Original Research Article

PRODUCTION AND CHARACTERIZATION OF PAPER BOARD MILL ETP SLUDGE DERIVED HYDROCHAR

ABSTRACT

Hydrothermal Carbonization an emerging technology for the conversion of biomass into carbon rich materials called as hydrochar. In this study, the paper board mill ETP sludge has been used for the production of hydrochar. The characterization of point of zero charge, Heavy metals, proximate and ultimate constituents, structural morphology (SEM), and molecular surface functionalities (FTIR) were also analysed. The results of Hydrochar showed slightly acidic pH (6.40), EC (1.33), and the pH_{PZC} (point of zero charge) of 7.8 and the heavy metals content were found to be below detectable limit. FTIR analysis revealed that, the produced hydrochar have oxygen containing functional groups (-OH, C-O-C, -C=O). SEM analysis has the morphological features such as spongy, fuzzy and fluffy porous network on surfaces. These results of hydrochar can be act as an active adsorbent with further activation.

Keywords: Hydrochar, Point of zero charge, Functional groups, Adsorbent

1. INTRODUCTION

The Paper production in the world was 413 million tonnes, with India accounting for 3.18 % of annual paper, paper board, and newspaper production [3]. These paper products are cycled thoroughly after handling by paperboard mill industries, resulting in recycled paper and packaging materials. These industries produce solid waste known as paperboard mill sludge from Effluent Treatment Plants (ETP), which is handled through landfill formation and incineration. Despite the strict policies of landfill and shortage of land, the paperboard mill sludge can be used for the production of hydrochar, with specific applications in energy generation and wastewater treatment [17].

Hydrothermal carbonization (HTC) is an emerging method, represents an efficient and valuable pre-treatment technology for the conversion of wet biomass into highly dense carbonaceous materials (Hydrochar) at relatively mild reaction temperatures that that could be used in wide applications such as environment, energy, soil improvement, and nutrients recovery [11]. Being a carbon compound with good aromaticity, hydrochar has a potential application due to the reduction of inorganic constituents and increased proportions of carbon compounds [2]. The surface modification such as coarseness and the formation of cracks, fissures on the hydrochar surface was caused by HTC. The synthesized hydrochars were acidic, had more dissolved organic carbon, greater surface area, more Oxygen functional groups, aromatic C=C and C-H bands when compared to the original feedstock [19]. This leads to the creation of remediation possibilities for wastewater-borne environmental pollutants. Due to the breakdown of organic polymers and the production of carbon compounds, hydrochar was shown to have more substantial adsorbent capabilities [14]. In addition to that an emerging field of research in recent days was hydrochar as a low cost adsorbent. As a result of HTC, pollutants such as organic contaminants, hazardous anions and toxic metals bind to oxygen functional groups on carbon surfaces, which operates as active sites for sorption [6, 18]. In this background, the current study was formulated to produce hydrochar from ETP paper board mill sludge and produced hydrochar was it characterized for environmental application feasibilities.

2. MATERIAL AND METHODS

The Paper Board mill ETP sludge was collected from Effluent Treatment Plant at TNPL Unit II, Mondipatti, Trichy and stored in sample containers at 4˚C. For the initial characterization, sludge was oven dried at 105˚C for moisture removal, ground, sieved through 2mm sieve and stored [9].

2.1 Production of Hydrochar

The PB-ETP Sludge was mixed to ensure homogeneity prior to the experiment. In a 100 ml hydrothermal autoclave reactor, 90g of fresh PB-ETP Sludge (with 1:9 sludge:water ratio) was placed and tightly sealed after homogenization [12]. After that, the reactor was positioned in a laboratory oven and heated to the specified temperature for various reaction time period [17]. After the completion of reaction, the reactor was immediately removed from the oven and immersed in the cold water to quench the reaction. The hydrochar was then filtered to separate the solid and liquid components before being dried overnight in a hot air oven at 105°C and kept in an airtight container for future analysis [1, 13]. The temperature level chosen for a 4 hour residence duration was 200°C, which is the optimized set temperature for the production of Hydrochar. The optimization was done using Stat-ease software (version 13), RSM tool.

