | - |
| pH | 7.50±0.20 | 7.74±0.23 | 7.91±0.20 | 7.99±0.19 | 8.14±0.73 | 8.47±0.23 | 5.5-9.0 |
| DO(mg L ⁻¹) | 6.48±1.02 | 5.26±1.14 | 4.56±1.11 | 2.41±1.19 | nil | nil | - |
| BOD(mg L ⁻¹) | 3.90±0.29 | 131.26±7.43 | 307.98±10.35 | 620.27±6.82 | 925.84±6.83 | 1230.50±8.81 | 100 |
| COD(mg L ⁻¹) | 5.88±1.18 | 280.25±4.65 | 707.50±5.69 | 1420.00±8.12 | 2124.75±4.43 | 2839.00±11.17 | 250 |
| Cl ⁻ (mg L ⁻¹) | 15.88±1.68 | 105.99±7.24 | 215.82±7.43 | 323.52±2.66 | 635.27±4.14 | 840.77±4.64 | 500 |
| HCO ₃ ⁻ (mg L ⁻¹) | 237.94±3.81 | 279.73±7.33 | 307.22±10.74 | 372.26±7.23 | 418.51±5.69 | 553.00±13.83 | - |
| Na ⁺ (mg L ⁻¹) | 9.65±1.25 | 62.51±3.85 | 128.25±5.02 | 246.12±5.93 | 367.60±7.25 | 481.5±5.87 | - |
| K ⁺ (mg L ⁻¹) | 5.54±2.25 | 23.06±2.84 | 41.29±3.82 | 77.99±2.90 | 99.54±4.00 | 126.75±6.98 | - |
| Ca ²⁺ (mg L ⁻¹) | 24.34±3.39 | 71.96±4.81 | 141.54±4.60 | 254.33±8.85 | 347.98±6.75 | 441.75±9.97 | 200 |
| Mg ²⁺ (mg L ⁻¹) | 13.24±1.60 | 25.57±1.95 | 35.87±4.10 | 51.50±2.53 | 64.49±4.57 | 75.66±5.22 | - |
| TKN(mg L ⁻¹) | 26.30±6.06 | 40.27±2.98 | 52.56±4.97 | 69.85±7.61 | 81.99±10.92 | 94.11±4.94 | 100 |
| PO ₄ ³⁻ (mg L ⁻¹) | 0.04±0.02 | 19.40±3.69 | 42.91±2.38 | 82.63±4.45 | 126.40±5.50 | 166.39±5.56 | - |
| SO ₄ ²⁻ (mg L ⁻¹) | 17.42±3.12 | 79.97±5.88 | 176.91±7.97 | 330.49±11.09 | 478.72±6.74 | 635.60±6.93 | 1000 |
| Fe ²⁺ (mg L ⁻¹) | 0.29±0.02 | 1.62±0.18 | 3.75±0.30 | 7.63±0.74 | 11.77±0.41 | 15.97±2.13 | 1.0 |
| Zn (mg L ⁻¹) | 0.06±0.03 | 0.64±0.06 | 1.53±0.07 | 3.14±0.83 | 4.56±0.68 | 6.49±1.27 | 15 |
| Cd (mg L ⁻¹) | 0.01±0.00 | 0.11±0.03 | 0.20±0.12 | 0.54±0.06 | 0.75±0.06 | 1.01±0.15 | 2.00 |
| Cu (mg L ⁻¹) | 0.04±0.02 | 0.19±0.08 | 0.37±0.03 | 0.73±0.08 | 1.11±0.16 | 1.37±0.06 | 3.00 |
| Ni (mg L ⁻¹) | 0.04±0.02 | 0.09±0.01 | 0.23±0.11 | 0.47±0.04 | 0.72±0.07 | 0.95±0.09 | 1.00 |
| Cr (mg L ⁻¹) | 0.03±0.01 | 0.05±0.01 | 0.10±0.01 | 0.19±0.02 | 0.30±0.03 | 0.40±0.08 | 2.00 |

Mean ±SD of four values; BWW - Borewell water; BIS- Bureau of Indian standards

Table 2. Physico-chemical characteristics and heavy metals of soil before and after irrigation of *V. unguiculata* with

