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Hydrothermal Carbonization of Paper Mill ETP Sludge and Assessing its Potential Application in Agriculture

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ABSTRACT

Effluent Treatment Plant Sludge (ETPS) from pulp and paper mill is produced in larger quantities and its disposal has the major problem faced by the industries. The conversion of paper mill sludge into hydrochar through the process of Hydro Thermal Carbonization (HTC) has wider opportunities in agriculture. This study explored the optimization processes which influence the preparation of hydrochar from ETPS through the approaches of Response Surface Methodology (RSM). The optimized temperature and time were 220 °C and 4 hours, respectively for hydrochar production based on higher carbon and nitrogen content. The hydrochar and ETPS was characterized using Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) surface area and Fourier Transform Infra-Red Spectroscopy (FTIR) for its structural morphology. Based on the optimized parameters, the hydrochar was produced and used in the pot culture experiment to study the impact of the hydrochar on bhendi (*Abelmoschus esculentus*) crop growth. Different concentrations of hydrochar were applied as basal in the pot. The treatment with 4% hydrochar germinated first show the good shoot and root length and 11% increase in germination percentage and 22% increase in vigour index when compared with control due to its higher nutritives which is on par with the results of 5% hydrochar.

Key words : *Hydro Thermal Carbonization, Hydrochar, Paper mill sludge, RSM, Bhendi and Germination.*

Introduction

Pulp and paper mill industry in India are one of the high consumers of fresh water and they release enormous amount of effluent and solid wastes as sludge. India's core industrial areas are ranked 15th among the world's paper-producing countries. At present, there are 665 pulp and paper mills in India, of which 632 units are agro residue and recycled fibre-based units with manufacturing capacity of 7.6 million tons.

The world demand for paper has grown rapidly and was around 5-6% per year. The per capita consumption of paper in India is 2.5 kg per year, while the Asian average is 18 kg. The paper mills have a larger investment and provide employment to 2 lakh peoples. It is estimated that the capacity of the mills increased from 8.3 million tonnes in 2010 to 14 million tonnes in 2020 (Khan *et al*., 2011).

The production of 1 ton of paper generates 250 kgs of sludge during the treatment process. The direct application of ETP sludge to the crop will cause adverse effects to the soil (land) as well as crop. The sludge from the biological treatment plants, mixed with sludge from primary treatment have potential nutritive value as a soil amendment in agriculture. A limiting factor to the agricultural utilization of the pulp and paper mill sludge is the nitrogen immobilization due to a very high C:N ratio (Beyer *et al*., 1992), especially sludge from primary treatment processes. Nitrogen immobilization after pulp and paper mill sludge application may in some circumstances be useful in reducing nitrate leaching. Sludge from paper mill is produced upto 23.4 percent per unit of manufactured paper, accounts for the bulk of waste created from paper manufacturing and recycling process, the quantity depends on the paper production process (Miner *et al.*, 1996 and Lacour *et al*., 2005). Hence the effective way of utilization of sludge can be planned and identified as conversion of sludge into hydrochar.

Hydrothermal carbonization (HTC) is a novel technique for turning wet biomass into a coal-like material termed hydrochar, at relatively moderate reaction temperatures. The transformation is worked out for half an hour to ten hours at temperature ranging from 180 °C to 260 °C, with such a biomass to water ratio of 1:92. (Oumabady *et al*., 2020). During the HTC process, pathogens are destroyed and thermally unstable contaminants will be decomposed. HTC can convert organic waste / biomass into char (carbonized material), whose application is diverse, and a study hasbeen carriedout onthe use of hydrocarbon as carbon and as an adsorbent to extract emerging impurities (Wang *et al.*, 2018). During the hydrothermal carbonization of biomass, the hydrolysis and dehydration process produces oxygenated functional groups, making it an excellent substrate for chemically activated carbon (Jain *et al.*, 2016).

The transformation techniques comprise chemical conversion, thermal conversion and thermo chemical conversion. Part of the heat conversion process includes pyrolysis, gasification, carbonization and combustion, each of which takes place over different temperature ranges. Among the thermal conversion processes, hydrothermal carbonization is superior to the management of solid feedstocks with high moisture content. And also, the release of nitrogen will be slow down in plants (Bargmann *et al*., 2014).Hence, the present study has been planned to optimize the process parameters for hydrochar production and study the effect on hydrochar on germination of Okra (bhendi) crop.

