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Biochar-assisted aerobic granulation in enhanced biological treatment of landfill leachate with municipal wastewater for sustainable resource recovery: A biorefinery approach

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ABSTRACT

The current study deals with aerobic granular technology (AGT) for the simultaneous treatment of landfill leachate and municipal wastewater in a stirred tank reactor in SBR mode with biochar-assisted granulation of sewage sludge. This study incorporated a strategy to shorten granulation time while increasing its stability for the efficient removal of pollutants. In this work, the sewage sludge-derived biochar, mesoporous in nature with surface area of 71.5 m^2/g was used to assist the granulation process of the sludge in a Sequential Batch Reactor (SBR). High removal of total phosphorous (~70 %) and nitrogen was observed along with COD removal (80 %) during the experimental study. After the treatment process, the sludge was retrieved from both reactors R1 and R2 and subjected to a hydrothermal liquefaction (HTL) process to obtain bio-oil. Therefore, this study proved to be a suitable example for generations of an alternative form of bio-fuel from industrial wastes thus establishing a biorefinery approach.

1. Introduction

Land-filling is the most common, convenient, and widely used approach for the disposal of municipal solid waste across the globe [1]. However, the lack of availability of space stands out to be the main drawback for population-dense countries like South Korea. Additionally, traditional landfills demand significant or prolonged periods for their stabilization and maintenance [2]. Leachate is the by-product of such landfills and because of its large concentration of pollutants, it should be treated before being discharged into the environment. Biological treatment of such wastes and using this as a substrate for cultivating microorganisms for bio-energy generation would help to overcome environmental hazards due to waste discharge.

The liquid that leaks through landfills as a result of precipitation, decomposing trash, and other circumstances is referred to as landfill leachate. It may contain a variety of contaminants, such as microorganisms, heavy metals, and organic/inorganic substances. Leachate from landfills needs to be managed properly to avoid damaging effects on the environment and public health. Due to South Korea's dense population and constrained land supply, the problem of landfill leachate has been a concern. Landfilling has traditionally been a major source of garbage disposal in South Korea. Since 1992, Incheon's Sudokwon landfill has handled all the garbage in an environmentally responsible manner. It was just recently reported that this landfill had reached capacity and was no longer accepting waste. Landfill management raises environmental concerns and controls greenhouse gas emissions. Despite progress in recycling, achieving high rates remains a challenge. Food waste remains a significant issue in South Korea. Therefore, this megacity is looking forward to other sustainable options in this regard. However, recognizing the environmental risks associated with landfill leachate, the government has taken steps to address the issue and promote more sustainable waste management practices. Government efforts include improving infrastructure, increasing public awareness, and promoting public participation in waste separation and recycling. However, immediate attention needs to be drawn toward sustainable landfill leachate management. Anaerobic digestion of landfill leachate can be carried out for bio-hydrogen and biomethane production. This leachate can however be re-circulated in an anaerobic reactor. Additionally, recirculation of the landfill leachate has been reported to substantially increase the biomethane content in the biogas produced [3]. Besides, an in-situ lab or pilot scale aeration on the landfill leachate poses a significant impact on the stabilization of the aerobic microbial

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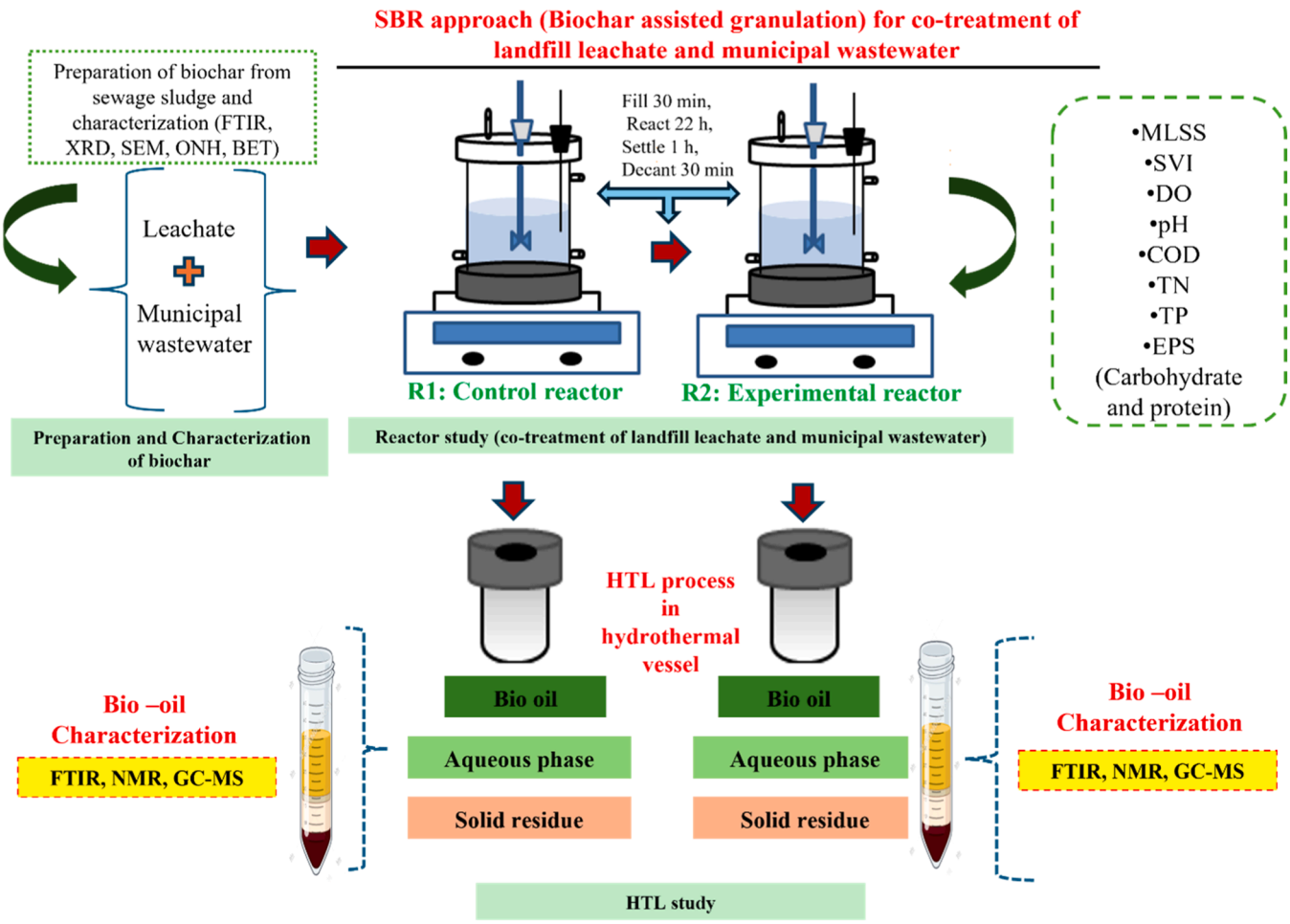


Fig. 1. Schematic showing the entire work plan for simultaneous leachate and municipal wastewater treatment using assisted granulation.

community [4].

Despite so many challenges, this country has been actively exploring waste-to-energy technologies to minimize the amount of waste sent to landfills, as an alternative and sustainable approach for solid waste management. However, the expansion of waste-to-energy facilities has faced some opposition from local communities due to concerns about emissions and their environmental and health impact. Hence, balancing waste-to-energy initiatives with environmental considerations and public acceptance stands out to be the most challenging issue. Therefore, the search for alternatives for solid waste management is the only option to solve this issue. For decades, extensive research has been done in this direction for the aerobic landfill leachate degradation of toxic compounds in an aerobic bioreactor under SBR mode.

The sequencing batch reactor is a fill-and-draw activated sludge system for wastewater treatment successfully used to treat both municipal and domestic wastewater. The term SBR was coined by R.L. Irvine [5]. Landfill leachate is known to have a high degree of variation in its quality and quantity, and hence the sequencing batch reactor (SBR), has great process flexibility among biological methods, therefore well fitted for leachate treatment [6]. It has several advantages such as simple operation and low capital cost, efficiency in the removal of organics, flexible nature fill/react ratios and time of aeration, ease in installation, needs fewer channels and pipes, easily scalable and expandable, flexibility in operating parameters, easy understanding of fundamental mechanisms of the process, etc. [7]. Since leachate has high organics, a combination of biochemical processing is required and hence this study aims to supplement leachate with municipal wastewater and simultaneously treat it biologically under aerobic conditions. Also, limited literatures are available on co-digestion of leachate and municipal wastewater as the BOD/COD ratio (0.09–0.37) of leachate can only be treated by SBR. Also, the use of biochar which can be produced by different thermochemical processes such as pyrolysis, hydrothermal carbonization, etc. is widely used for enhanced granulation in biological treatment using floccular sludge in SBR.