| Parameters | Before effluent irrigation | After effluent irrigation | | | | | | | r - value | F-calculated | CD |
|--|----------------------------|----------------------------|----------------------|-------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|-----------|--------------|------|
| | | Effluent concentration (%) | | | | | | | | | |
| | | 0 (BWW) | DAP | 10 | 25 | 50 | 75 | 100 | | | |
| Soil moisture (%) | 44.24±4.40 | 43.81±4.88 | 40.42±3.86 (-7.73) | 39.05±3.74 (-10.86) | 38.15±3.77 (-12.91) | 36.80±3.55 (-16.00) | 34.55±5.18 (-21.13) | 32.65±1.71 (-25.47) | -0.98 | 0.97NS | 5.36 |
| WHC (%) | 52.25±1.69 | 48.76±1.08 | 51.46±1.18 (+5.53) | 49.08±1.85 (+24.65) | 47.95 ^b ±3.47 (-1.66) | 46.67 ^b ±2.07 (-4.28) | 45.04 ^{ab} ±2.20 (-7.62) | 43.63 ^{ab} ±2.63 (-10.52) | -0.99 | 5.72** | 3.24 |
| BD (gm cm ⁻³) | 1.55±0.01 | 1.53±0.06 | 1.52±0.04 (-0.65) | 1.51±0.01 (-1.30) | 1.50±0.04 (-1.96) | 1.49±0.04 (-2.61) | 1.47±0.02 (-3.92) | 1.45±0.03 (-5.22) | -0.99 | 2.10NS | 0.05 |
| EC (dS m ⁻¹) | 2.19±0.84 | 2.10±0.09 | 2.42±0.03 (+15.23) | 2.62 ^{ab} ±0.06 (+24.65) | 2.74 ^{ab} ±0.04 (+30.47) | 2.92 ^{ab} ±0.12 (+39.24) | 3.04 ^{ab} ±0.14 (+44.76) | 3.12 ^{ab} ±0.18 (+48.57) | 0.88 | 36.49*** | 0.18 |
| pH | 8.28±0.05 | 8.21±0.24 | 8.25±0.03 (+0.48) | 8.22±0.16 (+0.12) | 8.20±0.29 (-0.12) | 8.17±0.16 (-0.48) | 8.15±0.06 (-0.73) | 7.81±0.30 (-4.87) | -0.82 | 2.19NS | 0.3 |
| OC(mg Kg ⁻¹) | 0.52±0.10 | 0.45±0.10 | 1.53±0.25 (+240) | 2.97 ^{ab} ±0.51 (+560) | 4.19 ^{ab} ±0.18 (+831.11) | 5.06 ^{ab} ±0.16 (+1024.44) | 7.62 ^{ab} ±0.04 (+1593.33) | 9.92 ^{ab} ±0.77 (+2104.44) | 0.98 | 319.35*** | 0.55 |
| Cl ⁻ (mg Kg ⁻¹) | 92.53±4.53 | 89.05±1.82 | 104.87±4.27 (+17.76) | 114.97 ^{ab} ±2.09 (+29.10) | 143.19 ^{ab} ±2.44 (+60.79) | 156.77 ^{ab} ±5.52 (+76.04) | 162.52 ^{ab} ±2.46 (+82.50) | 174.74 ^{ab} ±6.22 (+96.22) | 0.92 | 274.52*** | 5.75 |
| Exc. Na ⁺ (mg Kg ⁻¹) | 21.81±2.84 | 18.32±3.09 | 24.34±3.49 (+32.86) | 25.03±3.52 (+36.62) | 27.53 ^a ±4.31 (+50.27) | 28.84 ^a ±5.15 (+57.42) | 31.49 ^{ab} ±5.15 (+71.88) | 35.00 ^{ab} ±5.43 (+91.04) | 0.93 | 6*** | 6.46 |
| Ava. K+ (mg Kg ⁻¹) | 164.25±2.70 | 154.09±6.70 | 166.47±3.24 (+8.03) | 171.09 ^a ±2.78 (+11.03) | 184.61 ^{ab} ±4.07 (+19.80) | 209.95 ^{ab} ±4.17 (+36.25) | 217.78 ^{ab} ±3.47 (+41.33) | 225.97 ^{ab} ±5.71 (+46.64) | 0.96 | 154.51*** | 6.62 |
| Ca ²⁺ (mg Kg ⁻¹) | 18.58±1.44 | 14.40±2.79 | 34.59±4.54 (+140.20) | 37.55 ^a ±4.15 (+160.76) | 73.10 ^{ab} ±3.31 (+407.63) | 109.43 ^{ab} ±2.99 (+659.93) | 133.41 ^{ab} ±2.60 (+826.45) | 150.20 ^{ab} ±6.19 (+943.05) | 0.98 | 710.98*** | 5.85 |
| Mg ²⁺ (mg Kg ⁻¹) | 1.74±0.11 | 1.68±0.60 | 4.48±0.86 (+166.66) | 4.75±0.51 (+182.73) | 9.59 ^{ab} ±0.90 (+470.83) | 12.30 ^{ab} ±1.86 (+632.14) | 15.55 ^{ab} ±2.79 (+825.59) | 22.79 ^{ab} ±4.88 (+1256.54) | 0.99 | 40.97*** | 3.39 |
| TKN(mg Kg ⁻¹) | 31.46±4.24 | 29.22±3.85 | 51.78±4.86 (+77.20) | 59.90 ^{ab} ±2.62 (+104.99) | 119.31 ^{ab} ±2.44 (+308.31) | 175.14 ^{ab} ±4.59 (+499.38) | 242.36 ^{ab} ±3.60 (+729.43) | 282.60 ^{ab} ±10.92 (+867.14) | 0.99 | 1344.16*** | 7.95 |
| PO ₄ ³⁻ (mg Kg ⁻¹) | 56.19±5.03 | 52.45±3.64 | 73.12±7.37 (+39.40) | 74.93±1.87 (+42.85) | 93.88 ^{ab} ±1.99 (+78.98) | 107.40 ^{ab} ±2.22 (+104.76) | 115.94 ^{ab} ±2.23 (+121.04) | 122.98 ^{ab} ±4.54 (+134.47) | 0.94 | 151.39*** | 6.22 |
| SO ₄ ²⁻ (mg Kg ⁻¹) | 76.08±5.05 | 73.05±6.57 | 77.03±5.26 (+5.44) | 80.20 ^a ±5.68 (+9.78) | 81.99 ^a ±3.33 (+12.23) | 93.74 ^{ab} ±2.99 (+28.32) | 103.15 ^{ab} ±3.30 (+41.20) | 105.87 ^{ab} ±5.02 (+44.92) | 0.98 | 30*** | 7.01 |
| Fe ²⁺ (mg Kg ⁻¹) | 2.95±0.45 | 2.63±0.99 | 3.78±0.13 (+43.72) | 3.80 ^a ±0.14 (+44.48) | 5.08 ^{ab} ±0.05 (+93.15) | 5.26 ^{ab} ±0.05 (+100) | 5.58 ^{ab} ±0.15 (+112.16) | 5.74 ^{ab} ±0.56 (+118.25) | 0.86 | 30.59*** | 0.62 |
| Zn (mg Kg ⁻¹) | 1.07±0.12 | 0.78±0.16 | 1.96±0.09 (+151.28) | 2.22 ^{ab} ±0.07 (+184.61) | 2.38 ^{ab} ±0.04 (+205.12) | 2.49 ^{ab} ±0.06 (+219.23) | 2.61 ^{ab} ±0.02 (+234.61) | 2.77 ^{ab} ±0.26 (+255.12) | 0.75 | 233.43*** | 0.14 |
| Cd (mg Kg ⁻¹) | 0.08±0.06 | 0.02±0.01 | 0.04±0.01 (+100) | 0.11 ^a ±0.01 (+450) | 0.14 ^{ab} ±0.01 (+600) | 0.15 ^{ab} ±0.01 (+650) | 0.16 ^{ab} ±0.01 (+700) | 0.18 ^{ab} ±0.02 (+800) | 0.82 | 134.53*** | 0.02 |
| Cu (mg Kg ⁻¹) | 2.11±0.34 | 1.99±0.33 | 3.20±0.21 (+60.80) | 3.41 ^a ±0.45 (+71.35) | 5.16 ^{ab} ±0.23 (+159.29) | 5.68 ^{ab} ±0.47 (+185.42) | 6.07 ^{ab} ±0.16 (+205.02) | 6.65 ^{ab} ±1.06 (+234.17) | 0.90 | 104.14*** | 0.49 |
| Ni (mg Kg ⁻¹) | 0.05±0.01 | 0.06±0.02 | 0.07±0.01 (+16.66) | 0.54 ^{ab} ±0.03 (+800) | 0.68 ^{ab} ±0.08 (+1033.33) | 0.83 ^{ab} ±0.09 (+1283.33) | 1.01 ^{ab} ±0.04 (+1583.33) | 1.97 ^{ab} ±0.46 (+3183.33) | 0.94 | 52.7*** | 0.26 |
| Cr (mg Kg ⁻¹) | 0.12±0.06 | 0.11±0.06 | 0.23±0.01 (+109.09) | 0.29 ^{ab} ±0.03 (+163.63) | 0.50 ^{ab} ±0.02 (+354.54) | 0.60 ^{ab} ±0.03 (+445.45) | 0.85 ^{ab} ±0.03 (+672.72) | 0.90 ^{ab} ±0.07 (+718.18) | 0.97 | 199.97*** | 0.06 |