Materials and Methods

i) Collection and storage of ETP sludge from pulp and paper industry

The paper mill sludge was collected from ETP of SPB Seshasayee Paper Boards Ltd., Pallipalayam, Erode, Tamilnadu, India. The collected sample was stored in cold storage @ 4 °C. Later, the PBETP sludge was dried at 105 °C in hot air oven. After the complete removal of moisture from the sludge, it was ground and sieved through 2mm size sieve for further processing (Lin *et al.*,2015).

ii) Hydrothermal carbonization process

The ETPS was varied to receive the homogeneity in advance to conduct the experiment. After integration, 60g of initial ETPS (containing 1:9 sludge:water portion) was taken in a 100 ml hydrothermal autoclave reactor and closed tightly with a given rod (Lin *et al.,* 2015). Nitrogen gas was sprayed into the reactor to cleanse the reactor for developing the devoid of oxygen content in the hydrothermal carbonization (HTC) autoclave reactor (Lin *et al.,* 2017). Then, kept the reactor in the oven by fixing the temperature under different residence time interval. Then, the reactor should be kept in a cool water to decrease the reactor temperature rapidly (Nakason *et al.,* 2018). The produced hydrochar was strained through filter paper to get the solid portion. The separated solid portion was dried in the 110 °C hot air oven and utilized for further analysis.

iii) Characterization ofhydrochar

ThepH and EC of the samples were examined at a solid to water ratio at 1:5 using the digital pH and conductivity meter respectively. The proximate properties of ETPS and hydrocharwere analyzes by standard (ASTM) American Society for Testing and Materials protocol (ASTM-E871-82, ASTM-D3175-07 andASTM-D3174-04). The surface area and pore volume were carried out by the BET surface area analyzer. The surface arrangement was studied through Scanning Electron Microscope (Kliewer, 2009 and Oumabady *et al*., 2020). FTIR Fourier Transform Infrared Spectroscopy (Model 6800 Jasco Asia Portal) was used to identify the functional groups across a wave number range of 400–4000 cm^{-1} (Trakal *et al.,* 2014) The organic carbon, total nitrogen, total phosphorus and total potassium content was determined in the ETP sludge and hydrochar using standard protocol of hydrochar production (Oumabady *et al.*, 2020).

iv) Optimization of hydrochar production

For the hydrothermal carbonization of ETPS, the Integrated optimum (I-optimal) design of response surface approach was used (Mohammed *et al.*, 2020). The I-optimal design has been chosen because it matched a quadratic polynomial model with the fewest number of experiments, making it easier to investigate interactions between process parameters and indexing the most important element for response optimization. The optimization for the parameters and their levels were given in Table 1. Carbon content and nitrogen content were fixed as key factors for the optimization process. Sixteen runs of the experiments were given by the design expert. Every run's reaction was evaluated with Stat-Ease Inc.'s design expert software version 13, which was released in 2000. It led to the tuning of process parameters (temperature and time) in order to achieve desired goal characteristics including maximum carbon and nitrogen content (Oumabady *et al.*, 2020).

Germination test

The germination test was done by sowing the bhendi crop in the pot experiment. The bhendi (Okra) Co4 Bh hybrid was sowed in the pot based on the (STCR) Soil Test Crop ResponseNPK requirement. Based on the STCR requirements NPK calculation for the bhendi crop was calculated as 117 kg ha^{-1}, 67 kg ha^{-1} and 137 kg $ha^{-1}$of N, P, and K respectively. Four kilograms of black clay soil is filled in each pot. Based on the content of the soil filled in pot, NPK fertilizer is applied to the crop. The calculated value of NPK is 0.68g, 1.10g and 0.5g per pot respectively. The treatments were T1, T2, T3, T4, T5 and T6 that is control, 1%, 2%, 3%, 4%and 5% of hydrochars respectively. Germination rate is an appraise of the viability of a seed population.The vigour index (VI) of the seedlings can be estimated as below :

$$VI=(RL+SL)\times GP$$

where RL is root length (cm),
SL is shoot length (cm) and
GP is germination percentage.
Results and Discussion

Properties of ETPS and hydrochar

ETP sludge is a semi-solid substance derived as a waste from the effluent treatment plants of paper mill. The main composition of paper mill sludge includes the organic complexes derived as a result of microbial metabolism. These complexes include cellulose, hemicellulose and other derivative materials. The characterization of sludge depicted its potential for its usage because of its carbon content (23.68%). The pH of the ETPS was neutral with an electrical

Table 1. Experimental runs with their results (RSM). (Samples analyzed under dry weight basis and average of three samples)

