Hydrochar derived from sewage sludge and water hyacinth and its characterization

Abstract

Population and urbanization increase the sewage generation. Sewage treatment plant (STP) generates the sewage sludge. Agricultural runoff and sewage water discharge into water bodies proliferates the growth of water hyacinth and creates environmental issues. Managing the sewage sludge and water hyacinth are difficult task because of high water content, environmental concerns, regulatory measures and high operational cost. Hydrothermal carbonization (HTC) converts the wet biomass into condensed solid product called hydrochar at moderate temperature range of 180 – 250°C under auto generated pressure. Through HTC process, the sewage sludge and water hyacinth were mixed and converted into hydrochar @ temperature of 200℃ and 4h resident time with L/S ratio of 9:1. The produced hydrochar showed desired functional groups viz., CH – methyl groups, C-O-C – alcohol groups, esters, ethers and Oxygenic functional groups (-C=O, -OH, -CO-O, C-O-C) with particle size of 494.8 nm, BET surface area of 369.70 m^2 g^{-1}, Zeta Potential of -27.9 mV. The hydrochar recorded slightly acidic pH(5.8) with appreciable levels of C, N, P, K, Ca, Mg. These properties of sewage sludge and water hyacinth derived hydrochar exhibits its potential use in agricultural and environmental applications.

Keywords : Sewage sludge, water hyacinth, hydrothermal carbonization, hydrochar

Introduction

In India, the sewage sludge generation is about 19,127 t day^{-1}. It contains organic carbon (9.75-15.88%), Nitrogen (2.05-3.87%), Phosphorus (1.62-2.47%), Potassium (0.98-1.96%), Zn (1332.1-2584.6 mg kg^{-1}), Pb (309.6-608.5 mg kg^{-1}), Ni (125.5-388.5 mg kg^{-1}), Cu (136.6-451.7 mg kg^{-1}) and Cd (3.22-10.09 mg kg^{-1}) (Saha et al., 2018). Water hyacinth weed occupies almost every waterbody and creates environmental problems. The multiplication rate is very high and reaches 125t of wet biomass within 6-month period in 1ha of area. The biomass contains carbon from 30-49%, cellulose from 30-40%, hemicellulose from 31-40% and lignin 10-15%. It contains total nitrogen of 1.12%, total phosphorus of 0.38%, total potassium of 1.24%, total calcium of 0.82% and total magnesium of 0.54% (Prasad and Prasad, 2019). Due to the biochemical properties of the above said wastes *viz.*, Sewage sludge and water hyacinth have the potential to synthesise the novel carbon material which is having multidimensional utility. This approach will give concurrent benefits in both disposal and obtaining high value products.Hydrothermal carbonization (HTC) is an emerging effective thermochemical process for production of hydrochar by converting wet biomass at relatively mild reaction temperatures *i.e*.180-250˚C and self-generated pressure into a coal-like material along with aqueous products and gases-primarily CO_2**.** Materials are having high water content (more than 90%), direct pyrolysis is not economically viable. Hence, it was treated using the hydrothermal carbonization (HTC) process. According **to** Garlapalli*et al.* (2016), the low-quality hydrocharwas improved by higher HTC temperature (260˚C), followed by pyrolysis temperature (800˚C) and the subsequent pyro-HTC char had the following characteristics: highest BET surface area (63.5 m^2 g^{-1}); mild basic pH (9.34); and no PAH and phenolic compounds. Mixed feedstock (40% corn silage + 30% grass silage + 30% cattle manure) digestate from a biogas plant was used to produce activated carbon. The HTC process (temperature: 190-250˚C; residence time: 3-6 h; pH: 5-7) converted the digestate into hydrochars, and it was chemically activated (impregnated with KOH) to enhance the surface area. The surface area increased from 8-14 m^2g^{-1} (hydrochars) to 930-1351 m^2g^{-1} (activated carbon). The activated carbon was a very effective adsorbent for carbon dioxide (CO_2) since it has large micropore volumes (0.35–0.50 cm^3g^{-1}) (Rodriguez Correa *et al.*, 2017). Jin *et al.* (2018)analyzed the conversion of digestate of swine manure and rice straw to hydrochar, and these materials were subjected to HTC-treatment at 190°C with a ratio of biomass and water at 1:4 and 1:9. The synthesizedhydrochars were acidic, dissolved organic carbon, dissolved organic carbon, BET surface area, more O functional groups, and aromatic C=C and C-H band, when compared to the original feedstock and pyrochars. Sadish *et al.* (2019) also studied the characterization of optimized hydrochar from paper board mill sludge using Response Surface Methodology. Phytotoxic property of hydrochar was eliminated by thermal treatment below 300 °C (Hitzl et al., 2018). Sludge hydrothermal carbonization resulted the P rich char (total P up to 25,175 mg kg^{-1}) but the free P were fixed in char but most of the free fractions were transformed and thehydrochars showed a high phosphate adsorption capacity (up to 23,815 mg kg^{-1}) and the adsorbed P could be readily released (Fei et al., 2019). The wetland biomass wastes derived hydrochars had a moderate pH (5.0-7.7), more oxygen-containing groups, and higher energy density (18.0-27.1 MJ kg^{-1}) and high water-soluble P in biomass (71.0-73.2% of total P), more recalcitrant P species formed in hydrochars, implying that HTC treatment could achieve P immobilization and reduce P leaching loss. HTC is a promising treatment technique for wetland plants to produce valuable char with P reclamation (Cui *et al*., 2020). In this prelude this work has been taken to obtain hydrochar from the sewage sludge and water hyacinth biomass in order to find out the effective solution for managing the waste biomass.