AGS technology has been proven to be the most promising system for biological wastewater treatment systems with high resistance to toxicity load and a wide variety of microorganisms. Activated sludge has low settling flocculent biomass, low MLSS, and demanding high-energy systems. It also increases the hydraulic retention time) (HRT). On the other hand, AGS settles fast, with optimal MLSS concentration thus reducing the requirement of a secondary clarifying system. The granulation process can be termed as a complex phenomenon involving a series of events that takes place to form granules mostly accelerated by exopolysaccharides (EPS) secreted by the microorganisms. Granular formation involves few stages: cell-to-cell attachment, cell attachment, and microaggregate formation. Physical forces like hydrodynamics, diffusion, gravity, and Brownian movement stimulate movement. Recently, more focus was given to reduce the start-up time of the aerobic granulation process such as bioaugmentation and optimization of parameter conditions such as cycle time, settling time and organic loading rate. Short cycle and starvation time is reported to enhance granulation, while on the other hand bioaugmentation through inoculation of strains can also facilitate smooth granulation process. Biochar, a biostable carbon material offers several advantages when used in various fields such as, soil amendment, carbon sequestration, granulation processes, particularly in wastewater treatment processes. It

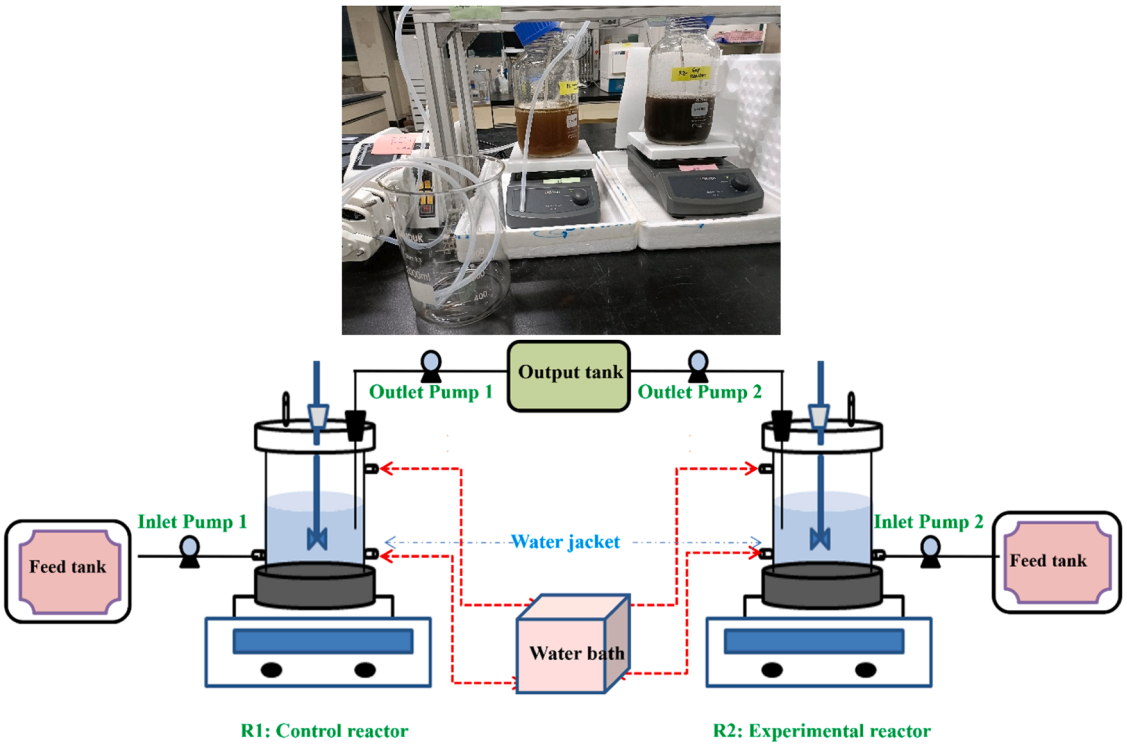


Fig. 2. Image showing the experimental set-up for cotreatment of landfill leachate and municipal wastewater in an SBR system.

involves the formation of larger particles or granules from smaller particles enhancing the efficiency of various treatment methods. Some of the advantages include high adsorption capacity, physical stability, removal of contaminants, physical stability, enhanced settling, and the ability to be customized, showing ease in handling.

In this study, the biological treatment of the landfill leachate and municipal wastewater, in a Sequential Batch Reactor (SBR) and energy recovery was carried out in three phases (I-III). The first phase involved the preliminary characterization of sludge/leachate and municipal wastewater along with the optimization of the landfill leachate: wastewater ratio for efficient COD removal and sludge production followed by biochar preparation from sewage sludge via pyrolysis and its characterization, etc. The second phase dealt with the performance evaluation of a simple completely stirred tank reactor (CSTR) under batch and SBR mode for simultaneous treatment of landfill leachate and municipal wastewater treatment and enhanced granulation using biochar. The effect of biochar for granulation and efficient COD reduction with different OLRs of landfill leachate and municipal wastewater was also emphasized in this phase. Finally, in the last phase, the residual sludge post-treatment was subjected to hydrothermal liquefaction (HTL) for potential bio-oil, aqueous phase, and bio-char production, its process optimization, and characterization. The schematic workflow of the entire experiment is depicted in Fig. 1. The novelty of this work lies in the fact of utilizing industrial and household liquid waste as a cheap source of both carbon, nitrogen and trace elements that support microorganisms for providing nutrition for growth and metabolism followed by subsequent biofuel (bio-oil) production. This work focused on establishing an effective method for enhanced granulation by the addition of biochar during co-treatment of landfill leachate and municipal wastewater. The co-relation between EPS (along with its composition *viz*. carbohydrate and protein) production and granulation has also been successfully established in the study from the obtained results and analysis. This study also tried to derive an integrated zero-waste eco-friendly strategy by applying waste utilization, waste valorization and energy generation from industrial waste (waste-to-energy approach) without generation of any hazardous compounds in the environment.

2. Materials and methods

2.1. Sewage sludge-derived biochar preparation

The sewage sludge was obtained from the Jangrim wastewater treatment plant in Busan, South Korea. The biochar was prepared as described by Wang et al. [8]. Briefly, the raw thickened sludge was initially oven-dried at 80℃ and then pyrolyzed at 700℃ for 1.5 h under N_2 conditions (Supplementary data). The pH was maintained at 7.0 and the oven dried again. The raw biochar was then sieved using 100–200 mm mesh sieves and kept until further use.

2.2. Leachate and municipal wastewater

The leachate was obtained from a landfill site in Busan and analyzed as mentioned following standard protocols (Humas). The synthetic municipal wastewater was prepared in the laboratory as mentioned by Shah et al. [9]. Different ratios of leachate and wastewater were optimized to start the reactor and maintain the OLR. The leachate provided nitrogen, and municipal wastewater provided all the necessary nutrients and carbon required for the growth and metabolism of microorganisms present in the sludge. Furthermore, biological treatment of old leachate seems to be inefficient due to the presence of high BOD/COD. Hence, pre-treatment techniques are often coupled with the mainstream to achieve efficient removal. In this regard, co-treatment can be a viable option for the treatment of leachate and municipal wastewater as dilution favors enhanced degradation. Moreover, municipal wastewater supports the growth of microorganisms owing to the presence of salt and minerals. The composition of municipal wastewater and characterization of the leachate and municipal wastewater are mentioned in Supplementary data.

2.3. Reactor configuration and operating conditions

Simultaneous treatment of leachate and municipal wastewater was carried out in an indigenously prepared laboratory SBR reactor with one reactor as a control (R1) and another as an experimental reactor (R2). The treatment process was assisted by enhanced granulation of sewage-derived biochar. The sewage-derived biochar was prepared as mentioned above in Section 2.1 and used in the reactor (1 % *v/v*) [10]. The reactor's total volume was 2 L with 1 L working volume. The air was pumped inside the reactor to maintain proper aeration using an air pump. The dissolved oxygen (DO) concentration was maintained at 6.5–8 mg L^{-1} throughout the experiment. The influent and output of the reactor were maintained using a peristaltic pump when required. The volumetric ratio was maintained at 50 % ratio. The sequencing batch reactor was maintained at a filling phase of 15 mins followed by a reaction phase of 23 h. The settling phase was kept for 30 mins followed by decanting for 15 mins. The experimental period consisted of three phases with start-up and acclimatization of 1–18 days. The shock loading phase with different OLRs (different ratios of landfill leachate and municipal wastewater) were carried out within 18–90 days. The recovery phase would be within 90–120 days. During the start-up of the reactor, the OLR was maintained as 500–700 mg L^{-1}. The initial SVI and MLSS were maintained at 150 ml g^{-1} and 2000 mg L^{-1} respectively. The schematic of the experimental set-up is shown in Fig. 2. The experimental and working conditions of the SBR for treating landfill leachate and municipal wastewater are mentioned in Supplementary data.

2.4. Hydrothermal liquefaction of sewage sludge biomass for potential bio-oil production

2.4.1. Sewage sludge biomass characterization

For a detailed characterization of the sewage sludge biomass grown in landfill leachate and municipal wastewater as the substrate, the biomass was first washed with Milli Q water and then the biomass was analyzed for its ash content, volatile matter (VM), moisture content (MC) and fixed carbon content (FC) according to ASTM standards E870–82 [11]. The elemental composition of the biomass was analyzed by CHNS analyzer (EuroEA3000 Elemental Analyzer, EuroVector, Italy); and high heating value (HHV) was calculated by using the following empirical formula:

$$HHV\ (MJ/Kg) = (0.3419)\ C + (1.11783)\ H + (0.1005)\ O\text{-}(0.1034)\ N \quad (1)$$

For determining the biochemical composition of the biomass, the total carbohydrate and protein contents were analyzed [12]. All these analyses were done in triplicates and average values were accordingly reported in the manuscript.

2.4.2. HTL experiments

HTL experiments were carried out with the residual sewage sludge biomass using a 200 ml non-stirred stainless steel batch reactor of 100 ml working volume. The HTL reactor was fabricated with a thick seamless tube containing Teflon inside for high-temperature reactions. Prior to the experiments, the vessel was loaded with 50 ml of deionized water and preheated to 220℃ (This step can be skipped). The required amount of biomass (~10 g) was mixed with distilled water before loading into the reactor. The reactor was then operated at a desired temperature. After completion, the entire reaction vessel was cooled accordingly to stop the HTL reaction. After cooling down the contents inside, samples taken from the reactor were extracted using dichloromethane. The solvent extract was then added with deionized water followed by centrifugation of the mixture to obtain a solvent phase containing bio-oil and water-soluble by-products. The solid residues obtained during the solvent extraction step were also recovered, and heated at 105°C. The bio-oil, aqueous phase, and biochar obtained were kept for further characterization and applications.