Paper mill effluent i.e. after crop harvesting of 90 days

Mean ±SD of three values; Significant F - ***P - 0.01%, **P - 0.1% level; r-Coefficient of correlation; % Increase or decrease in comparison to control given in parenthesis; a-significantly different to the control; b- significantly different to the control + DAP; NS - Not Significant; BWW - Borewell water; CD -Critical difference.

Statistical analysis

Data were analyzed for one way analysis of variance (ANOVA) for determining the difference between soil parameters before and after irrigation of crop as per concentrations of PME and DAP treatment. Standard deviation, coefficient of correlation for soil and crop parameter and effluent concentration were also calculated with the help of MS Excel, SPSS12.0 and Sigma plot, 2000.

RESULTS AND DISCUSSION

Effluent characteristics

The mean \pm SD values of physico-chemical and heavy metals parameters TDS, EC, pH, DO, BOD, COD, Cl^- , HCO_3^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , TKN, PO_4^{3-} , SO_4^{2-} , Fe^{2+} , Zn, Cd, Cu, Ni and Cr of PME (black liquor) are given in Table 1.

The results revealed that the effluent was alkaline in nature (pH, 8.47). Among various parameters of effluent (100%), TDS (2681.60 mg L^{-1}), BOD (1230.50 mg L^{-1}), COD (2839.00 mg L^{-1}) Cl^- (840.77 mg L^{-1}), Ca^{2+} (441.75 mg L^{-1}) and Fe^{2+} (15.97 mg L^{-1}), were not found in the prescribed limit of Indian irrigation standards (BIS 1991). The higher values of TDS (2681.60 mg L^{-1}), BOD (1230.50 mg L^{-1}) and COD (2839.00 mg L^{-1}) indicated the higher amount of inorganic and organic load in PME.

Soil Characteristics

The mean \pm SD values of various physico-chemical and heavy metals parameters viz. moisture content, WHC, BD, soil texture, EC, pH, Cl^- , OC, exchangeable Na^+ , available K^+ , Ca^{2+} , Mg^{2+} , TKN, PO_4^{3-} , SO_4^{2-} , Fe^{2+} , Zn, Cd, Cu, Ni and Cr of the soil before and after irrigation with different concentrations viz. 10%, 25%, 50%, 75% and 100% of PME along with control (Bore well water) and DAP for 90 days are given in Table 2.

The authors (20) reported that distillery effluent (spent wash) contained various nutrients and toxic chemicals that could contaminate water and soil and may affect the common crops if used for agricultural irrigation. The authors [35] reported that paper mill effluent irrigation significantly decreased the moisture content, WHC, bulk density and pH and significantly increased the EC, Cl^- , K^+ and Ca^{2+} , Na^+ , NO_3^{2-} , PO_4^{3-} and SO_4^{2-} in the soil.