Run	Factor 1 A: Temperature Degree Celsius	Factor 2 B: Time Hour	Response 1 Carbon %	Response 2 Nitrogen %
1	260	5	32.41	2.82
2	200	3	31.23	2.79
3	200	5	31.87	2.84
4	240	8	28.13	2.76
5	240	1	26.71	2.81
6	200	5	31.87	2.84
7	180	8	24.36	2.67
8	180	5	24.79	2.69
9	260	3	32.14	2.74
10	180	1	23.86	2.45
11	240	8	28.13	2.76
12	200	8	32.45	2.81
13	180	3	25.45	2.47
14	240	1	26.71	2.81
15	200	5	31.87	2.84
16	200	5	31.87	2.84

conductivity of 5.24 dS m^{-1}. The pH of the hydrochar was decreased from 6.49 to 5.63 after hydrothermal carbonization of ETP sludge which depicts slightly acidic nature of hydrochar. ETPS (6.68 dS m^{-1}) has a higher electrical conductivity than its hydrochar (5.24 dS m^{-1}). The sorption of dissolved salts from the raw resources during hydrothermal carbonization resulted in an increase in electrical conductivity (Chen *et al.,* 2017 and Jin *et al*., 2018). This reduction was due to the production of organic acids during hydrothermal carbonization process (Table 2). The proximate analysis showed the volatile matter has been decreased from ETPS (Oumabady *et al.,* 2021). The nutrient content of total nitrogen (8%), total phosphorus (3%) and organic carbon content (34%) has been increased in the hydrochar.

Characterization of surface morphology

The SEM images of ETPS and its derived hydrochar were taken at a high voltage of 8kV with 10,000 x

Table 2. Characterization ofETPS raw and hydrochar

Parameters	ETP sludge	Hydrochar
pH	6.49	5.63
EC (dS m^{-1})	5.24	6.68
Bulk density (gcm^{-3})	0.91	0.82
Particle density(gcm^{-3})	1.54	1.57
Porosity (%)	40.91	37.73
Volatile matter (%)	55.6	49.6
Ash content (%)	32	34.6
Organic carbon (%)	23.68	31.87
Nitrogen (%)	2.65	2.87
Phosphorus (%)	1.58	1.64
Potassium (%)	0.79	0.84
Sulphur (%)	0.81	0.62

magnifications and appraised for surface modifications (Figure 1). It was seen that hydrochar has formed a coarser surface as compared to its smooth surface of raw biomass. The existence of a linked porous network of surfaces on the hydrochar was suggested by small cavities, fissures, pores, and rough surfaces. These rugged surface structures were clearly apparent in micrographs, which also reduction in particles (3.806 µm to 496 nm) were also observed after hydrothermal carbonization. Moreover, the surface of hydrochar exhibits particle dispersions in the form of fluffy sponges and spherical shaped particles with deeper cleavage (Gai *et al.,* 2016). In order to confirm the presence of higher carbon of hydrochar, EDAX analysis was performed. During this measurement, different areas were focused and the peaks of ETPS and hydrochar were compared in Figure 2. In ETPS and hydrochar, the quantity of C, O and Mg were 55.71%, 30.14%, 0.80% and 74.12%, 23.28%, 0.18% respectively. Details of two spectra of the ETPS and hydrochar values were measured in weight % and atomic % are listed in the Table 3. The increase in surface area of hydrochar from 0.78 to 3.55 m^2 $g^{-1}$and reduction in pore volume of hydrocharfrom 0.230 to 0.089cc g^{-1} using Brunauer-Emmett Teller (BET) analysis of surface area was limned.

Surface functionalities of hydrochar

The FTIR spectra of ETPS and hydrochar depicted a broad band with variable stretching around 3200-3600 cm^{-1} which was due to the presence of cellulose in the paper mill sludge. The OH stretching of phenolic OH groups were represented by a rounded tip