2.4.3. HTL product characterization and analysis

2.4.3.1. HTL product analysis. The yield of Bio-oil (BOY) and other by-products *viz.* Solid Residue (SRY) and Water Soluble Product (WSPY) were calculated as % (*w/w*) of initial biomass loaded in the HTL reactor. The yield of this different products were determined as per the following Equation:

$$BOY\ (wt\%) = \text{Mass of bio-oil/Mass of residual sewage sludge biomass} \times 100. \quad (2)$$

The elemental composition of the bio-oil was determined by an elemental analyzer (EuroEA3000 Elemental Analyzer, Euro Vector, Italy) to evaluate its properties as a biofuel. The HHV of bio-oil obtained was estimated using the Dulong formula [12] as given by Eq. (1)

The gas Chromatography-Mass spectroscopy (GC–MS) technique was used in this study to analyze the bio-oil (main product) derived from hydrothermal liquefaction (HTL) of residual sewage sludge biomass treating landfill leachate and municipal wastewater. The GC–MS (Shimadzu (GCMS QP-2020 NX)) was equipped with a column of dimensions (30 *0.25 *0.25) and was maintained at an initial oven temperature of 50 °C for 2 min and then ramped to 320 °C with a heating value of 10 °C. The injector temperature and detector temperatures were initially set to 280°C and 250°C, respectively. For analysis, samples were injected at the split ratio of 10:1 with He (99.99 %) as the carrier gas. Individual compounds that are present in the obtained bio-oil were eventually identified by comparing the obtained GC–MS results with the data available in the MS library (WILEY and NIST (WI2N20)) of pure standard compounds.

2.5. Analytical methods

The parameters associated with the sewage sludge were analyzed initially. The mixed liquid suspended solids (MLSS) concentration was calculated based on the protocol after drying the sample at 105°C [13]. For treatment efficiency, chemical oxygen demand (COD) was analyzed. The chemical oxygen demand (COD) analysis was carried out using the standard dichromate method [14]. Total nitrogen (TN) and total phosphorous (TP) were analyzed using an analysis kit by HUMAS water quality analysis KIT [15].

Extracellular polymeric substances (EPS) are a critical parameter governing membrane granule formation and were analyzed according to the modified version of the protocol described by Shah et al. [16]. For this, 15 ml of mixed liquor was centrifuged at 4000 rpm (2951 × g) for 20 mins and filtered through a 0.45-μm membrane filter (Millipore). EPS (EPS-C and EPS-P) was extracted from the cell pellet by resuspending the pellet in 0.9 % NaCl. The resuspension solution was then kept in a water bath at 90°C for 30 mins. After cooling, the sample was then centrifuged and the obtained supernatant was filtered (0.45-μm) before analysis. Finally, the carbohydrate content in this study was measured by the widely used phenol-sulfuric acid method (standard used-glucose) and the protein content in EPS was analyzed by a modified Lowry method kit respectively [17].

The functional group of biochar and bio-oil were determined using an FT-IR spectrophotometer (JASCO). The surface area and porosity of the biochar were determined using a surface area analyzer (Anton Par, Quantachome, Autosorb-IQ). The biochar morphology and elemental composition of the biochar was analyzed using Field Emission Scanning Electron Microscope (FESEM-EDX, JEOL, JSM-6700F). The crystallinity of the biochar was analyzed by a Real-time X-ray Diffraction analyzer (EMPYREAN, Malvern Panalytical).

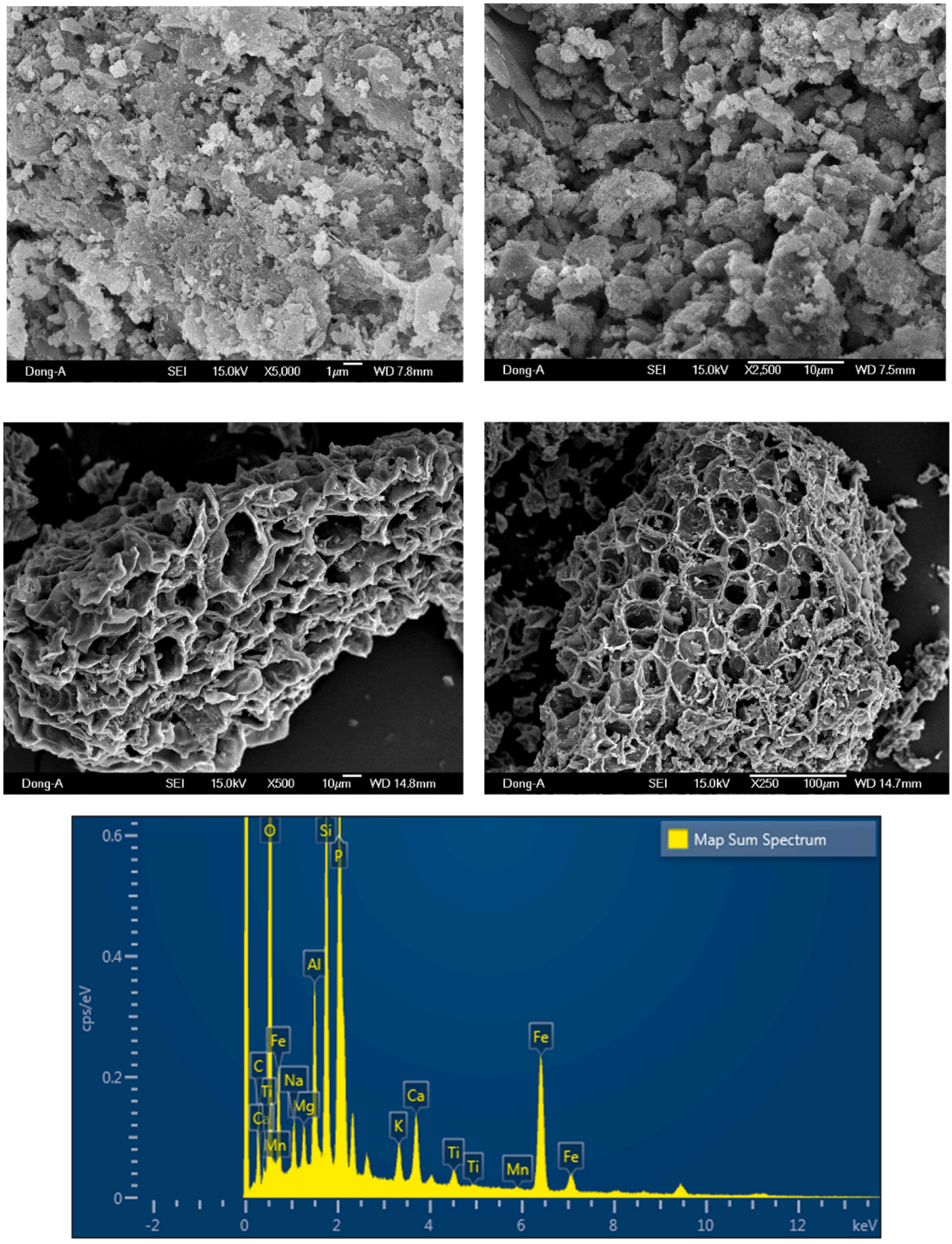


Fig. 3. (a) FESEM images of biochar produced from sewage sludge Fig. 3 **(b)**. FESEM-EDX image of biochar.

3. Results and discussion

3.1. Biochar characterization

3.1.1. FTIR analysis

FT-IR spectroscopy of the sewage sludge-derived biochar was carried out which showed the presence of a wide range of functional groups on its surface. The FT-IR spectra is shown in Supplementary data. The peak 3433.64 cm^{-1} is strong and broad which could be the hydroxyl groups originating from alcohols and carboxylic groups [18]. The small speak at 2341.16 cm^{-1} might correspond to the C═C bond which is found in very small quantities. However, a comparatively sharper peak could be seen at 1637.27 cm^{-1} and a weaker peak at 1400.07 which might correspond to C═O bonds from aromatic rings [19]. However, the peaks from 1400.26 cm^{-1} and 465.72 cm^{-1} are the results of Si-O-Si vibrations [20]. It has been widely reported that biochar having peak intensities with functional groups corresponding to C═O on their surface have high abilities to remove toxic pollutants. Biochar is highly suggested to be used as direct interspecies electron transfer which further accelerates the biodegradation of toxic chemicals [21].

The presence of nitrogen and oxygen-containing functional groups determines the hydrophobic nature of the biochar. The presence of less functional groups makes it more hydrophobic and thus absorbs more pollutants. Hydrophilic biochar adsorbs water forming hydrogen bonds which leads to competitiveness between water and adsorbates for the available sites on the surface of the biochar [22].

3.1.2. XRD analysis

A dried sample of biochar was placed in the sample holder of the autosampler of the XRD machine and analyzed under the range of 5–80 θ (Supplementary data). The results showed that biochar is semi-crystalline in nature. The 2 theta value of 26 ° shows signification diffraction and the presence of graphite, which is crystalline facets, mainly monoatomic carbon layers. 2θ values of SiO_2 50 degrees and $CaCO_3$ 35.9, NaCl 31.6, 31.4 chlorapatite, 27 gibbsite minerals. The pyrolysis was carried out at 700 ℃, with a variation of peak and their intensities change with temperature. Yuan et al. [23] reported that an increase in temperature for biochar from 300 to 500 ℃ had changed the mineralogical heterogeneity of biochar.