The authors [4] reported that the range of pH from 6.0 to 8.3 enhanced the nutrients availability for the growth of plants. A change in pH beyond this limit inhibited the availability of nutrients for the plants as soil tied up large quantities of these nutrients and thus would not be available for plants, even though they remain in the soil [10]. It is reported that paper mill effluent irrigation added the significant amount of salt to the soil environment. Higher values of EC indicated the enrichment of soluble cations and anions such as Cl^- , PO_4^{3-} , SO_4^{2-} , Mg^{2+} , exchangeable Na^+ , available K^+ and Ca^+ through incessant use of effluent in different concentration (28; 35). The increase in organic carbon content may be due to continued addition of organic matter through effluent irrigation, the same was reported by [2]. The authors [21] also reported that paper mill effluent irrigation significantly increased the total nitrogen in the soil.

The small amount of heavy metals found in industrial effluents acted as growth stimulants and played a very significant role in enzymatic reactions, photosynthesis and chlorophyll content. These elements present in the soil provide nourishment to plants and hence increased its productivity [14; 24]. The higher content of Zn, Cd, Cu, Ni, Pb and Cr had been reported earlier in effluent irrigated soil by [14].

In the present study the 100% concentration of PME decreased soil moisture content, WHC, bulk density, pH and increased EC, Cl^- , Mg^{2+} , OC, exchangeable Na^+ , available K^+ , Ca^+ , TKN, PO_4^{3-} ,

and SO_4^{2-} (Table 2). Soil moisture content ($r = -0.98$) and bulk density ($r = -0.99$) were recorded to be negatively correlated with different concentrations of the PME. The WHC was significantly affected ($P < 0.01$) and it was negatively correlated ($r = -0.99$) with different concentrations of PME. Among various concentrations of PME, 25% to 100% concentrations showed significant ($P < 0.01$) effect on WHC in comparison to control and DAP treated. After 90 days of the effluent irrigation on *V. unguiculata*, no any change was observed in the soil texture. Soil was loamy sand in nature and its particles size remained unchanged after applying all the concentrations of PME separately throughout the period.

The soil pH was recorded to be negatively correlated ($r = -0.82$) with different effluent concentrations and it was found slightly basic in nature on irrigation with 100% concentration of PME. The EC ($r = +0.88$), Cl^- ($r = +0.92$), Mg^{2+} ($r = +0.99$), OC ($r = +0.98$), exchangeable Na^+ ($r = +0.93$), available K^+ ($r = +0.96$), Ca^+ ($r = +0.98$), TKN ($r = +0.99$), PO_4^{3-} ($r = +0.94$), SO_4^{2-} ($r = +0.98$), Zn ($r = +0.75$), Cu ($r = +0.90$), Fe ($r = +0.86$), Cd ($r = +0.82$), Ni ($r = +0.94$) and Cr ($r = +0.97$) of the soil were shown their positive correlation with different concentrations of PME.

The ANOVA indicated that PME concentrations 10-100% had significant ($P < 0.001$) effect on the EC, Cl^- , TOC, HCO_3^- , exchangeable Na^+ , available K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , TKN, NO_3^{2-} , PO_4^{3-} and SO_4^{2-} , Fe, Zn, Cu, Ni, Cr and Cd of the soil in comparison to control and DAP (Table 2).

Exchangeable Na^+ was found to be significantly ($P < 0.001$) different at 10%, 25% and 50% concentrations of PME to the control and it was also found to be significantly ($P < 0.001$) different with 75% and at 100% concentration of PME in comparison to control and DAP. Available K^+ and Ca^{2+} was recorded to be significantly ($P < 0.001$) affected with 10% concentration of PME in comparison to control. The significant ($P < 0.001$) change was observed in Mg^{2+} and PO_4^{3-} with 25% to 100% concentration of PME in comparison to control and DAP. The SO_4^{2-} was found to be significantly ($P < 0.001$) affected in effluent irrigated soil with 10% and 25% concentration of PME in comparison to control and 50%, 75% and 100% concentrations in comparison to control and DAP. The significant ($P < 0.001$) change was noted in Zn, Ni and Cr with 10% to 100% of the PME irrigated soil. The content of Fe, Cu, and Cd were found to be significantly ($P < 0.001$) affected with 10% concentration of PME in comparison to control and with 25% to 100% concentration of PME in comparison to control and DAP treatment.

Agronomical characteristics

Germination stage

The results of the seed germination of *V. unguiculata* with different concentrations viz. 10%, 25%, 50%, 75% and 100% of PME along with control and DAP are shown in Fig. 1.

In the present study, the maximum percentage of seed germination *V. unguiculata* was recorded with 25% concentration of PME. The statistical analysis revealed that seed germination percentage was found to be negatively correlated ($r = -0.60$) i.e. it was decreased with increase in the effluent concentrations. It may be due to the higher amount of salt in PME which hardens the soil and affects the seed germination. The higher concentration of Na, SO_4^{2-} and TDS in the effluent at the time of irrigation move in accordance with water and due to evaporation they get accumulated in the soil and inhibit seed germination as stated earlier [35].

