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ORIGINAL ARTICLE

Dual biogas/biochar production from anaerobic co-digestion of petrochemical and domestic wastewater: a techno-economic and sustainable approach

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Abstract

This study investigates the utilization of petrochemical and domestic wastewater (PCW and DW) for dual biogas and biochar production, focusing on the economic and sustainable development criteria. Biogas yield by anaerobic co-digestion of a 0:1 (PCW:DW) feed was 306.4±11.8 mL per g chemical oxygen demand (COD) removed, which dropped by 12.7% with changing PCW:DW to 1:0. The results indicated that increasing the DW fraction in the feed encouraged the conversion of COD into more biogas and sludge amounts. The anaerobic sludge was subjected to pyrolysis to generate biochar with a yield of 0.6 g/g dry sludge. The delivered biochar showed appropriate surface morphology, elemental composition, physical properties, and surface functional groups, as demonstrated by SEM/EDX, XRD, and FTIR characterizations. The COD mass balance estimation of the anaerobic digestion system, with biochar yield, was used to determine the economic feasibility of treating 30 m^3/day of wastewater. The 1:0 (PCW:DW) condition provided the most feasible scenario, with profits of 3340, 192, and 2819 USD/year for energy income, biochar selling, and pollution reduction, respectively. This economic benefit was equivalent to a payback period of 5.38 years. The fulfillment of multiple sustainable development goals (SDGs) related to clean and renewable energy production, human health protection, and economic growth was highlighted.

Keywords Biochar characterization · Cost-benefits · Co-substrate PCW:DW · Pyrolysis · Sustainable development

Highlights
- Biogas/biochar production from petrochemical (PCW) and domestic (DW) wastewater co-digestion
- Biogas yield (in mL/g $COD_{removed}$)= 306.4 at 0:1 (PCW:DW) and 267.3 at 1:0 (PCW:DW)
- Characterization of biochar from pyrolysis of anaerobic sludge by BET, SEM/EDX, FTIR, and XRD
- Payback period of 5.38 years from energy income, biochar selling, and pollution reduction
- Defining SDGs related to renewable energy, human health, and economic growth

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1 Introduction

Petrochemical industries generate large amounts of wastewater, containing aromatic hydrocarbons, oil and grease, heavy metals, and complex organic compounds [1]. The uncontrolled release of petrochemical wastewater (PCW) into the environmental matrix has been associated with serious human health risks [2]. For instance, individuals exposed to PCW pollution could suffer from acute irritative, asthma, nasal, respiratory, and wheezing symptoms, both for adults and children [3]. Moreover, soils and vegetation near the petrochemical industrial areas would receive unacceptable levels of metals and toxic and airborne trace elements [4]. In parallel, recent studies have revealed the utilization of PCW to produce valuable byproducts such as bioethanol and biogas, achieving more economic profit [5]. The profitability analysis of the entire PCW treatment system should cover the initial investment and net profits to estimate the payback period (which should be shorter than the project lifetime) [6]. Hence, further studies are required to reduce the pollution of PCW, with a focus on the economic feasibility of generating and selling the delivered byproducts.

Recently, several researchers have employed the biological-based systems to treat PCW before reaching the environment [5, 7]. Anaerobic treatment of PCW has the advantages of reducing the organic fraction, expressed by chemical oxygen demand (COD), and generating energy such as CH_4 and H_2 gasses [8]. Due to the complex composition of PCW, the addition of organic fractions (co-substrate) such as domestic wastewater (DW) to the feed would enhance the entire biodegradation system [9]. This co-digestion process would facilitate the utilization of carbohydrates and protein, production of methane-rich biogas, and anaerobic sludge stabilization [10]. Moreover, adding a co-substrate to the PCW digestion system would encourage pollution minimization by reducing the inhibitory substance formation, which further elevates the economic profits (e.g., earn 0.15 USD by eliminating 1 kg of COD) [11].