3.1.3. SEM-EDX analysis`

The surface morphology and the elemental composition of sewage sludge derived biochar in this study were determined using a scanning electron microscope (SEM), equipped with an energy-dispersive X-ray analyzer. For this, required amount of dried sample was placed in a stub with carbon tape fixed. It was coated with platinum for 60 sec (single platinum coating) and analyzed using FESEM-EDX. FESEM images showed that biochar obtained in this study had a porous structure. The EDX analysis showed that the biochar contained C, O, Mg, Ca, Na, Fe, and Mg which are primarily required for EPS production for an enhanced granulation process. Additionally, the SEM images of sewage sludge-derived biochar revealed that they have a rough surface with a highly developed porous structure (Fig. 3a).

The porous structure of biochar is reported to accumulate more toxic chemicals increasing bacterial survival in the niche. The EDX analysis of the sewage sludge-derived biochar also showed significant findings related to the role of biochar in granulation for the treatment of leachate and municipal wastewater (Fig. 3b). Various metals including C, O, Na, Mg, Al, Si, P, K Ca, Ti, Mn, and Fe were observed to be present on the surface of the biochar. The presence of certain metals such as Mg, Ca, and Fe can stimulate EPS production which highly stimulates granule formation [24]. The addition of biochar to the reactor assists in the granulation process by not only stimulating EPS production but also helping in attaching beneficial microbes for forming stable granule formation. Certain minerals' presence in the biochar can also enhance microbial activity. Also, the porous structure of the biochar helps in the adsorption of toxic pollutants helping accelerate and efficient removal of COD from the leachate and municipal wastewater.

3.1.4. BET analysis

It has been reported that biochar consists of a wide range of pores, ranging from nanometers to micrometers. Pores can be divided into three groups according to the standard of the International Union of Pure and Applied Chemistry (IUPAC): micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). The internal structure of biochar can be evaluated by pore size distribution, which is said to have a complex pore structure in real solids and could be represented by a model with equivalent interactions and regular-shaped pores [25]. The distribution of pore size is a significant parameter for the characterization of the pore structural heterogeneity of biochar. The surface area value is strongly associated with its porosity, of which micropores make the greatest contribution. In this case, the surface area of the biochar was found to be 71.497 m^2/g with a pore size of 3.1 nm which shows it is mesoporous in nature. Furthermore, the pore volume was found to be 0.122 cc/g (Supplementary data).

The C and H are considered essential elements of organic matter, and the reduction of their content indicates its conversion. The H/C and (N + O)/C molar ratios of a substance are often used to evaluate the aromaticity and polarity of adsorbent materials. As seen from Table 1, the H/C molar ratio of biochar is 0.064, indicating high aromaticity. Besides, higher (N + O)/C molar ratios indicate that biochar had stronger adsorption capacity. Therefore, a low H/C molar ratio and high (N + O)/C molar ratio of biochar is considered more favorable for subsequent utilization, because it has stronger resistance to decomposition and higher adsorption capacity.

Table 1
BET and elemental analysis of sewage sludge derived biochar.

BET analysis		Elemental analysis	
Surface area (m^2/g)	71.497	C%	16.554
Pore diameter (nm)	3.1	H%	1.072
Total pore volume (cm^3/g)	0.122	O%	25.956
		N%	2.142
		H/C	0.064
		O/C	1.567
		(O+N)/C	1.697

However, the surface area and total pore volume of biochar are commonly found to be within the range of 8–132 m^2/g and 0.016–0.083 cm^3/g, respectively [26]. When a suitable precursor for biochar preparation and preferable pyrolysis parameters are selected, the surface area and total pore volume of biochar can reach up to 490.8 m^2/g [27] and 0.25 cm^3/g [28], respectively. After an effective post-treatments, e.g., KOH activation, the total pore volume and surface area of biochar can even be increased to 3263 m^2/g and 1.772 cm^3/g, respectively [29], which is comparable to or even higher than commercial activated carbon. Micropore and mesopore volumes are two major parts of the biochar pore volume. In this case, effective treatment can increase the surface area and pore volume of the obtained biochar in this study, for targeting further specific applications in the near future.

3.2. Evaluation of the reactor performance

3.2.1. Organics, TN and TP removal

The indigenously prepared experimental system for simultaneous co-treatment of leachate and municipal wastewater was started in a stirred tank reactor under batch mode with leachate and wastewater in the ratio (1:1) for 18 days. Two reactors were used R1 and R2 which are control (without biochar) and experimental (with biochar), respectively. The initial COD of the experimental system during the acclimatization phase was found to be 800 ± 100 mg L^{-1} in both reactors R1 (control) and R2 (experimental). After 7 days of treatment, the COD was found to be reduced from 827 mg L^{-1} to 650 ± 100 mg L^{-1} in both R1 and R2 showing ~20 % removal of COD in both R1 and R2. These results showed that the initial 1–2 weeks usually consists of the acclimatization phase where the microorganisms adapt to the environment consisting of toxic pollutants. Several physiological and genetic changes take place within microorganisms during this phase for the degradation of the toxic compounds present in the environment.

It is usual to note that the COD removal percentage during the initial period was negligible as compared to the values obtained in the entire experiment [8]. The initial value was around 10–20 % which then further increased to 40 % after 30 days of operation when the reactor was supplemented with shock loading conditions with a COD inlet concentration similar to that of the start of the experiment along with the start in the SBR cycle. Hence, during the initial phase of the shock loading the percentage removal was around 50 % which further increases to ~80 % during the first phase of shock loading. The COD removal efficiency increased in this phase slowly as the microorganisms slowly acclimatized with the COD concentration (Fig. 4a). The main composition of the compounds leading to the COD could be toxic pollutants present in the leachate. The municipal wastewater which was supplemented along with leachate consisted of salts which basically act

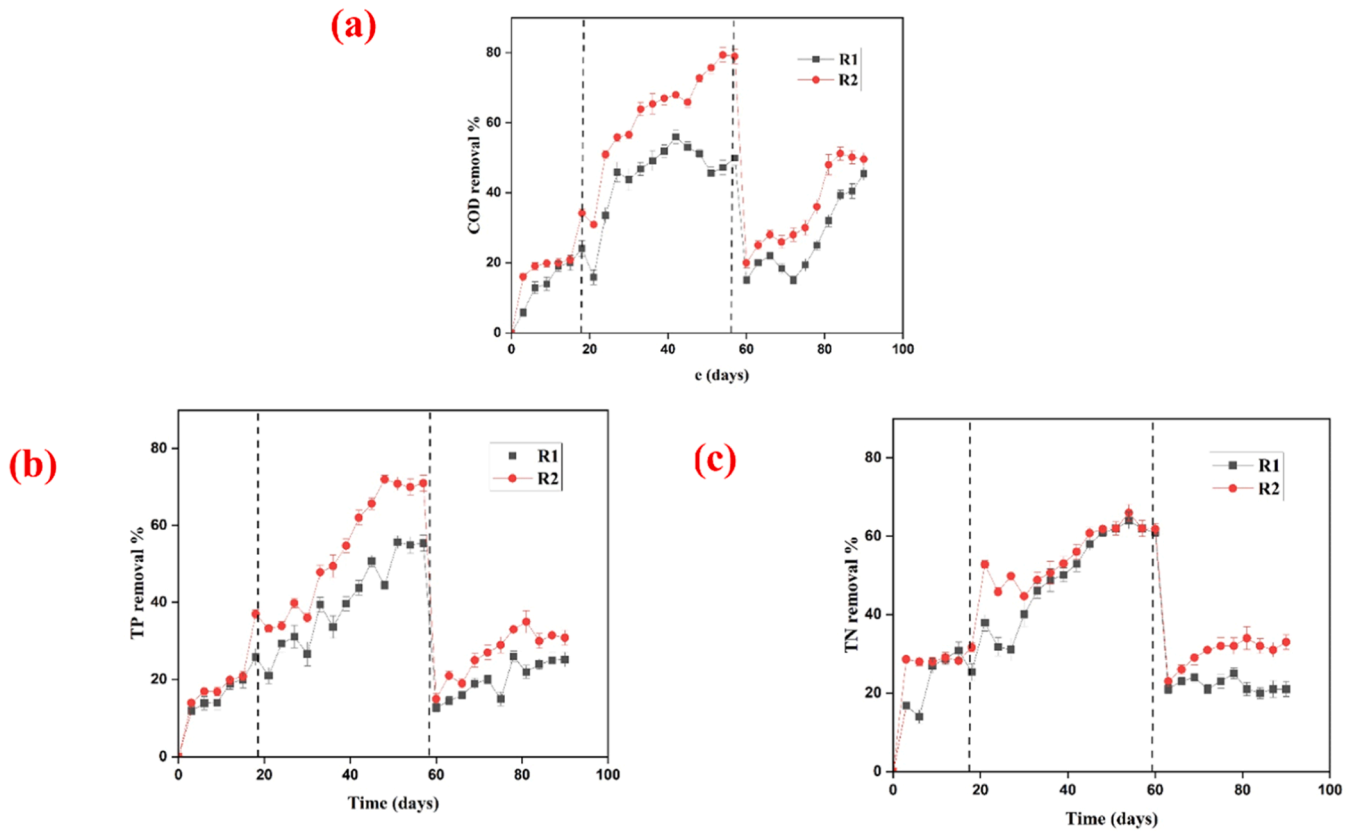


Fig. 4. (a) COD removal profile, (b) TP removal profile, and (c) TN removal profile in R1 and R2 reactor during 90 days operation of an SBR treating leachate and municipal wastewater.

as nutrients for microbial growth and metabolism. The addition of municipal wastewater is hence considered as a viable option for co-treatment owing to the presence of salts and further favoring dilution [30]. The toxicity of landfills and their treatment is further challenging due to their variation in quality and quantity. Operational flexibility is one of the key features of SBR for treating recalcitrant-containing landfill leachates [31].