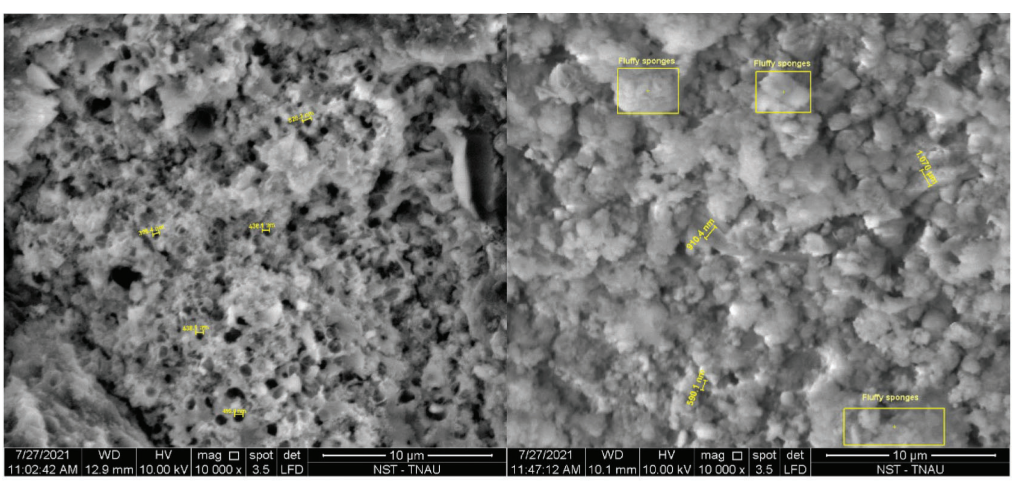
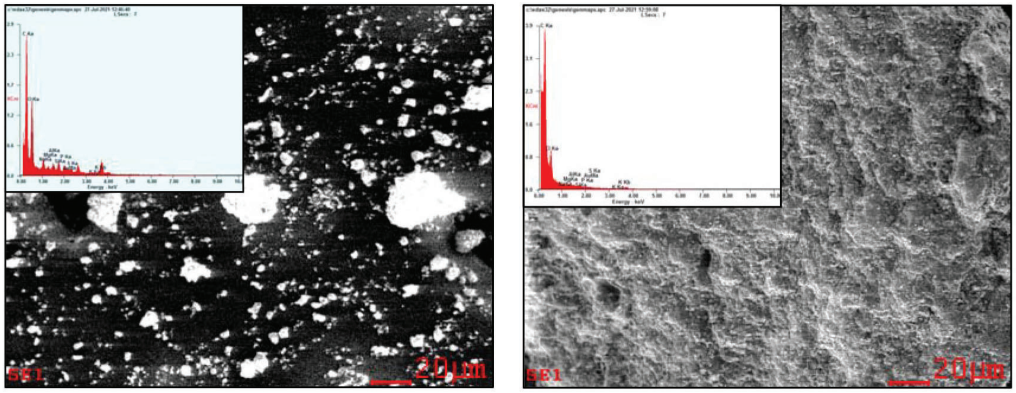


Fig. 1. SEM micrographs of ETPS and hydrochar



ETPS with EDAXhydrochar with EDAX

Fig. 2. ETPS and hydrochar with EDAX graphs

band at 3260 cm^{-1} (Figure 3). The resonance of aliphatic methyl groups was assigned to the band between 2800 and 3000 cm^{-1}, with a centroid at 2920 cm^{-1} representing the oscillation of asymmetric C-H stretching, identify the existence of amino acids (Kim *et al.*, 2014; Sevilla and Fuertes, 2011 and Oumabady *et al.*, 2020).

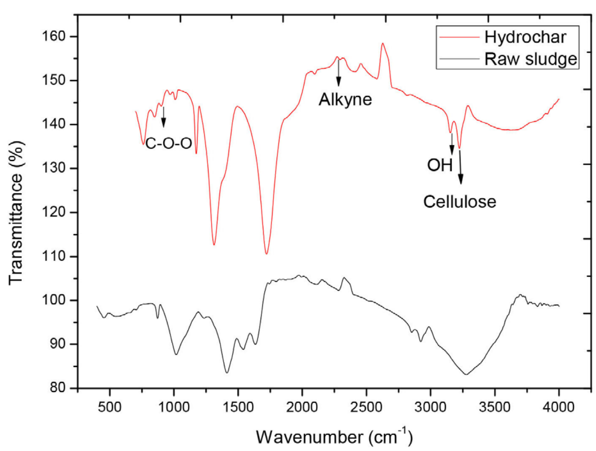


Fig. 3. FTIR spectra of ETPS and hydrochar

Process optimization of hydrochar production

Figure 4 shows a plotted graph displaying anticipated vs experimental values, *i.e.*, the relationship between the actual and predicted values for each response. The experimental response values were found to be closer to the anticipated values, indicating that the created model had a strong connection between the process parameters and their responses. Using perturbation plots (Figure 5) and three-dimensional response surface plots, the influence of process parameters and their interaction on hydrochar production was evaluated. The perturbation plots assist in assessing the influence of all process parameters at a given moment and monitoring their behaviour to evaluate the changes that each response undergoes in response to a change in process parameter. In three-dimensional graphs (Figure 6), the red zone represents the greater response value, while the blue region represents the lower response value (Oumabady *et al.*, 2020). Due to its highest predicted probability of 89 percent, the statistical optimization resulted in the projection of some solutions (optimized process parameters), among which the process temperature of 220 °C and time of 4.25 h was concluded to be the optimized process parameter for the production of hydrochar. The optimized hydrochar has 31.87 % organic carbon and 2.84 % total nitrogen content.