After the anaerobic treatment of PCW, the generated sludge (containing inorganic elements, aromatic compounds, and acidic species) requires an appropriate management strategy [12]. For instance, the generated sludge could be converted into bioenergy using thermal treatment [13]. Pyrolysis, i.e., a thermal decomposition process under an oxygen-deprived condition, has been proposed as a viable sludge management process to deliver biochar [14]. Biochar is a carbon-rich material that contains a large specific surface area, multiple functional groups, and a proper elemental composition [15]. These features allow the application of biochar for adsorbing metal ions from industrial effluents via surface complexation, ion exchange, electrostatic attraction, and pore-filling mechanisms [16]. Moreover, the biochar material has been used in agricultural practices via improving the soil's physical and hydraulic properties [17]. Owing to the aforementioned biochar applications, the selling price of biochar reached 0.4–0.6 US$/kg [18].

Currently, there is a lack of studies describing the economic feasibility of the PCW co-digestion to generate biogas, followed by biochar synthesis from sludge pyrolysis. Hence, the study objectives are fourfold: (i) investigate the effect of various PCW:DW fractions on COD mass balance bioconversion, (ii) estimate the kinetics of bio-CH_4 productivity via the Gompertz model application, (iii) prepare and characterize biochar from the pyrolysis of anaerobic sludge, and (iv) estimate the economic feasibility and payback period from selling biogas and biochar, with pollution reduction.

2 Materials and methods

2.1 Wastewater and sludge inoculum preparation

Synthetic PCW was prepared to simulate purified terephthalic acid (PTA) wastewater, as reported previously [19]. A stock solution of wastewater was composed of terephthalic acid (2000 mg/L), benzoic acid (600 mg/L), acetic acid as a carbon source (2000 mg/L), and xylene (400 mg/L), with NH_4CL, KH_2PO_4, and $MgCl_2$ as micronutrients. The PCW characteristics in Table 1 were prepared by diluting the stock solution in appropriate amounts of distilled water. Each batch of synthetic wastewater was stored at 4 °C to avoid further undesirable biodegradation activities. All reagents used were of analytical grade.

Sewage sludge was collected from a wastewater treatment plant located in Borg El-Arab, Alexandria, Egypt [8]. The sludge samples were kept in a cooler box and transported directly to the laboratory for analysis. Sludge as inoculum had total solid (TS) and volatile solid (VS) concentrations of 21.95 g/L and 14.91 g/L, respectively (Table 1). The inoculum was acclimatized to the PCW feed gradually for 120 h at 37 °C before use in experimentations.

2.2 Experimental setup

Figure 1 shows the experimental work of this study designed to produce biogas (1st experiment) and biochar (2nd experiment).

In the 1st experiment, PCW was co-digested with DW in three different PCW:DW ratios of 2:1, 1:1, and 1:2. The control assays were performed using PCW-to-DW proportions of 1-to-0 and 0-to-1. Batch experimentations were performed using 250 mL bottles with 200 mL working volume and 37 °C water path. Methane-rich biogas was obtained by connecting the gas outlet of each digester to an alkaline solution (0.5 M NaOH) [18]. An inverted 50-mL measuring cylinder was used to quantify the biogas volume by water displacement.

Table 1 Characteristics of petrochemical wastewater (PCW) and sludge inoculum

Parameter	Value	Unit
Petrochemical wastewater (PCW)		
Total chemical oxygen demand (COD_{total})	2720	mg/L
Soluble chemical oxygen demand ($COD_{soluble}$)	1900	mg/L
Terephthalic acid (TA)	40.65	mg/L
pH	3.3	pH unit
Total organic carbon (TOC)	3800	mg/L
NH_3-N	0.84	mg/L
Volatile fatty acids (VFA_{total})	1390	mg/L
Sludge inoculum		
Total solids (TS)	21.5	g/L
Volatile solids (VS)	14.8	g/L
Moisture content	71.8	%
Ash content	20.7	%
Volatile matter	61.7	%