The efficiency of the indigenous SBR decreased drastically with increasing shock loading concentration in the next shock loading phase, where the leachate and municipal wastewater were added in the ratio 4:1. Due to the presence of excess COD concentration, the initial removal efficiency got reduced (20–30 %) and then eventually increased to ~50 % by the end of the second shock loading phase (Fig. 4a). It is quite evident that the COD% removal was quite higher during the first shock loading condition in R2 as compared to R1. This shows that the addition of biochar for enhancing granule formation was successfully initiated, and thus helped to achieve a comparatively higher reduction in COD. However, in due course of time, the COD % removal started increasing during the second phase of shock loading as observed in Fig. 4a.

Nitrogen is considered to be one of the key nutrients which causes eutrophication. Biological treatment of wastewater usually consists of nitrification and denitrification which are the two basic steps for nitrogen removal. Denitrification demands an anoxic environment which is the rate-limiting step of the process. So far, many literatures are available on the removal of nitrogen in SBR using sewage sludge following alternating oxic/anoxic mode, continuous on/off operation for simultaneous nitrification and denitrification. The granular nitrogen removal process shows efficient nitrification due to the sufficient presence of oxygen in the reactor system. However, anoxic zones that are formed in the system because of the hindrance caused in the mass transfer efficiency owing to the formation of a big-size floc or granule, is, however, the most suitable requirement for nitrogen removal by denitrification process [32]. Shock loading conditions are reported to drastically affected the nitrogen removal efficiency of the reactor. In this study, it is evident from the figure that both the control reactor (R1) and experimental reactor (R2) removed nitrogen efficiently until the first dose of shock loading. But, the total nitrogen removal by the end of the first phase of the study was around 60 % in R1 (Fig. 4b). This result is in accordance with the reported literature [33]. However, TN removal efficiency was comparatively lower than the other reported literature [33] owing to the presence of sufficient oxygen supply which didn't allow for the formation of anoxic zones within the reactor.

The results obtained in this study were further confirmed by analyzing the DO level of the reactors, which were quite high (~ 6 mg L). During the first phase of shock loading (leachate: wastewater, 1:1), the removal percentage was low, but eventually seem to increase with an increase in time in both the reactors. Following acclimatization for almost 2 weeks, the first phase of shock loading started around the 18th day and ended around the 57th day. The TN % removal was ~60 % both in R1 and R2. These could be due to the reasons already mentioned above in this section. However, during the 2nd phase of shock loading, where the leachate and wastewater were added in the ratio (4:1), the TN removal % drastically reduced and didn't reach a substantial amount until the 90th day of the reactor operation (Fig. 4c). This show that excess COD supplementation hindered the nitrogen removal efficiency in this experimental study. Even after the 90th day of operation, ~30 % removal could be achieved. This shows that further increment in the shock load would be unsuitable and not recommended for maintaining the treatment efficiency of the SBR. Further acclimatization is required to enhance the efficiency of the SBR in terms of COD, TN and TP removal. The nitrogen removal efficiency of R2 was however, slightly higher than that of R1, which could be due to the fact that the presence of biochar can create a provision of axonic shelter for the denitrifies [8], [33]. However, tt has been reported that anaerobes need a longer time

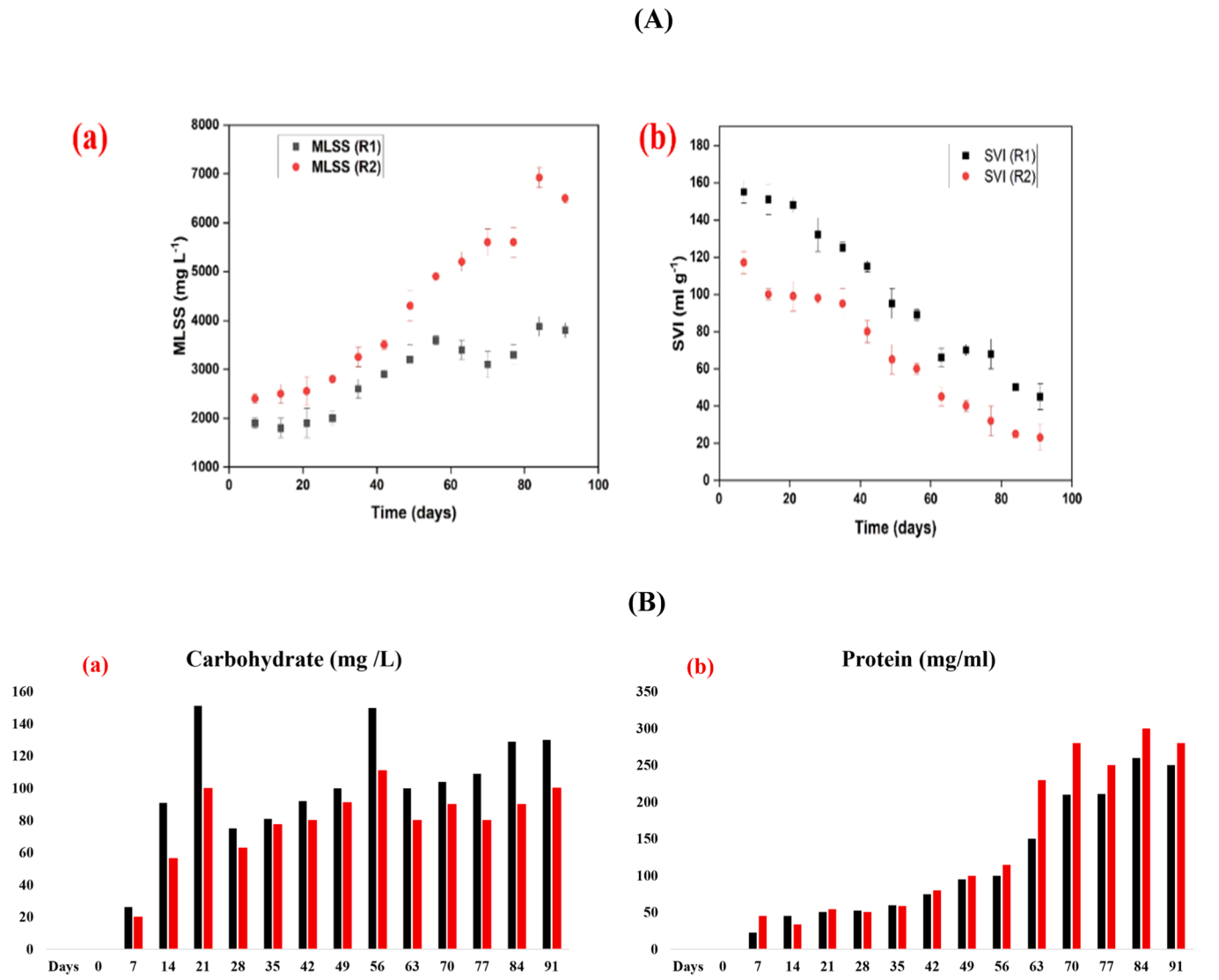


Fig. 5. **(A)** (a) MLSS and (b) SVI profiles **(B)** (a) Polysaccharide profile and (b) Protein profiles in R1 and R2 reactor for 90 days operation of an SBR treating leachate and municipal wastewater.

for a generation period with less reproductive capacity. Ming et al. [33] reported that lowering the COD helped in achieving high removal efficiencies of SBR up to 89.50 %, 90.33 and 87.57 % in Rrh, Rrb, and Rws respectively.

However, the phosphorous removal was observed to be more than 30 % in just 30th day in the case of R1 and 37 % in R2 (Fig. 4b), respectively, which is excellent in terms of effective phosphorous removal from wastewater. It was observed that the removal of phosphorous was comparatively slower in the case of R1. Interestingly, the addition of biochar is reported to enhance the shock-loading ability of sludge, which would be further analyzed in the experiments. Hence, during the end of the first shock loading phase, R2 witnessed nitrogen removal up to 70 % which was quite higher than R1. Fast-settling biomass and slow-settling sludge were used for selective utilization of organic carbon in this case. The AGS reactor, dominated by small granules, usually donot exhibit simultaneous nitrification and denitrification due to limited anoxic volume or organic substrate availability. Nevertheless, an excellent effluent quality with high COD removal was achieved during the initial change in the phase of OLR. Hence, to summarize, the treatment of landfill leachate and municipal wastewater in a sequencing batch reactor achieved successful granulation with improved settling properties. Therefore, this study served to be an excellent example of solving two issues: first concerning the landfill problem and second, successfully establishing the waste biorefinery: a sustainable waste to biofuel approach.

3.2.2. *Biomass profile and settling property of aerobic granules*

During the startup of experiments in this study, the sludge inoculated was dark brown in appearance and loosely bound. Visible granules were observed in R2 after ~20 days of SBR operation whereas in R1 which was without biochar, granule formation was not observed then. It was observed that the experimental reactor (R2) experienced more granule formation which was around ~15–20 % more. This proved that the addition of biochar promoted granulation of the aerobic sludge which further improved its settling ability. Granular sludge is often considered as a potential indicator for high biomass retention. The efficiency of biomass settling and granulation can be evaluated by calculating the presence of Mixed Liquor Suspended Solids (MLSS) and Sludge volume index (SVI) in the reactor [34].