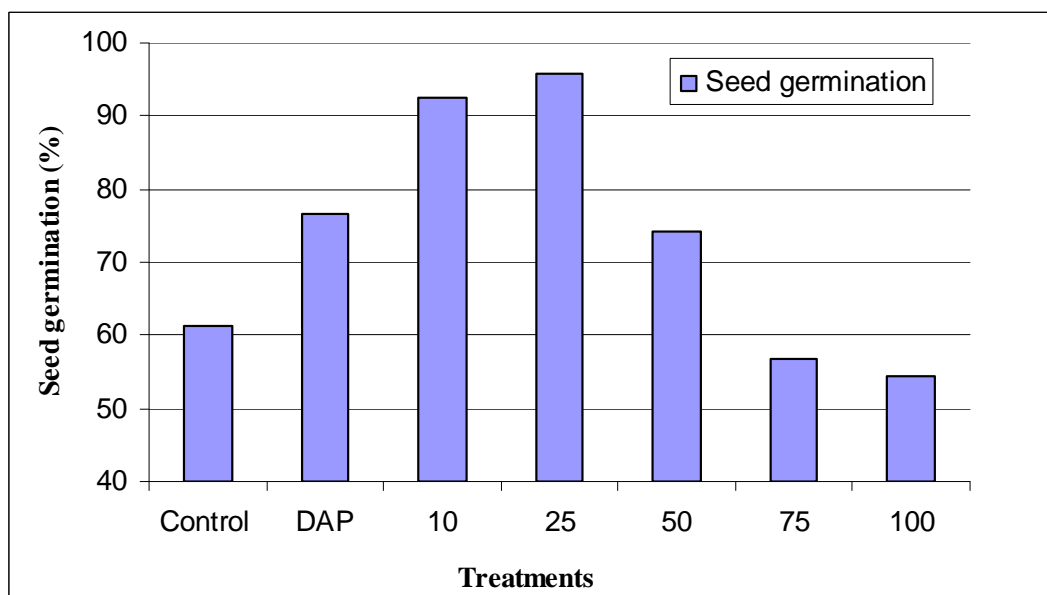


Fig.1 Seed germination of *V. unguiculata* after irrigation with paper mill effluent.

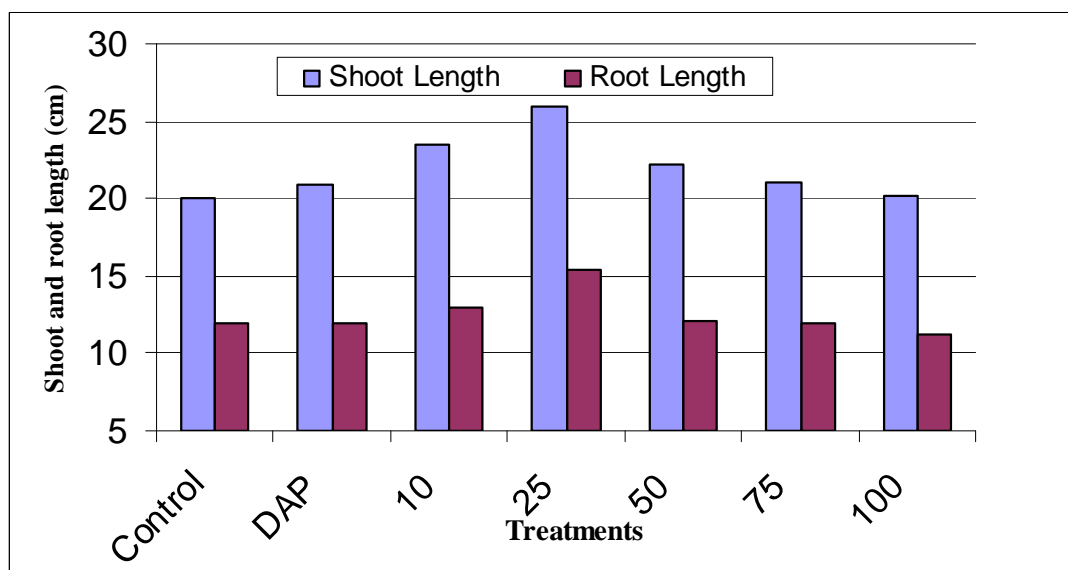


Fig.2 Shoot and root length of *V. unguiculata* after irrigation with paper mill effluent

The ANOVA showed that seed germination percentage of *V. unguiculata* was recorded to be significantly ($P < 0.05$) affected with different concentrations of PME irrigation. The seed germination was recorded to be highly significantly ($P < 0.001$) different with 10% and 25% concentration of PME in comparison to control and DAP. The 50% concentration of PME also showed highly significant ($P < 0.001$) effect on seed germination of the crop in comparison to control. It was observed that as the concentration of effluent increased from 75% to 100%, the retarding trend in percentage seed germination in contrast with control and DAP was noted. This type of germination pattern can be attributed to the presence of bio-toxic substances present in the effluent which might had inhibited seed germination at higher concentration by altering the

interaction of seed and water which is necessary for triggering enzyme activity [6; 35]. The authors [30] had also reported that the 25% concentration of paper mill effluent was better for both emergence period and seed germination of *Trigonella foenum graecum*. This might be due to that lower concentration of effluent enhanced the fertilizing effect and provided optimum condition for germination.