Materials and Methods

Hydrochar production from ETP sludge

Hydrochar, a product of Hydrothermal Carbonization is found to possess wide range of environmental and agricultural application. The purpose of this work is to produce the hydrochar from sewage treatment plant sludge and water hyacinth biomass and assess its efficiency in sodic soil reclamation. The materials used and methods adopted in these experiments are given below. In order to produce hydrochar, Sewage sludge was collected from Sewage Treatment Plant (STP) Ukkadam, Coimbatore and water hyacinth was collected from Koraiyar, Trichy. The sample of sewage sludge and water hyacinth were dried @ 105°C in oven, powdered sieved through 2mm sieve and stored and their chemical properties were analyzed (Lin *et al*., 2015).

Characterization of Sewage sludge, water hyacinth biomass and hydrochar

The Carbon, Hydrogen, Nitrogen and Sulphur composition were determined using Elemental Vario EL III CHNS analyser(Kalderis *et al*., 2020). The surface texture and morphological features of the samples were identified by scanning electron microscope (M/s. FEI – Quanta 250, Czech Republic)(Kliewer *et al*., 2009). The internal morphology of the samples was determined by transmission electron microscope (M/S FEI - Technai Spirit G2) at an accelerating voltage of 120KV(Kliewer *et al*., 2009). Fourier Transform Infrared Spectroscopy (FTIR) technique was used to determine the functional groups present in the sample (Trakal *et al*., 2014). The Particle size was measured in the particle size analyzer (Horiba Scientific Nanopartica SZ-100, Japan) (Kuzniatsova *et al*., 2008). The surface charges of sample were determined by measuring the zeta potential (Asadi *et al*., 2009). The BET surface area and pore volume were analyzed by Smartsorb 92/93 surface area analyzer under nitrogen environment (Brunauer *et al*., 1938; Yang and Qiu, 2010). In addition to this, the other essential characterizations were carried out as per the standard methodsandthe analytical data are presented in table 1.