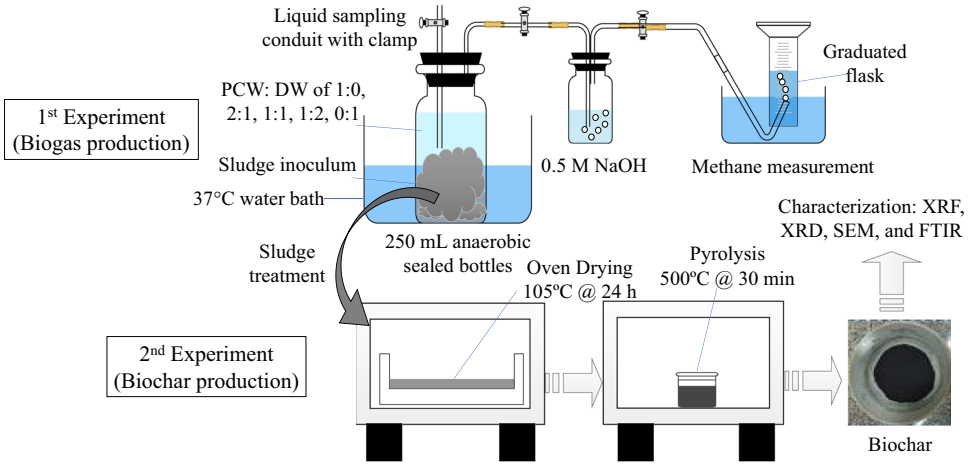

Fig. 1 Schematic diagram of the two experimentations used for dual biogas/biochar production from petrochemical wastewater (PCW)

In the second experimentation, anaerobic sludge (AS) was collected after the termination of PCW digestion and then subjected to thermal treatment. For this purpose, the sludge samples were dewatered through centrifugation (6000 rpm @ 10 min), and the supernatant was decanted carefully [20]. The dehydrated sludge was inserted in an oven at 105 °C within 24 h for drying. The samples were withdrawn, and then crushed, sieved to a size of less than 1.00 mm, and stored in zip-locked plastic bags for subsequent studies. A suitable amount of AS (50 g) was placed in an autoclave and heat-treated in a muffle furnace at 500 °C @ 30 min at an oxygen-free environment. The delivered biochar, i.e., sludge biochar (AS-BC), was allowed to cool at room temperature in a desiccator, and used for characterization studies.

2.3 Analytical analysis

Wastewater samples were analyzed for chemical oxygen demand (COD), total organic carbon (TOC), ammoniacal nitrogen (NH_3–N), and volatile fatty acids (VFA_{total}) according to standard APHA methods [21]. COD was measured with the Hach DR900 Multiparameter Portable Colorimeter. The soluble fraction was determined by passing the wastewater samples through a syringe filter (0.45 µm). The terephthalic acid content was determined using high-pressure liquid chromatography (Prominence HPLC, Shimadzu, Kyoto, Japan) at a 254 nm wavelength. The sludge samples were analyzed for total solids (TS) and volatile solids (VS) following APHA [21]. Sludge pyrolysis was conducted in a muffle furnace (Linn High Therm) at 500 °C (rate of 12 °C/min), where an autoclave was used to maintain an oxygen-free atmosphere. The solid samples (sludge and biochar) were characterized following the procedures reported in our previous research [18]. For instance, a scanning electron microscope (JCM-6000PLUS NeoScope Benchtop SEM, Japan) was used to determine the surface morphologies of the AS and AS-BC samples. Moreover, the samples' main elemental composition was detected by an energy dispersive X-ray (EDX) spectroscopy (JEOL JSM-6510LV, Japan). The minerals present in the solid samples were identified using the X-ray diffractometer method (XRD-6100, Shimadzu, Japan). Fourier transform infrared (FTIR) spectroscopy (Bruker ALPHA, Germany) was used to record the variation in the surface functional groups of AS before and after pyrolysis. The X-ray fluorescence (XRF) elemental composition was determined by a wavelength-dispersive XRF spectrometer (Rigaku NEX CG, Japan). All pH monitoring was done using a portable multimeter (Lutron, YK-2001PHA, Taiwan). All measurements were recorded in triplicate, and average values were used in the analysis.