The variation of MLSS and SVI during the 90 days of SBR operation is shown in Fig. 5 A (a and b). The initial MLSS of reactor R1 was around ~1.9 g L^{-1}, whereas the MLSS of the R2 was ~2.4 g L^{-1} which might be also due to the presence of biochar and its enhanced effect on the granulation of the sludge [34]. Hence, the initial MLSS concentration of

R1 and R2 before treatment is not drastically different. However, the marginal difference observed in the values of MLSS of R1 and R2 might be due to the presence of biochar added, which further showed an increase in MLSS. Meanwhile, the SVI of R2 was found to be ~150 ml/g which is (<150 ml/g) and is not favorable for effective wastewater treatment as reported by researchers. As mentioned earlier, the inoculating sludge was loosely bound and hence showed an SVI value of 155 ml/g revealing its poor settling quality. The rate of biomass increment is less which might be also due to the biomass washout taking place while maintaining the SBR cycle. The MLSS continued to increase gradually till 56 days in both the reactors. After that, the shock loading conditions affected the MLSS slightly as seen from Fig. 5 A (a). However, the final MLSS concentration in the control reactor (R1) was found to be ~3.8 g L^{-1} whereas in the experimental reactor (R2) with biochar was ~6.5 g L^{-1} which is remarkably higher than the experimental reactor. Additionally, a decreased SVI 40 ml/g in R2 shows an excellent settling property of the sludge and thus efficient achieving COD removal. It is well known that granule formation is extensively favorable for the efficient treatment of wastewater in an SBR reactor which is reflected from the results of this current study. Moreover, compact granule structure can help to protect the microorganisms from the toxic effects of the recalcitrant compounds particularly in the shock loading conditions [35]. The settling time can be further evaluated to be increased or decreased in due course of time in order to monitor the granulation process. Nevertheless, a short settling time is a prerequisite for facilitating the granulation process of sludge followed by changes in physiological changes leading to microbial aggregation [8]. The pH and DO in both reactors R1 and R2 were maintained as ~7 and 5.5–6 mg L^{-1} respectively.

EPS is often regarded as the important mediator responsible for the addition of bacteria into carrier surface during biofilm formation [34]. Carbohydrates and proteins are considered as the main components of EPS with lipids, nucleic acids, and other inorganic compounds as minor components [36]. However, the production of EPS and its variation in its components are largely dependent on various factors including culture conditions, bioreactor type, growth phase, process parameters, and the method employed for its extraction. In this study, the initial polysaccharide concentration was found to be 22 and 15 mg L^{-1}, which increased to 140 mg L^{-1} and 100 mg L^{-1} in R1 and R2 respectively (Fig. 5B (b). Polysaccharides are hydrophilic molecules that absorb and exude water, thus contributing to water retention [37,38]. An increase in water content decreases the property of the floc to settle. It has been reported that an increase in the water-soluble EPS results in the deterioration of the stable floc structure [39]. Additionally, proteins are hydrophobic molecules that are suggested to enhance sludge stimulation. Already reported literature supports the results establishing a close correlation between protein and EPS fraction hydrophobicity, resulting in high settling of sludge [40]. Owing to the presence of a high content of negatively charged amino acids in the proteins, it forms electrostatic bonds with multivalent cations, which has been regarded as the key factor for stabilizing the aggregate structure, thus maintaining the cell cohesion property [41]. It has been observed that proteins are found in more quantities in sheared granules as compared to carbohydrates. Additionally, an increase in PN/PS ratio in EPS results in a decrease in negative charge thus increasing hydrophobicity in the sludge surface, enhancing the flocculation and stability of the granules. Higher PN/PS values show the presence of the formation of stable aerobic granules [34]. Hence it is evident from the Figure and also from the reported literature that protein concentration increases in R2 from 50 to ~300 mg ml^{-1} which is higher than R1 (200 mg ml^{-1}) (Fig. 5B b). Also, the concentration of carbohydrates decreased after the addition of biochar in R2 and showed low values of less than 100 mg L^{-1} as compared to R1 (~150 mg L^{-1}) by the end of the second phase of shock loading.

It was reported that the addition of biochar might also stimulate enzyme production and stabilize extracellular enzymes. It is well known that the role of biochar is important in granule formation in a wastewater treatment process for the removal of toxic substances. Sewage-derived biochar having pores and high surface area can contribute to the adhesion of the different microorganisms. During the early stages of the granule formation, the porous structure of the biochar helps to provide shelter in adverse conditions. Cationic metal ions that are present on the surface of the biochar (confirmed by FESEM-EDX) analysis accelerated microbial adhesion on the surface of negatively charged cellular components [42]. Moreover, EPS secreted by the microorganisms functions as a bridge to form granules. So, in this case. the microorganism first adheres to the surface of the biochar owing to its physicochemical behavior. The EPS produced then modifies the surface chemistry, particularly its charge and hydrophobicity, further enhancing the microbial aggregation. These aggregates then act as a precursor for granule formation and then mature into a complete granule.

Table 2
Results of alpha diversity analysis.

Sample name	Shannon	Gini-Simpson
R1	5.700714458	0.937150518
R2	5.962765302	0.964806349

3.2.3. *Effect of biochar on microbial community analysis*

The richness and diversity in the microbial communities of the control reactor (R1) without biochar and the experimental reactor (R2) with biochar were carried out on the 90th day of the reactor operation for treating leachate and municipal waste using sewage sludge. The richness and diversity measured by index are presented in Table 2. The relative abundance of the bacterial 16sRNA gene at the phylum and genus level were evaluated to investigate the microbial community present in the control and in the reactor after the addition of biochar. Sequencing results indicated the bacterial community consisted of 12 phyla in R1 while R2 showed the presence of 14 phyla. As evident from Fig. 6(a) the phyla present abundantly were *Pseudomonadota, Bacteroidota, Bacillota, Actinomycetota, Abditibacteriota, Chloroflexota, Thermomicrobiota, Verrucomicrobiota, Planctomycetota* dominated in both the reactor R1 and R2. The relative abundance of the phylum *Pseudomonadota* was 48.99 % and 45.94 % in R1 and R2 respectively. However, the phylum *Bacteroidota* and *Actinomycetota* showed less abundance in R1 at 17.59 % and 11.07 % respectively, which was slightly higher in the case of R2, 21.70 and 13.75 % for *Bacteroidota* and *Actinomycetota* respectively. Significant changes in the phylum level were not observed after biochar addition. In this study, *Actinobacteria*, *Verrucomicrobia*, *Chloroflexi*, *Bacteroidetes*, *Chlorobi*, and *Planctomycetes* phyla were present in both the control reactor (R1) and the experimental reactor (R2) and matched with the already reported literature [8,33].

However, the most abundant phyla were found to be *Pseudomonadota* and the least was *Bdellovibrionota*. It was interesting to note that the phylum classification showed almost similar results in both the reactors but in case of genus, it showed the presence of wide variety of genus in R2 (experimental reactor), which revealed that in genus level, change in the microbial community occurred after addition of biochar that enhanced the granulation process. The alpha diversity of both the cases were analyzed by Shannon and Gini-Simpson (Table 2). For Gini-Simpson, the range varies from 0 to 1 where 0 indicates maximum diversity with all the species being equally present and abundant in the community. 1, however, refers to one species that dominates the community and others are absent. On the other hand, Shannon index ranges from 0 to infinity. When the value is 0, it means there is no diversity, however the value increases with an increase in the diversity in the community. In this case, the Shannon index was 5.700 and 5.96 for R1 and R2 respectively. The Gini-Simpson values were 0.937 and 0.964 for R1 and R2 respectively showing maximum diversity amongst the population [8]. It is also reported that biochar might provide a favorable