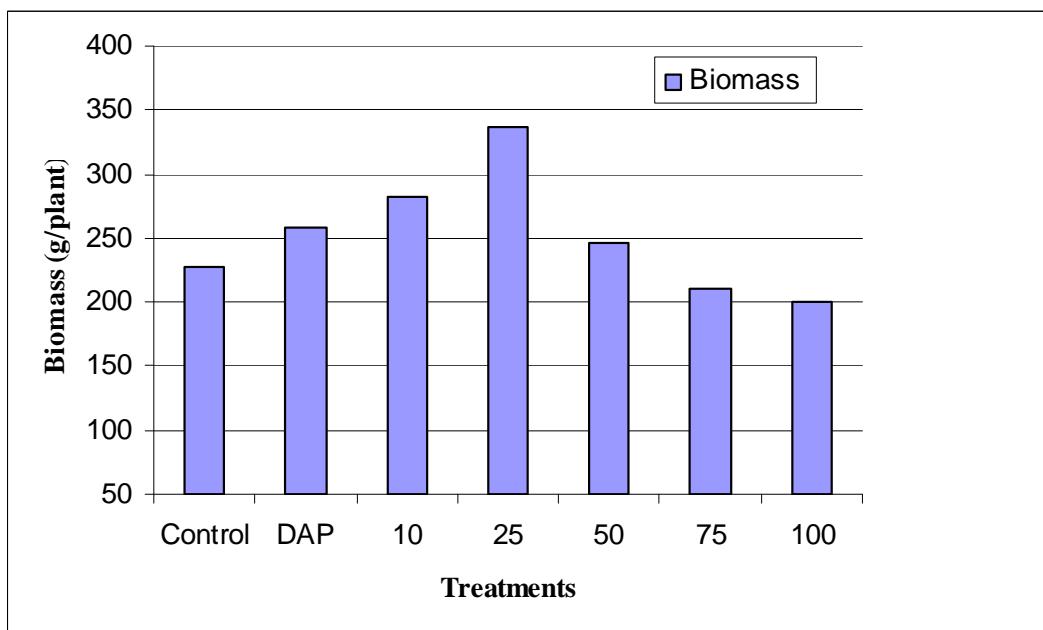


Fig.3 Biomass of *V. unguiculata* after irrigation with paper mill effluent

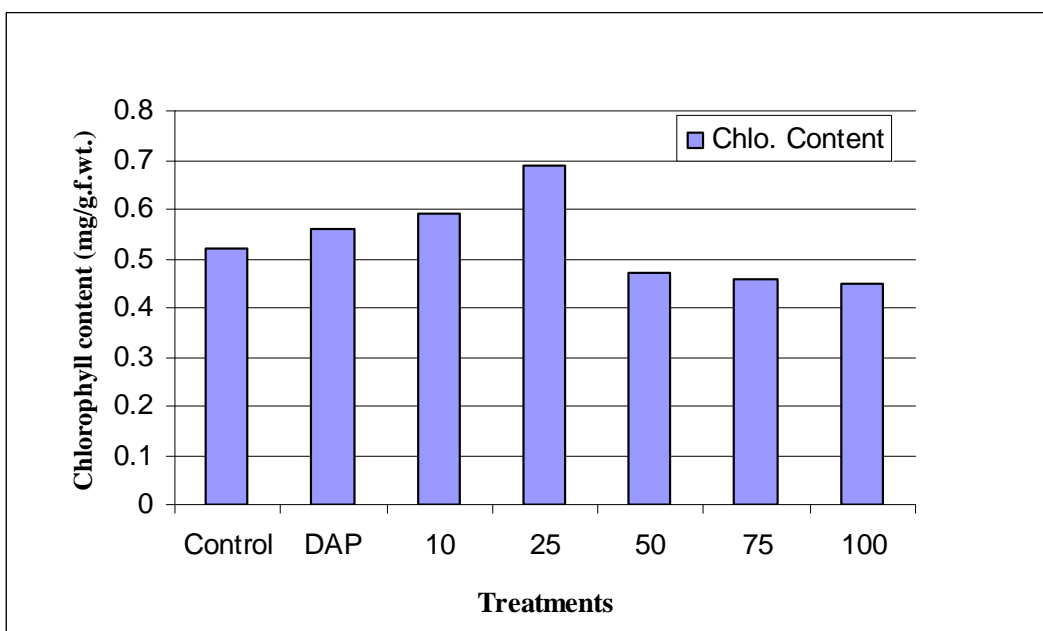


Fig.4 Chlorophyll content of *V. unguiculata* after irrigation with paper mill effluent

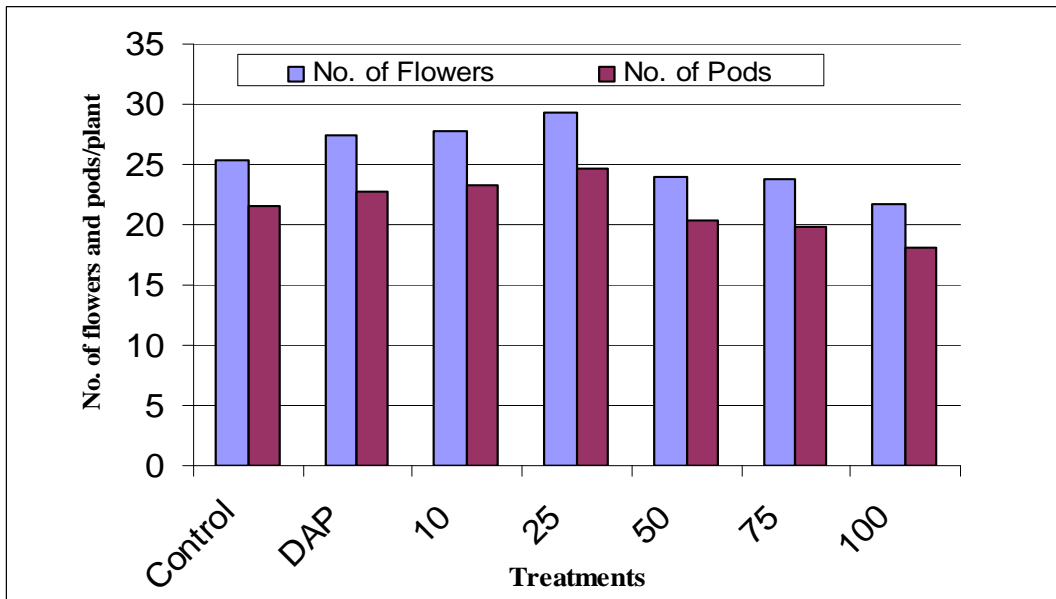


Fig.5 No. of flowers and pods of *V. unguiculata* after irrigation with paper mill effluent