2.4 Kinetic analysis

A modified Gompertz model (Eq. (1)) was used to evaluate the bio-CH_4 production curves obtained at different PCW:DW ratios.

$$H = Pexp\left\{-\exp\left[\frac{R_m e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

where H is cumulative CH_4 production (mL), P is CH_4 potential (mL), R_m is the maximum CH_4 production rate (mL/d), e is the Euler's number (2.71828), and t and λ are the time (day) of anaerobic digestion and lag phase to initiate bacterial growth, respectively

3 Results and discussion

3.1 Anaerobic co-digestion of PCW:DW for biogas production

3.1.1 Biogas production and fitting with Gompertz model

Figure 2(a) shows the cumulative CH_4 values derived from the anaerobic batch assays for treating PCW. A modified Gompertz model was able to fit the CH_4 production data for the different PCW:DW ratios, with high fitting accuracy (R^2 0.991–0.995). The bio-CH_4 productivity initiated to increase after about 3 days of a lag phase, probably due to the acclimatization of microorganisms to the operating environment [9]. The duration range of 3–12 days was used to describe the CH_4 productivity in the exponential phase culture. Extending the treatment time over 12 days displayed insignificant ($p > 0.05$) improvement in biogas productivity. The maximum CH_4 production rate (R_m) varied among the PCW:DW conditions (Fig. 2b), showing the highest value of 12.8 mL/day at 1:0 (PCW:DW). This value was significantly ($p < 0.05$) higher than R_m= 9.8 mL/day for the 0:1 (PCW:DW) condition. A similar pattern was noticed for the *P* data, giving the highest and lowest values of 62.6 mL at 1:0 (PCW:DW) and 49.1 mL at 0:1 (PCW:DW), respectively. The PCW:DW= 1:0 condition contained a high amount of carbonaceous organic matter, represented by a COD concentration of 2720 mg/L that could be converted into biogas. It has been reported that a high COD concentration of PCW would provide a positive potential for methane production [10]. A comparable study by Tan et al. [2] had revealed that CH_4-rich bioenergy could be recovered from the utilization of soluble organics in PCW under an anaerobic condition. Their study demonstrated that the increased biogas productivity from PCW was assigned to the secretion of extracellular biopolymers by anaerobic microorganisms to degrade the soluble COD fraction [2]. In another study, Maletić et al. [22] used the Gompertz model to fit the biogas productivity from the anaerobic degradation of petroleum hydrocarbons, in which acetate and glucose were used as co-substrates to enhance the biodegradation activity. Hence, it is suggested that increasing the biogas productivity from PCW could have been supported by adding co-substrate (e.g., acetate/glucose) to increase the microbial communities for organic matter degradation. In addition, the kinetic parameters estimated from fitting the Gompertz model could be further used to design an efficient scale-up digester receiving PCW [23].