Production of Hydrochar from Sewage sludge and Water hyacinth through Co-Hydrothermal carbonization process

Hydrochar, a carbonized material was produced from the raw sludge and water hyacinth by heating the material to different temperatures ranges (180°C, 200°C, 220°C, 240°C) and time 1hr, 2 hr, 4 hr and 6 hr) at self-generating pressure. Hydrochar production parameter optimization (Resident time and Temperature) was fixed by adopting RSM methodology. Sewage sludge and fresh water hyacinth biomass @ 1:1 ratio weremixed thoroughly before the experiment for attaining homogeneity. After homogenization, 90 g of Sewage sludge and fresh water hyacinth (i.e., 9g solids and 81g water) (maintained L/S ratio of 9: 1 in HTC reactor) were taken in a 100 ml hydrothermal autoclave reactor and sealed. The reactor was then placed in the laboratory oven and heated to the specified temperatures for different reaction times. After the reaction has been completed, the reactor was removed immediately from the oven and placed in cold water to quench the reaction. The formed hydrochar was filtered through Whatman no. 40 filter paper to separate the solid and liquid portion, after that the suspended hydrochar was dried overnight at 105˚C in oven and analysed (Sadish et al., 2020).

Details of Experiment

List 1. Experimental Design

Factors	Levels	Level 1	Level 2	Level 3	Level 4
Temperature	4	180 ˚C	200 ˚C	220 ˚C	240 ˚C
Time	4	1h	2h	4h	6h

Number of Factors: 2 (Temperature & Time)

Results and Discussion

Co-hydrothermal Carbonization of Sewage sludge and fresh water hyacinth biomass

Based on the values of the individual responses and the predetermined optimization parameters (boundaries and goals), the optimization was carried out by the software. A set of optimized process parameters with presumed responses were generated after optimization. The predicted parameters with the highest desirability (towards 1) can be confirmed as an optimized run for the design. The process temperature of 200℃ and time of 4h were shown a highest desirability and it was set as optimum process parameter for the production of hydrochar from Sewage sludge and fresh water hyacinth biomass.This was supported by Ferrentino *et al.* (2020) Sabarish *et al.* (2021) and Parameswari et al. (2023). The production of hydrochar from date palm waste for adsorbent preparation was optimized at 200^{0}C for 2h (Ferrentino *et al.*, 2020). Oumabady *et al.* (2020)reported the optimized parameter, 200^{0}C for 10 h for hydrochar production from paper board mill sludge.

Characterization of Sewage sludge and fresh water hyacinth biomassderived hydrochar

The physical, chemical, physico-chemical, proximate, ultimate and surface characterization of Sewage sludge and fresh water hyacinth derived hydrochar (Plate 1) were analysed and their results are presented in table 1.The production of acidic groups like acetic acid, glycolic acid, formic acid, and levulinic acid as a result of the breakdown of organic molecules depicted the acidic pH of the Hydrochar(Jin *et al.*, 2018; Oumabady *et al.*, 2020). The Structural and morphological characteristics of Sewage sludge and water hyacinth derived Hydrochar (SSWHH) were given in table 3.The zeta potential value of hydrochar was decreased. The establishment of cross linking electrophilic bonds with oxygenic functional groups (OFG) (hydroxyl, carboxylic and phenolic) through the surface deprotonation, explains the decrease in surface's zeta potential. The structural features like surface area and pore volume of the hydrochar produced showed the increase in surface area and pore volume. The findings of Sadish *et al.* (2019) revealed the same as the HTC reaction resulted in reduced oxygen, hydrogen, nitrogen and sulfur content with increase in carbon content. Similar results were also reported by Wang *et al.* (2021), Ramesh *et al.* (2019),Marx and van der Merwe (2021), Sabarish *et al.*(2021)and Parameswari *et al.*(2023).

FTIR spectra analysis

FTIR spectral analysis (fig. 1) revels that depicts to the presence inter/intra-hydrogen bonded (O-H) stretching vibration of alcohols, phenols, and carboxylic acids as in cellulose and lignin, which indicating the presence of free hydroxyl groups on the surface. In addition to this, the hydrochar is having other functional groups viz., -CH – methyl groups, C-O-C – alcohol groups, esters, ethers and Oxygenic functional groups (-C=O, -OH, -CO-O, C-O-C).Dehydration, polymerization reaction and aromatization are increased the functional groups in hydrochar. The presence of the functional groups was supported by Reza (2013),Saha *et al.* (2019), Nguyen*et al.* (2021), Sabarish *et al.* (2021),Parameswari *et al.*(2023).