2.2 Analytical procedures

The pH and electrical conductivity of the Sludge and Hydrochar were measured using a digital pH meter and a conductivity meter at a solid-to-water suspension ratio of 1:2.5, respectively. The point of zero charge (pH_{PZC}) was determined by Drift method. The standard ASTM (American Society of Testing and Materials) analytical methodologies have been followed for the determination of proximate composition (ASTM D3173 for moisture content, ASTM D3175 for volatile matter, ASTM D3174 for ash content and ASTM D3172 for fixed carbon content) of the samples [1]. The samples were acid digested for the determination of the heavy metals (Cd, Cr, Ni and Pb) and estimated using Atomic absorption spectrophotometer (Perkin Elmer AA analyst 400).The ultimate composition (C, H, N and S) of the raw sludge and hydrochar were determined using Elementar Vario EL III at CHNS operating mode with digestion temperature of 950-1200℃. The functional characteristics were determined using FTIR (Model 8400 S of Shimadzu, Japan) over the wavenumber range of 4000–400 cm^{-1}. The surface morphologies and texture characteristics of the samples were interpreted by scanning electron microscope M/s. FEI - Quanta 250, Czech Republic taken at a high voltage of 8 kV with 5000x magnification.

3. RESULTS AND DISCUSSION

The color of sludge and hydrochar was visually observed (**Figure 1**). The hydrochar produced has obtained brown colour compared to sludge with black colour [21].