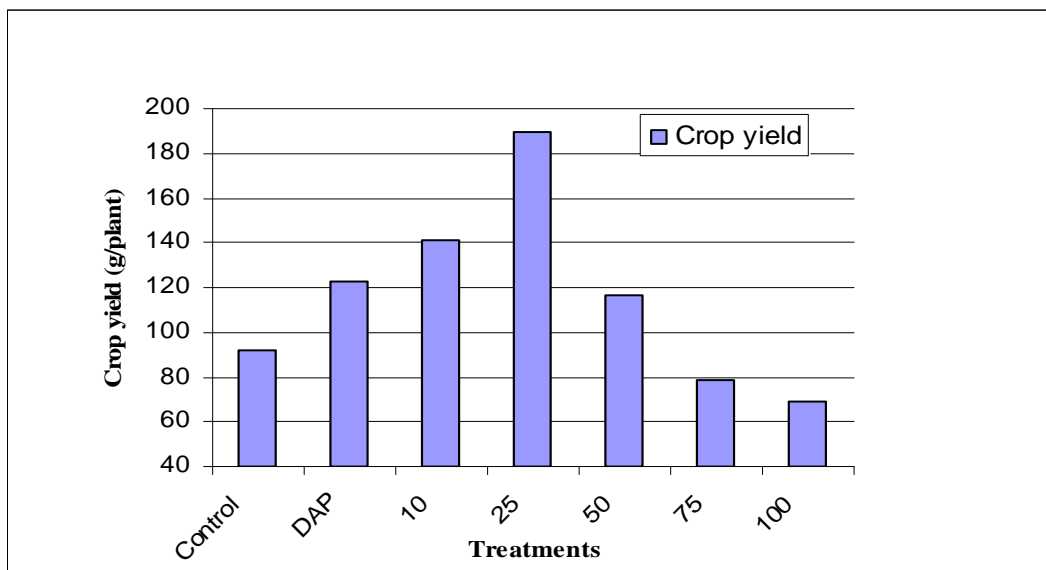


Fig.6 Crop yield of *V. unguiculata* after irrigation with paper mill effluent

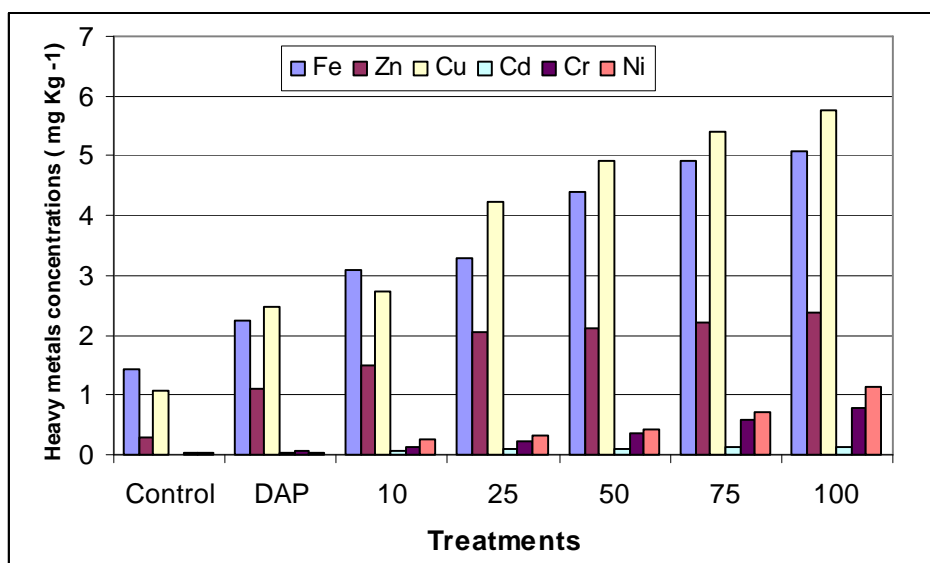


Fig.7 Heavy metals in *V. unguiculata* after irrigation with paper mill effluent.

Maturity stage

At maturity stage (90 days), the parameters such as shoot length, root length, biomass, chlorophyll content, number of flowers, number of pods, and crop yield of *V. unguiculata* with different concentrations viz. 10% to 100% of PME along with control and DAP are given in Figs. 2- 6.

The results indicated that the maximum performance of the crop at maturity stage was recorded at 25% concentration of PME irrigation. The statistical analysis on data at the maturity stage parameters showed that the shoot length/plant ($r = -0.37$), root length/plant ($r = -0.48$), biomass ($r = -0.58$), chlorophyll content ($r = -0.64$), number of flowers/plant ($r = -0.77$), number of pods/plant ($r = -0.79$) and crop yield/plant ($r = -0.57$) of *V. unguiculata* were negatively correlated with different concentrations of PME.

The ANOVA showed that the shoot length, root length, biomass, chlorophyll content, number of flowers, pods and crop yield/plant of *V. unguiculata* were found to be significantly ($P < 0.05$) affected with different concentrations of PME. The shoot length was also noted to be significantly ($P < 0.01$) affected with different concentration of PME. The root length, chlorophyll content, biomass/plant, number of flowers, pods, and crop yield were also found more significantly ($P < 0.001$) different with different concentrations of PME.

The 25% concentration of PME showed significant effect on shoot length, root length, biomass, chlorophyll content, number of flowers, pods, and crop yield/plant in comparison to control and DAP. The 10% concentration of PME showed significant effect on shoot length, chlorophyll content, number of flowers/plant and number of pods/plant in comparison to control. The chlorophyll content, biomass and crop yield were also found to be significantly different with 10% concentration of PME in comparison to DAP.