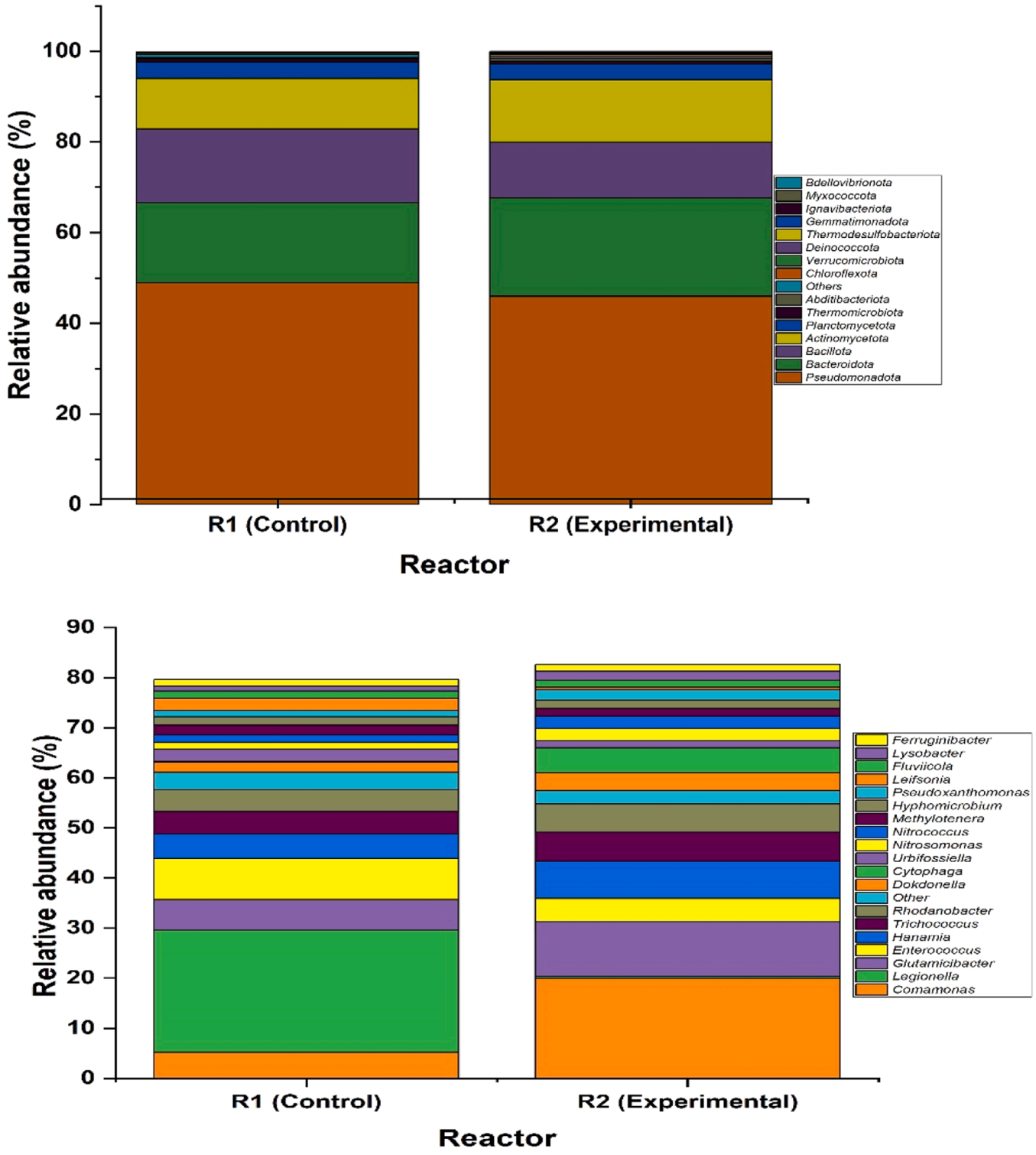


Fig. 6. The classification of microorganisms presented in R0 and R1 by phyla (a) and (b) genera.

niche to the microorganism for its growth and sustenance [43]. However, richness and diversity in the phyla were not affected by the addition of biochar in this study. Similar findings were also reported by Wang et al. [8]. However, decrease in bacterial abundance and altered communities were not observed during this experimental study. Although, biochar applications are reported to change (increase/decrease) the microbial flora. Nevertheless, the core genera involved in the degradation of toxins during the wastewater process were observed in this study and are similar to the already reported literature.

To achieve a deeper insight into the change in the microbial community structure, the sequences from the bacterial communities that are considered dominant were further analyzed at the genus level (Fig. 6b). The genus *Legionella* was found to be most abundant in R1 (24.40 %), however it decreased in R2 drastically after the addition of biochar. Additionally, relative abundance (%) of the genus *Comamonas* and *Glutamicibacter* increased from 5.23 % to 19 % in R1 and 6.09 % to 10.89 % in R2 respectively. WWTPs with aerobic biological treatment processes promote *Legionella* proliferation due to the presence of organic

Table 3 (a)
Tentative compounds present in bio-crude obtained from HTL of R1 residual sewage sludge.

No.	Time (min)	Compounds	Relative peak area (%)	Molecular formula
1.	27.035	2,5-Piperazinedione, 3-methyl−6-(1-methylethyl)-	5.56	$C_8H_{14}N_2O_2$
2.	28.162	3-Isopropyl−2,5-piperazine-dione	10.30	$C_8H_{14}N_2O_2$
3.	29.360	Cyclo(alanylleucyl)	7.20	$C_9H_{16}N_2O_2$
4.	29.958	Pyrrolo[1,2-*a*]pyrazine−1,4-dione, hexahydro-	12.08	$C_7H_{10}N_2O_2$
5.	30.218	3-Isobutyl−2,5-piperazinedione	8.51	$C_8H_{14}N_2O_2$
6.	31.175	Cyclo(L-prolyl-L-valine)	1.06	$C_{10}H_{16}N_2O_2$
7.	37.472	2,5-Piperazinedione, 3-methyl−6-(phenylmethyl)-	2.65	$C_{12}H_{14}N_2O_2$
8.	38.624	2,5-Piperazinedione, 3-(phenylmethyl)-	5.22	
		3-Butyl−6-methylpiperazine−2,5-dione		$C_9H_{16}N_2O_2$

Table 3 (b)
Tentative compounds present in bio-crude obtained from HTL of R2 residual sewage.

No.	Time (min)	Compounds	Relative peak area (%)	Molecular formula
1.	5.125	Butanoic acid, 3-methyl-	1.34	$C_5H_{10}O_2$
2.	8.658	Hexanoic acid	2.77	$C_6H_{12}O_2$
3.	9.016	1,2,3-Propanetriol	7.62	$C_3H_8O_3$
4.	27.048	2,5-Piperazinedione, 3-methyl−6-(1-methylethyl)-	4.07	$C_8H_{14}N_2O_2$
5.	28.164	3-Isopropyl−2,5-piperazine-dione	8.21	$C_8H_{14}N_2O_2$
6.	29.362	Cyclo(alanylleucyl)	6.51	$C_9H_{16}N_2O_2$
7.	29.961	Pyrrolo[1,2-*a*]pyrazine−1,4-dione, hexahydro-	9.24	:$C_{11}H_{18}N_2O_2$
8.	30.220	3-Isobutyl−2,5-piperazinedione	5.93	$C_9H_{16}N_2O2$
9.	31.799	Cyclo(L-prolyl-L-valine)	6.38	$C_{10}H_{16}N_2O_2$
10.	38.648	2,5-Piperazinedione, 3-(phenylmethyl)-	3.38	$C_{11}H_{12}N_2O_2$

matter, nitrogen, and phosphorus in the wastewater. Furthermore, it mainly occurs in clusters in activated sludge, using organic nitrogen as a source of amino acids. Dissolved oxygen concentrations in activated sludge tanks are ideal for *Legionella* growth, as they remove carbon and nitrogen, and the oxygen requirements for *Legionella* species are 0.3–2.2 mg L^{-1}. However, further studies are needed to validate this hypothesis [44].

Enhanced biological phosphorus removal (EBPR) is a process by phosphate-accumulating organisms (PAO) that develop in bioreactors under cyclically switched aerobic/anaerobic conditions. PAO consumes volatile fatty acids and stores them as polyhydroxyalkanoates, while aerobic conditions allow them to grow, consume orthophosphate, and synthesize intracellular polyphosphates. Other PAO also play a significant role in EBPR. *Candidatus Accumulibacter* (phylum *Pseudomonadota*) and members of the genus *Tetrasphaera* (phylum *Actinomycetota*) are considered to be the main agents of EBPR [45,46]. *Comamonas* sp. is reported to exhibit excellent nitrogen removal ability under low C/N conditions (C/N = 2.5), where 94.01 % of nitrate was removed within 18 h, with no accumulation of nitrite. These findings reveal that *Comamonas* sp. YSF15 can is robust and efficient for bioremediation of waterwater under low C/N conditions [47].

3.3. Characterization of bio-crude obtained from residual sewage sludge

The residual sludge biomass obtained in the experiments after the treatment of leachate and municipal wastewater was subjected to hydrothermal liquefaction (HTL) for bio-oil production where the carbonaceous sludge gets converted to a single monomer in the presence of water as a solvent at high temperature. The addition of solvent (DCM) leads to the separation of two phases (aqueous and oil phase) because of their different solubility in water. The yield of the sewage sludge-derived bio-oil obtained in this study was calculated based on the Eq. mentioned in the previous section and was found to be ~27 % (w/w), which is relatively higher than the yield obtained from microalgae by hydrothermal liquefaction [14]. The HHV of the bio-oil produced in this study was found to be 17 MJ/kg. Since this study is a preliminary analysis to evaluate the feasibility of biofuel production by utilization of waste, producing bio-oil as an alternative to commercial fuels, the estimation of the cost in this study would be sufficiently insignificant in this regard. More detailed sensitivity evaluations can be planned in the future for a pilot scale study which would provide a brief idea of the cost-benefit analysis of the entire process of producing bio-oil from wastes biomass treating wastewater. A detailed techno-economic feasibility study would be highly helpful for establishing the efficiency of the entire process in the long run.

The elemental analysis of the bio-oil produced from the residual sewage sludge post-treatment was found to be C (26.92), H (4.174), N (6.186, S (0.868) and O (33.00). A high content of oxygen in the bio-oil was observed and hence upgradation is highly suggested to improve the quality and HHV of the biofuel. The bio-oil derived from residual sewage sludge treating landfill leachate and municipal wastewater in this study contained a mixture of hydrocarbons as obtained by GC–MS analysis. The major composition present in the bio-oil is presented in Table 3 (a) showing a number of complex organic hydrocarbons with different structures and molecular weights present in the oil phase. These compounds can be further classified into different groups that are usually present in bio-oil such as mono aromatics, aliphatics, saturated/unsaturated fatty acids, and polyaromatics [11].

The retention time, peak area and chemical name of the significant components of the bio-oil produced after HTL of residual sewage sludge treating landfill leachate and municipal wastewater from both the reactors are mentioned in Table 3 (a) and (b). It is evident from the results that the composition of bio-oil was complex which included aldehydes, alcohols, organic acids and ketones, hydrocarbons, esters, phenols, and nitrogenous compounds such as pyrrolidones and pyridines which show high levels of nitrogenous compounds. This might be due to the fact that the sample was not subjected to any pre-treatment process, hence there was no denaturation of proteins into saturated and unsaturated acids prior to the experiments. Chen et al. [48] studied the HTL of sewage sludge by microwave pretreatment which showed that microwave pretreatment reduces the organic acids and nitrogenous compounds and promotes the formation of esters and hydrocarbons. The presence of hydrocarbons and esters are highly recommended for improving the quality of the bio-oil. Presence of esters showed that the bio-oil is esterified and is similar to bio-diesel. It is reported that low level of nitrogenous compounds and organic acids in the bio-oils leads to less corrosion and emission of NOx gas during the burning of the bio-oil. Hence, extensive work has been carried out to improve the quality of the bio-oil by blending, transesterification, etc. thus improving the economics of the biorefinery process[49]. Therefore, the bio-oil obtained in this study can be further trans esterified or pretreated to enhance its properties for the combustion process. Paul et al. [11] mentioned the estimated property values of the bio-oil obtained from the residual *R. opacus* biomass treating petroleum refinery wastewater.