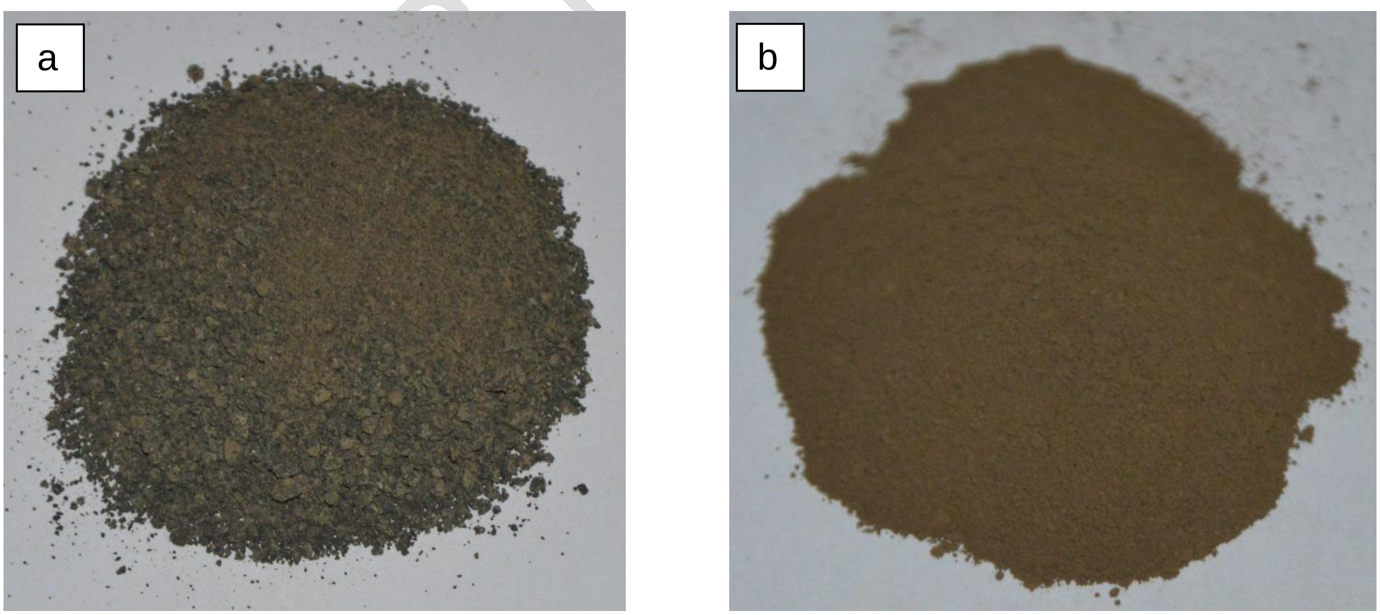

Figure 1. Visual Observation of (a) Sludge, and (b) Hydrochar

Table 1. Characteristics of Sludge and Hydrochar

Sl. NO	Characteristics	Sludge	Hydrochar
1.	pH	7.08	6.40
2.	Electrical Conductivity (dSm^{-1})	4.52	1.33
3.	pH_{PZC}	7.3	7.8
4.	Proximate Analysis (%)		
	i. Volatile matter	62.40	46.7
	ii. Ash content	30.25	37.2
	iii. Fixed carbon	7.35	16.1
5.	Ultimate Analysis (%)		
	i. Carbon	29.42	31.32
	ii. Hydrogen	5.56	2.70
	iii. Nitrogen	4.68	1.81
	iv. Sulphur	0.73	0.70
6.	Heavy Metals ($mgKg^{-1}$)		
	i. Nickel	32	BDL
	ii. Lead	184	BDL
	iii. Chromium	BDL	BDL
	iv. Cadmium	BDL	BDL

The pH and electrical conductivity of the sludge was 7.08 and 4.52 dSm^{-1}, respectively. Wherein, the Hydrochar showed the pH and EC of 6.40 and 1.33 dSm^{-1} respectively. The organic acids released during HTC catalyze the hydrolysis reaction which resulted in reduction of pH [24]. The Proximate characteristics such as volatile matter, ash content and fixed carbon content has been presented in **Table 1.** Hydrochar's volatile matter content has dropped considerably from 62.4 % to 46.7 % when compared to raw sludge, resulting in a 15.7 % reduction. Dehydration and decarboxylation processes resulted the volatile matter content reduction [8]. On the other hand, the fixed carbon percentage in Hydrochar increased from 7.35 % in sludge to a high of 16.1 %. However, the increase in fixed carbon was smaller than the decrease in volatile matter, indicating that volatile molecules were converted into liquid and gaseous products [9]. The organic composition of paper sludge, such as carbohydrates, proteins, cellulose, and hemicellulose compounds, decomposes and dissolves into liquid and gaseous portions of hydrothermal carbonization as glucose, fructose, amino acids, and phenolic compounds, resulting in the loss of volatile matter [16]. As a result of the loss of volatile matter and the retention of mineral matter, the ash content of Hydrochar increased from 30.25 % to 37.2 %. The ultimate characteristics of sludge revealed a carbon content of 29.42%, hydrogen content of 5.56%, nitrogen content of 4.68% and sulfur content of 0.73%, where hydrochar depicted carbon content of 31.32%, hydrogen content of 2.70%, nitrogen content of 1.81% and sulfur content of 0.70%. Among the heavy metals, the lead (Pb) and nickel (Ni) were detected in Sludge and were accounted for 184 mg kg^{-1} and 32 mg kg^{-1}, while cadmium and chromium were found to be below detectable limit (BDL). After hydrothermal carbonization, the lead and nickel content were found to be below the detection limit in Hydrochar, which may be due to lead and nickel leaching from solid to liquid fractions.