The agronomical performance of *V. unguiculata* at maturity stage was found to increase at lower concentration from 10% to 25% concentration of PME while it was gradually decreased at higher concentration from 50% to 100% concentrations of PME. This gradual decrease may be due to toxicity of heavy metals (Zn, Cd, Cu, Ni and Cr) at higher concentrations present in the PME that might have affected the crop performance at higher concentration. It implies that at lower concentration i.e. 10% and 25% of PME had noticeable growth promoting effect while at higher concentrations, effluent had inhibiting effect on *V. unguiculata*. The endorsement of plant growth at 25% concentration may be due to presence of most advantageous level of plant nutrients in the effluent [23; 35].

The authors [35] had reported the declined trend of shoot, root length, biomass, and chlorophyll content, number of flowers, pods and crop yield/plant of *Trigonella foenum-graecum* with 50% to 100% concentration of paper mill effluent irrigation. Similar findings had also been reported earlier using fertilizer factory effluent on crop productivity reported [32] and using polluted water on cereal crops [33].

The chlorophyll content of *V. unguiculata* was found maximum with 25% concentration of PME. This might be due to alkaline nature of PME which provided speedy transformation of magnesium, available potassium and exchangeable sodium, calcium, nitrogen and iron to the crops. At higher concentrations the reduction was observed in chlorophyll content which might be due to without dilution of PME. So that there would be an increase in the concentration of toxic ions in the effluent and would inhibit the photosynthetic activity of plants. The findings had been supported the assessment of the pulp and paper mill effluent on growth, yield and nutrient quality of wheat (*Triticum aestivum* L.) reported by [34].

Heavy metal concentration in *V. unguiculata*

The concentrations of heavy metals such as Fe, Zn, Cu, Cd, Cr and Ni in *V. unguiculata* after irrigation with different concentration of PME irrigation are given in Fig. 7.

The values of heavy metals viz. Fe, Zn, Cu, Cd, Cr and Ni in *V. unguiculata* were recorded to maximum at 100% concentration among different concentrations of PME. The statistical analysis on heavy metals Fe ($r = +0.92$), Zn ($r = +0.83$), Cu ($r = +0.90$), Cd ($r = +0.88$), Cr ($r = +0.99$) and Ni ($r = +0.97$) were shown their positive correlation with different concentrations of PME.

The ANOVA showed that heavy metals Fe, Zn, Cu, Cr and Ni of the crop were recorded to be significantly ($P < 0.05$) affected with different concentrations of PME in comparison to control and DAP. The 10% concentration of PME, also showed highly significant ($P < 0.001$) effect on copper in comparison to control. Though all the values of heavy metals were slightly higher in the effluent irrigation as compared to control and DAP. All the values of heavy metals at different effluent concentration of PME were under the permissible limits of FAO/WHO-Codex alimentarius commission [13]. Hence no significant risk was associated with the irrigation of the crops with diluted effluent as far as the heavy metals are concerned. The authors [22] was also observed the concentration range of various heavy metals such as Cd (0.011–0.073 mg Kg⁻¹), Cu (0.161–0.923 mg Kg⁻¹), Zn (0.361–1.893 mg Kg⁻¹) and Cr (1.121–2.254 mg Kg⁻¹) in Cabbage, Spinach, Lettuce and Cauliflower respectively which were less than the permissible limit as

recommended by maximum acceptable levels proposed by the Joint FAO/WHO Expert Committee on Food Additives.

Economical assessment of the cultivation of *V. unguiculata*

The comparative economical assessment of *V. unguiculata* at different treatments of PME with control (BWW) and DAP revealed that the maximum yield of the crop was recorded with 25% concentration of PME in comparison to control and DAP. This might be due to importance of nutritive value of PME. And its dilution provided a number of specific properties of irrigational water that are relevant in relation to the yield and quality of *V. unguiculata* and maintenance of soil productivity. Normally the nutritive elements required for agricultural crop production are supplied by the effluent. In addition, other valuable micronutrients and the organic matter contained in the effluent will provide additional benefits for the cultivation of crop. The maximum biomass (336.78 g) and crop yield (189.44 g) of the crop at 25% concentration of PME proved more economical in comparison to lower biomass and crop yield at higher effluent concentrations and also in association with control (BWW) and DAP treatment. Similar findings have been reported by [15, 37, 38] for domestic wastewater who also reported that need of water for irrigation crops is very essential and despite limited water resources, the reuse of wastewater is the appropriate selection in terms of economic value.

CONCLUSION

The present study concluded that Star paper mill effluent, Saharanpur (U.P.) had a substantial effect on soil properties. The WHC, pH, soil moisture and bulk density were found to be decreased. On the contrary, EC, Cl^- , Mg^{2+} , OC, exchangeable Na^+ , available K^+ , Ca^+ , TKN, PO_4^{3-} , and SO_4^{2-} were increased. The heavy metals such as Zn, Cu, Fe, Cd, Ni and Cr were also recorded higher in the soil after effluent irrigation. The agronomical characteristics of the crop *V. unguiculata* were significantly better at 25% concentration of PME in comparison to control and DAP. The maximum performance of *V. unguiculata* was based on the yield of crop and taking into account of the market price of the various treatments. The 25% concentration of PME was found more economical than that of the other concentrations of PME and synthetic nutrient (DAP) in the cultivation of this crop. Thus, the PME contained the nutrients and micronutrients which enhanced crop productivity of *V. unguiculata* and the effluent acted as liquid fertilizer. The use of such diluted effluent may minimize the need of chemical fertilizers and irrigation-water needs also.

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