The properties of bio-oil primarily depends upon the composition and source of the feedstock used for bio-oil production. In this study, the bio-oil obtained was from residual sewage sludge treating landfill leachate and municipal wastewater. The bio-oil pertaining to its biofuel properties can be analyzed after transesterification and matched with standards as demonstrated in the literature by Xu et al. [50]. Certain undesired properties of bio-oil such as high corrosiveness viscosity and

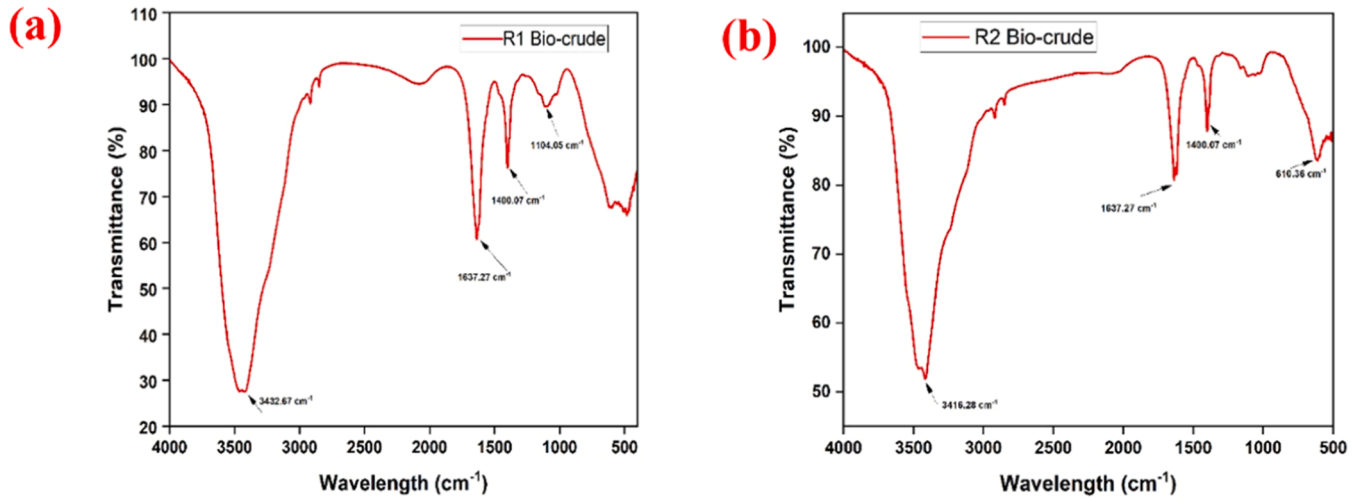


Fig. 7. FT-IR peaks of bio-crude obtained from residual sewage sludge of (a) R1 and (b) R2.

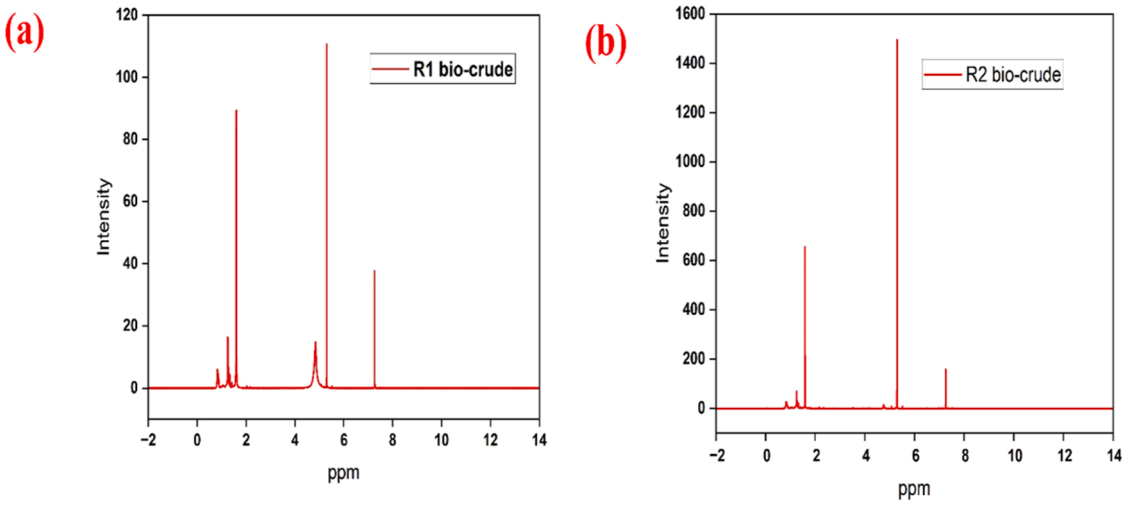


Fig. 8. NMR peaks of bio-crude obtained from residual sewage sludge of (a) R1 and (b) R2.

acidity can be improved by performing the appropriate upgradation process [51]. Additionally, high amounts of fatty acids might cause acidity and corrosiveness. Besides the main product, the HTL also produces certain by-products such as aqueous phase and solid residue [14]. The nutrient-rich aqueous phase can be reused again for culturing microorganisms and the solid residue is reported to have excellent absorbent properties which would help in toxic pollutant removal. Hence, this study has not only focused on the treatment of pollutants using sewage sludge but also focused on the valorization of the waste into valuable substances for further beneficial use.

FTIR spectroscopic technique was used in this study to determine the functional groups present in bio-oil derived from residual sewage sludge treating landfill leachate and municipal wastewater. Organic compounds that are present in bio-oil were analyzed accordingly and the scanning range selection was kept between 500 and 4000 cm^{-1}.FTIR analysis of the residual sewage sludge biomass derived from R1 (Control reactor) and R2 (experimental reactor) revealed identical spectra of the produced bio-oil treating landfill leachate and municipal wastewater (7 (a and b)). The OH stretching vibrations at 3432.67 cm^{-1} and 3416.28 cm^{-1} show the presence of alcohols and phenols. Furthermore, the carbonyl signal of ketones and aldehydes is obtained at 1637 cm^{-1}, which denotes the presence of fatty acids arising from the degradation of lipids. The absorbance peak at 1384.43 cm^{-1} shows the presence of esters, alcohols, and phenolic ethers. The presence of the functional groups obtained in this study matches well with the results already reported in the literature on bio-oil derived from sewage sludge produced by using the HTL process [48]. The bio-oil obtained in this study by the HTL thermochemical conversion process mainly showed the presence of alcohols, ketones, esters, carboxylic acids, nitrogen-containing compounds and hydrocarbons.

The chemical shifts in the proton (^{1}H) NMR spectrum of bio-oil can also vary widely due to the diverse range of organic compounds present in its composition (Fig. 8a&b). The proton (^{1}H) NMR spectrum of bio-oil is highly complex due to the presence of a wide variety of organic compounds derived from biomass. Bio-oil typically contains a mixture of aldehydes, ketones, acids, phenols, alcohols, furans, and other oxygen-containing functional groups, along with aliphatic and aromatic hydrocarbons [52]. ^{1}H NMR has been used to elucidate the complex structures of the compounds that are present in bio-oil obtained under different pyrolysis conditions and upgrading methods as well as those of chemicals extracted from bio-oils [53]. Hydroxyl protons (OH) from alcohols and phenols may appear as broad signals in the region of 3.0–5.0 ppm due to hydrogen bonding and exchange with the solvent. Proton shifts in ether groups (5.5 −3.0 ppm) and aliphatic OH groups (6.5 −4.0 ppm) overlap with those in nonconjugated alkenes (6.0 −4.0 ppm). Protons on carbons connected to a carbonyl group as well as

aliphatic protons can be attributed to the signals between 3.0 and 2.0 ppm. Aldehydes and carboxylic acids are allocated inside the 10.0 −8.3 ppm downfield zones. Aliphatic protons are assigned to 3.0 −0.5 ppm. ^{1}H NMR spectroscopy is unable to distinguish between primary, secondary, and tertiary protons. The most up field region of the spectra usually represents aliphatic protons that are attached to carbon atoms or heteroatom (O or N) as evident from the results obtained in this study and is also in accordance with the already reported literature [54].

4. Conclusions

The biochar obtained in this study by pyrolysis of sewage sludge has a porous structure with high surface area and pore volume with a wide range of functional groups and other metals. These properties helped the biochar to successfully help in the granulation process for achieving efficient COD removal upon granulation. Recently, biochar engineering has gained interest among researchers for optimizing biochar according to the need by adding the desired functional group for pollutant removal and changing its physicochemical characteristics to obtain the desired results. In this study, biochar shortened the time for the granulation process thus achieving efficient COD removal. Protein production is highly encouraged for enhanced granulation which was also observed during the granulation process while treating landfill leachate and municipal wastewater. Total nitrogen and phosphorous removal were successfully achieved in this study by raw unmodified biochar derived from sewage sludge. The probability of bio-oil production from the sewage sludge was shown as an alternative to commercial fuels. Hence, this study proved to be an excellent integrated approach for co-treatment of landfill leachate and wastewater using sewage sludge and sewage sludge-derived biochar for an enhanced granulation process. However, the bio-oil obtained in this study can be used upon upgradation using various upgraded technologies to increase its HHV value in the near future. Also, other ways for enhancing granulation using bio-augmentation can be explored in this field for developing insight into functional microorganisms.

CRediT authorship contribution statement

Jurng-Jae Yee: Supervision, Resources, Project administration, Funding acquisition. **Tanushree Paul:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sung-Hyuk Park:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.115330.

Data availability

The data that has been used is confidential.

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