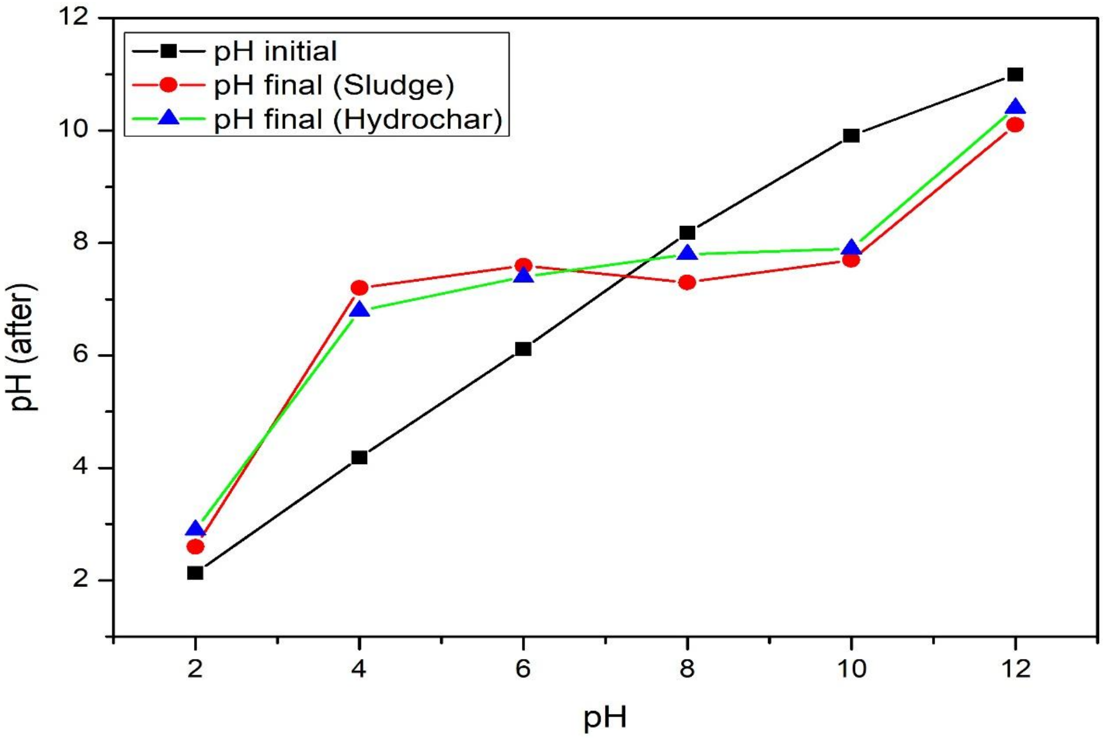

Figure 2. Point of Zero Charge of Sludge and Hydrochar

For the pH of Sludge and Hydrochar at the zero-charge point shown in **Figure 2**, the curve $pH_{initial}$ = f (pH_{final}) intersection with the bisector reveals that the pH_{PZC} of Sludge and Hydrochar equals 7.3 and 7.8, respectively. With the increase in HTC temperature, hydrochars are coming closer to neutral charge (equal amounts of positive and negative charge). Hydrochar surface is a negatively charged, if its pH is greater than that of pH_{PZC}. This form of hydrochar has the potential to interact with positively charged materials. Hydrochar, on the other hand, is positively charged with a pH lower than pH_{PZC}, which may interact with negatively charged materials [4, 18]. This means that below pH_{PZC}, the surface of Hydrochar is positive, promoting adsorption between Hydrochar and negatively charged molecules and vice-versa [10].