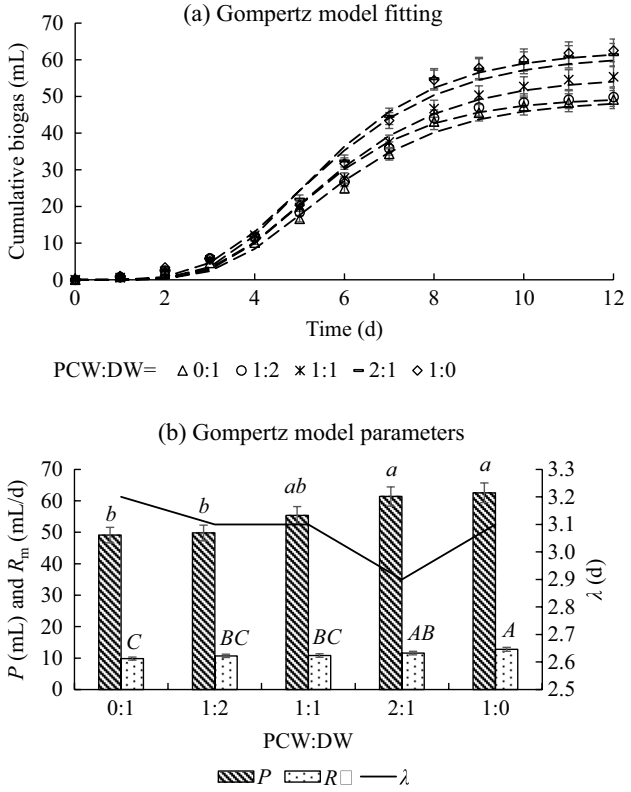

Fig. 2 Biogas production from different PCW:DW ratios of 0:1, 1:2, 1:1, 2:1, and 1:0 (a) Gompertz model fitting, and (b) Gompertz model parameters. The statistical significance of the difference between PCW:DW dilutions was derived using one-way ANOVA followed by Tukey's post hoc test. Groups sharing the same letter do not statistically differ from each other at the significance level of alpha = 0.05

3.1.2 COD mass balance

Table 2 lists the results of COD mass conversion into biogas, soluble byproducts, and biomass growth. The percentage of "$COD_{soluble}$ final/COD_{total} initial" showed the highest value of 44.9±2.2% at 1:0 (PCW:DW). Increasing the concentrations of complex compounds (hydrocarbons, phenol, organics, and oil and grease) in PCW encourages the microorganisms to release extracellular polymeric substances for facilitating substrate degradation [1]. These substances are accompanied by incrementing the soluble microbial products, which further raise the $COD_{soluble}$ concentration in the final supernatant. The highest fraction of CH_4/COD_{total} initial (60.5±2.3%) was observed for the 0:1 (PCW:DW) assay, probably due to the availability of readily biodegradable organic matter in the domestic waste source [5]. In particular, increasing the PCW fraction in the feeding wastewater tended to reduce the ability of microorganisms to degrade the complex compounds; hence, the biogas/COD_{total} fraction dropped at 1:0 (PCW:DW). It was also observed that the 0:1 (PCW:DW) composition provided a suitable environment for biomass growth, equivalent to biomass/COD_{total} initial of 13.3±0.6%. For example, terephthalic acid was not detected in the 0:1 (PCW:DW) bottle but showed the highest

Table 2 Estimation of COD mass balance during PCW:DW anaerobic treatment

PCW:DW	0:1	1:2	1:1	2:1	1:0
pH	7.3 ± 0.3	7.0 ± 0.2	6.9 ± 0.2	6.8 ± 0.1	6.6 ± 0.2
COD_{total} initial	1160 ± 54	1300 ± 62	1790 ± 78	2330 ± 112	2720 ± 132
COD removal (%)	69.1 ± 3.5	63.5 ± 3.3	54.9 ± 3.2	48.4 ± 3.5	43.0 ± 2.6
TA initial	ND	14.10 ± 0.70	24.21 ± 1.71	39.27 ± 1.88	46.60 ± 2.17
TA removal (%)	ND	88.98 ± 4.37	81.62 ± 4.11	80.06 ± 4.03	82.07 ± 4.65
VFA	102.6 ± 4.2	246.3 ± 11.7	420.7 ± 18.3	542.3 ± 24.1	821.4 ± 37.2
CH_4 gas (mL/g $COD_{removed}$)	306.4 ± 11.8	301.5 ± 12.2	282.0 ± 10.6	272.3 ± 10.8	267.3 ± 10.3
Sludge yield (g sludge/g COD_{total})	0.22 ± 0.01	0.16 ± 0.01	0.11 ± 0.01	0.09 ± 0.00	0.07 ± 0.00
$COD_{soluble}$ final/COD_{total} initial (%)	20.7 ± 1.2	29.2 ± 1.4	38.0 ± 1.8	42.5 ± 2.2	44.9 ± 2.2
Biogas/COD_{total} initial (%)	60.5 ± 2.3	54.7 ± 2.6	44.2 ± 2.2	37.6 ± 1.6	32.9 ± 1.7
Biomass/COD_{total} initial (%)	13.3 ± 0.6	9.3 ± 0.5	7.9 ± 0.3	6.9 ± 0.3	6.4 ± 0.3
COD mass balance (%)	94.5 ± 4.3	93.3 ± 3.8	90.1 ± 4.2	87.0 ± 3.6	84.1 ± 3.7