Analysis of Structural morphology

SEM image (Fig. 2) revealed that, hydrochar showed rougher surface, small cracks, fissures, pores, and grooves which indicates the existence of a linked porous network of surfaces. These rough surface morphologies were clearly apparent in micrographs, which also showed particle size decrease from µm to nm (hydrochar). In addition to that, the hydrochar surface from micrographs revealed the particle dispersions in the form of spongy, spherical shaped particles, fluffy and fuzzy nature with deeper fragmentation.The TEM images (Fig. 2) portrayed the formation of porous – spherical, hexagonal, tubular, and microsphere carbons. Spherical and tubular porous carbon (carbon nanotube) materials were formed from the irregular shaped precursor particles.Oumabady *et al.* (2020)reported that the surface morphologies of paper board mill ETP sludge (PBM-ETP) and PBM-ETP sludge derived hydrochar showed the smooth and coarser surface, respectively. The formation of the rougher surface with microspheres on the surface of PBSH was due to the decomposition of easily degradable compound hemicellulose and cellulose followed by softening of lignin(Boyjoo *et al.*, 2017; Sabarish *et al.*, 2021;Parameswari *et al.*, 2023).

Table 1.Characteristics of raw sewage sludge, water hyacinth, and Sewage sludge and water hyacinth derived Hydrochar (SSWHH)

Parameters	Sewage sludge	Water hyacinth	SSWHH
pH	6.01	6.68	5.80
EC (dS m^{-1})	3.70	1.72	3.00

C (%)	19.32	29.42	24.40
H (%)	2.66	5.56	3.28
N (%)	2.28	2.66	2.51
S (%)	0.99	0.73	0.97
P (%)	0.58	0.38	0.44
K (%)	1.70	1.24	0.98
Ca (%)	1.80	0.82	1.24
Mg (%)	1.20	0.54	0.68
Metals (mg kg^{-1})			
Cadmium	0.64	1.80	0.76
Chromium	6.5	BDL	1.80
Nickel	12.55	BDL	0.88
Lead	30.9	BDL	0.92
Iron	560	320.00	436.0
Zinc	980	37.6	440.00

Table 2. Structural morphology and textural characterization of Hydochar produced from sewage sludge and water hyacinth

Parameters	Value
BET Surface Area (m^2 g^{-1})	369.70
Pore Volume (cc g^{-1})	0.6790

Particle Size (nm)	494.8
Zeta Potential (mV)	-27.9

Conclusion

Based on the results obtained by the laboratory experiments, it could be concluded that the ideal parameters were set as 200°C temperature and 4h residence time for production of hydrochar fromSewage sludge and water hyacinth at self-generating pressure. The characteristicsfeaturesof produced hydrocharlikepH, C, S, N, P, K, Ca, Mg, BET surface area, particle size and zeta potential are showed the positive to used agricultural soil amendment and environmental application. This approach is used to convert the high wet organic waste materials into valuable carbon material as hydrochar.