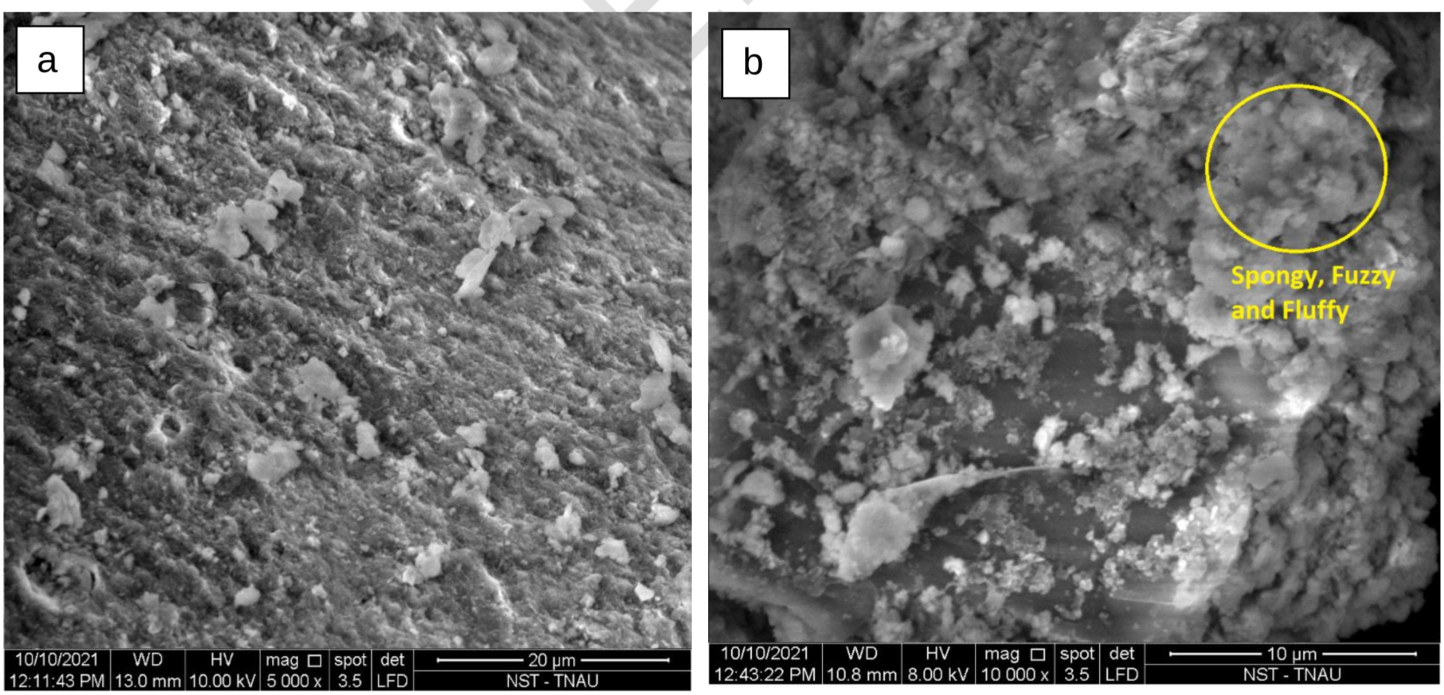

Figure 3. SEM images of (a) Sludge and (b) Hydrochar

The scanning electron microscopy revealed the surface morphology of Sludge and Hydrochar **(Fig.3)**. In comparison to smooth surface of sludge with microspheres, SEM image showed that Hydrochar had a rougher surface. On the hydrochar, small cracks, fissures, pores, and grooves showed the existence of a linked porous network of surfaces, as well as reduction in particle size from µm (sludge) 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 [5, 13]