Effect on germination of Bhendi crop

The bhendi (Co4Bh) was sowed in the pot experiment based on the treatment (1%, 2%, 3%, 4%, 5%).

Table 3. EDAX with weight percentage and atomic percentage ETPS and hydrochar

Samples	Carbon		Oxygen		Magnesium	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
ETP sludge raw	55.71	66.82	30.14	27.14	0.80	0.48
Hydrochar	74.12	80.12	23.28	18.92	0.18	0.10

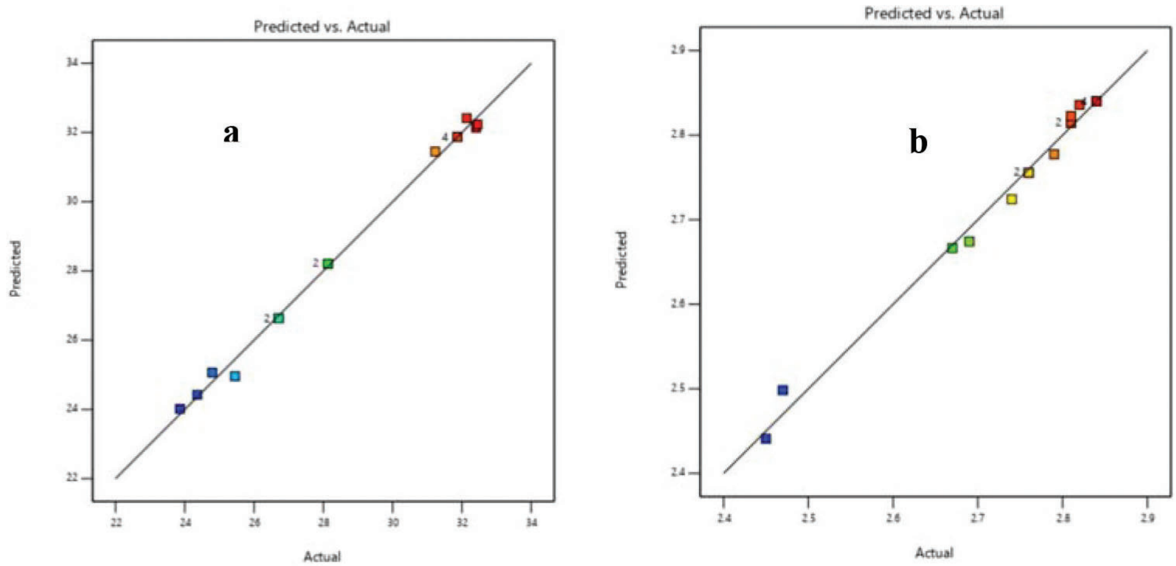


Figure 4. Relationship between actual and predicted values of (a) Carbon content (b) Nitrogen content

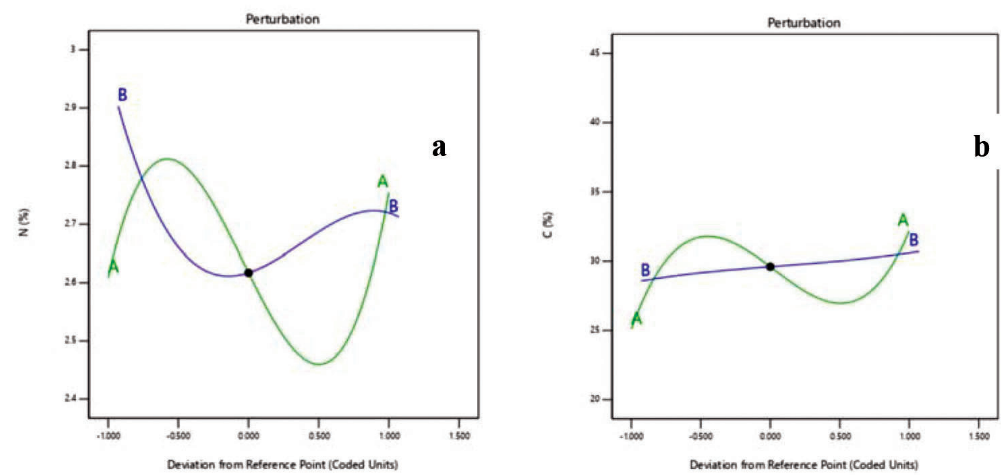


Fig. 5. Effect of perturbation plot on individual responses. (a) Carbon content, (b) Nitrogen content