Plate 1. Hydochar produced from sewage sludge and water hyacinth

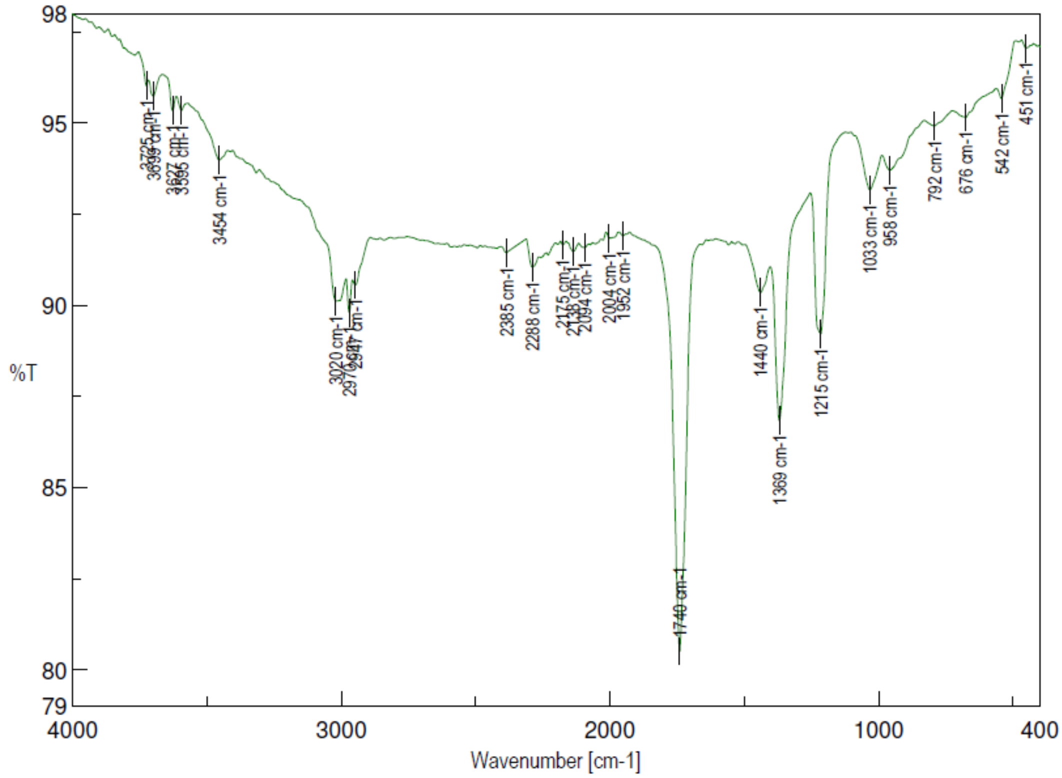
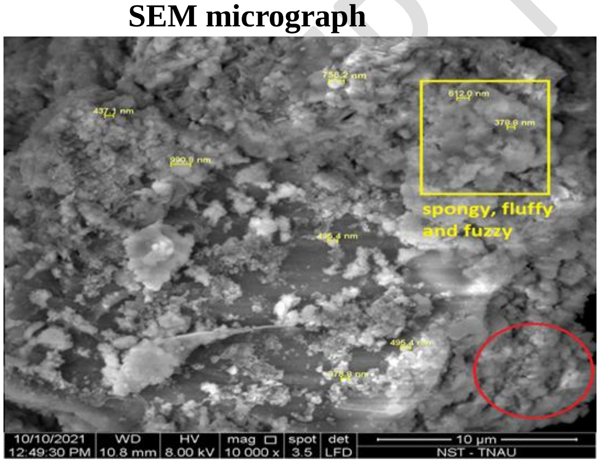


Figure 1. FTIR Spectra of Hydochar produced from sewage sludge and water hyacinth

SEM micrograph



TEM micrograph

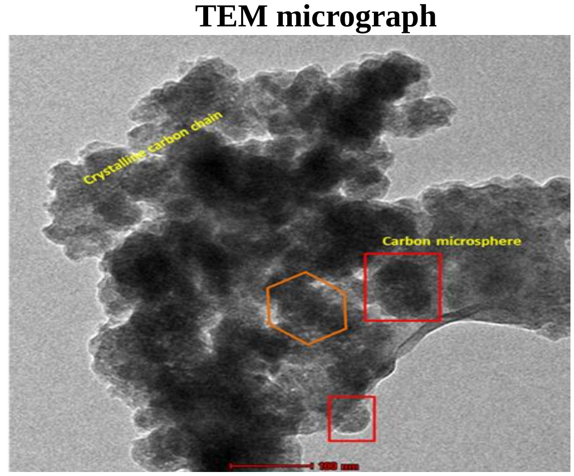


Fig. 2. Structural morphology of Hydochar produced from sewage sludge and water hyacinth

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