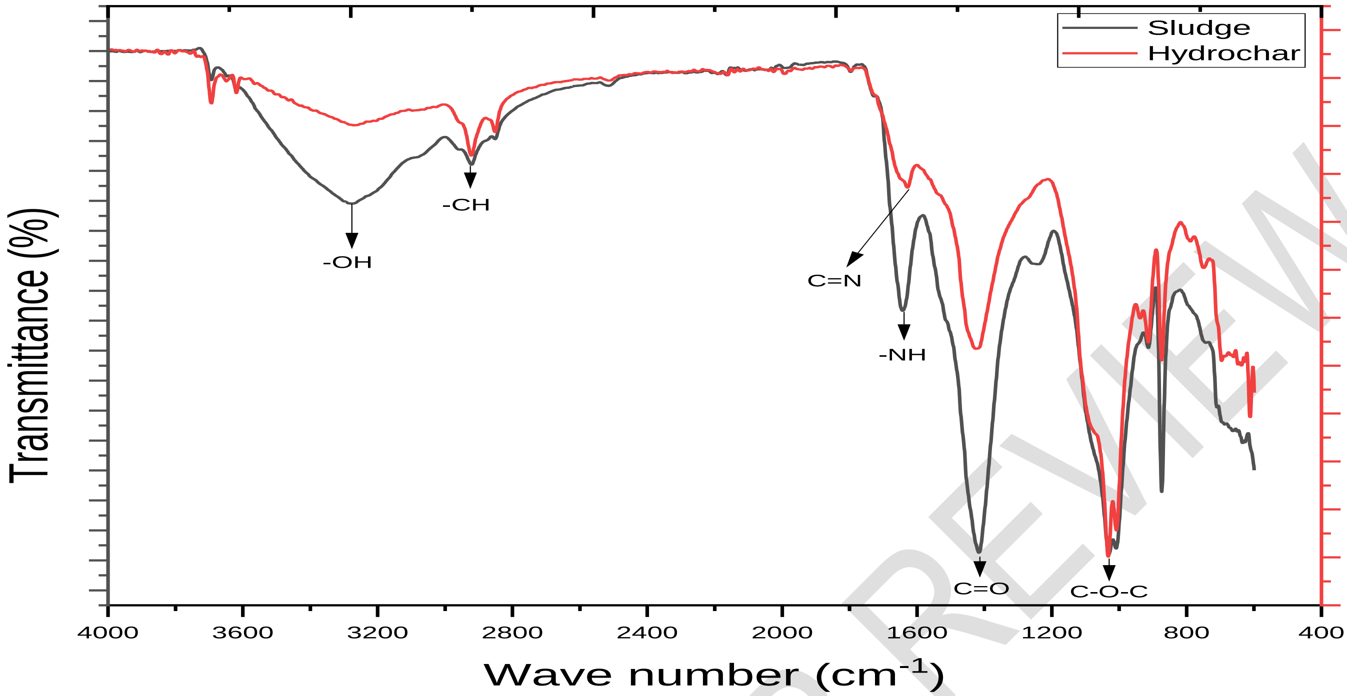

Figure 4. FTIR Spectra of Sludge and Hydrochar

The FTIR characteristics of Sludge and hydrochar were analysed over a band range of 4000-400 cm^{-1}**(Fig. 4)**. The intensity of the peaks for the prepared hydrochar are listed in the **Table 2**. The table shows the surface functionalities of Hydrochar. The peak of Slude and hydrochar at 2923 cm^{-1} attributed to the vibration of C–H stretching thereby indicating the presence of methyl groups $-CH_2$, $-CH_3$, or - $(CH_2)_{n.}$ The band at 1670 – 1530 cm^{-1} indicats the C=C stretching bends in lignin aromatic ring [23]. The characteristic NH deformation and C-N stretching band is around 1650-1520 cm^{-1}. The C=O stretching band at 1415 cm^{-1} related to the C–N stretching vibration of amides, and the drop was caused by decarboxylation processes that occurred during the hydrothermal carbonization [20]. The oxygen containing functional groups **(Table 2)** formed on the surface of the hydrochar may play an essential role as an adsorbent [7].

Table 2. Functional Characteristics of Hydrochar

Range (cm^{-1})	**Intensity**	**Functional Groups**	**Bond**	**References**
3383 – 3160	stretching vibration	-OH	Inter/intra-hydrogen bonded (O-H)	[22, 15]
1030 and 1018	stretching vibration	C-O-C	Ethers, esters	[23]
1415	stretching	-C=O	Ester groups	[20]
1670 – 1530	stretching bends	C=C	Lignin aromatic ring	[23]
2923	stretching vibration	C–H	methyl groups $-CH_2$, $-CH_3$, or - $(CH_2)_{n.}$	[13]

4. CONCLUSION

The production of hydrochar from the recycled paper board sludge is a better way of reducing solid wastes and its characteristics features shows effective utilization for environmental applications. The acidic properties of the hydrochar will also be used for the sodic soil reclamation. It can also be used in the efficient removal of heavy metals and pollutants from soil and waters. The hydrochar with pH_{pzc} (7.8) and its conditions below adsorb the molecules with opposite charges. The surface of hydrochar with oxygen containing functional groups paves the way for adsorption of pollutants from the environmental wastewater. Further detailed studies on hydrochar for characterization and activation can be performed for achieving the sustainability in wastewater treatment.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly used products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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