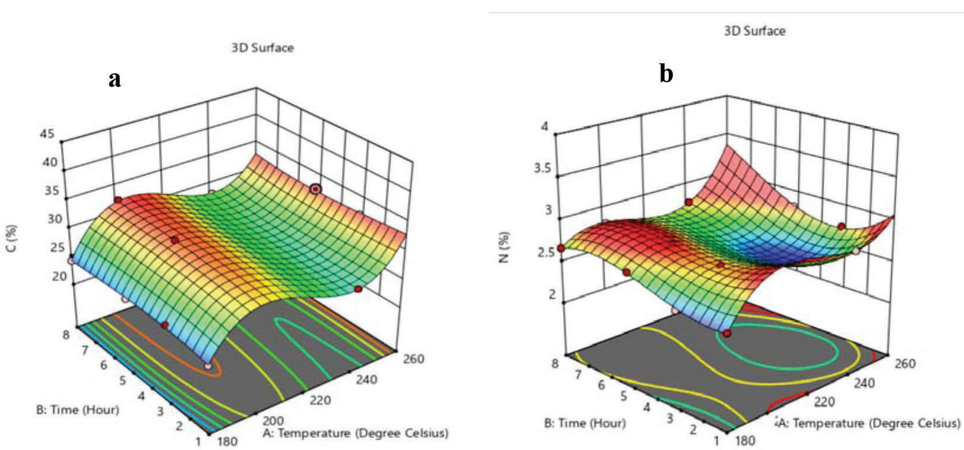


Fig. 6. Three-dimensional response surface curve of temperature and time on (a) Carbon content (b) Nitrogen content

The treatment (T5) which is 4% hydrochar showed germination of seed first among all the treatments which shows that the influence of hydrochar nutrient content (organic acids and nitrogen) on the bhendi seed (Bargmann *et al*., 2013). The germination percentage was noticed as 80% on fifth day in control (Figure 8). The vigour index also calculated for the hydrochar applied bhendi crop on the seventh day was 112. The germination percentage of 89% in T5 shows higher rate which was significantly different when compared to other treatments. The seed vigour index of T5 is 137.6 shows the higher vigour index which was on par with the treatment T4 and T6 (Figure 7). Thus, the germination test and vigour index show positive relationship in the application of hydrochar on the crop germination due to the presence of rich carbon content.

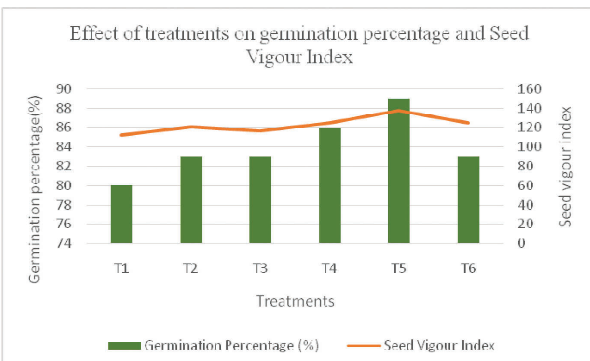


Fig. 7. Treatments showing germination percentage and vigour index

T1 - Control
T2 – 1% hydrochar
T3 – 2% hydrochar
T4 – 3% hydrochar
T5 – 4% hydrochar
T6 – 5% hydrochar

Fig. 8. Germination Experiment

Conclusion

The disposal of paper sludge is a major problem in paper industry. Conversion of sludge into eco-friendly value-added product with lesser energy is beneficial to environment. This current study indicated that production of hydrochar from the ETPS has the increased content of carbon content and slight rise in nitrogen content. This increase in carbon and nitrogen content makes an attempt for the crop application. The hydrochar amendment to the crop will be a viable option for the sustainable environment. This indicates that the effective utilization of the undesirable sludge as a product of carbon rich hydrochar. Further, this could act as an organic fertilizer for the crop and also will increase the organic content of the soil.

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