concentration of 40.66±2.10 mg/L in 1:0 (PCW:DW). A longer degradation period and specific microbial community, including *Syntrophorhabdus* members, were required to convert this aromatic compound to 206.1 mL CH_4/g $COD_{removed}$ [24]. Moreover, a lower percentage of biomass/COD_{total} initial at 1:0 (PCW:DW) could be related to the rupture and decay of bacterial cells due to the presence of inhibitory substances in PCW. This pattern would liberate intracellular substances, and further increase the $COD_{soluble}$ fraction in the final effluent. Other COD fractions such as CH_4 dissolved in the medium and substrate storage in the bacterial cells could not be detected in this mass balance equation. The estimated COD mass balance of an 84–94% range suggests a suitable validation procedure for the data, representing the anaerobic degradation of PCW-related organics. The findings also indicate that adding DW (as a co-substrate) to PCW enhanced the bioconversion of organic compounds to methane.

3.2 Pyrolysis of anaerobic sludge for biochar production

3.2.1 Physicochemical properties and elemental composition

The residual sludge of PCW anaerobic treatment was subjected to a pyrolysis process, and the obtained biochar (AS-BC) was characterized (Table 3). The physicochemical properties of AS-BC (biochar) were compared with anaerobic sludge (AS). The pH values were 5.8 for AS and 7.9 for AS-BC, implying that the sludge's pH increased following pyrolysis. The decomposition of the O-containing functional groups by pyrolysis is accompanied by the release of alkali metal salts from the pyrolytic structure (organic matrix) of AS [17]. This pattern further reduces the amount of acidic surface functional groups, making an overall alkaline feature. The zeta potential of AS-BC was highly negative (−20.2 mV), reflecting the presence of multiple negatively charged functional groups. This property tends to facilitate the deposition of positively charged pollutants onto the AS-BC material, which could be further used for heavy metal cations (Cd^{2+}, Cu^{2+}, and Pb^{2+}) removal from wastewater. For instance, an AS-BC material with pH= 6 and a zeta potential of −19.3 mV was able to remove Pb^{2+} from aqueous solutions with an adsorption capacity of 51.20 mg/g [25]. The BET values were 5.20 m^2/g for AS and 6.73 m^2/g for AS-BC, indicating that the sludge-specific surface area increased by 22.7% after pyrolysis. The derived biochar had a BET surface area comparable with 6.35 m^2/g for biochar prepared from aerobic granular sludge [16]. The increased pyrolysis temperature (i.e., 500 °C) would also ensure a larger BET surface area due to the aggravation of the biomass carbonization degree [8]. The results of sludge's pore size, which reduced by 81.1% after pyrolysis, agreed with

Table 3 Physicochemical properties and X-ray fluorescence (XRF) elemental composition of anaerobic sludge (AS) and sludge-based biochar (AS-BC)

Material	pH	Zeta potential (mV)	BET (m^2/g)	Pore size (nm)	Elemental composition (wt%)											
					Sc	Cu	Ni	Zn	Co	P	Mg	Mn	Ti	K	Zr	Fe
AS	5.8	−16.4	5.20	93.79	0.32	0.18	0.03	0.69	0.03	0.63	0.19	0.20	1.97	1.35	1.40	20.5
AS-BC	7.9	−20.2	6.73	17.71	0.27	0.15	0.04	0.74	0.10	0.89	0.35	0.13	1.97	1.78	1.32	19.6

the BET analysis (Table 3). Apparently, the sludge structure shifted from macropores (> 50 nm) to mesopores (2–50 nm), owing to the carbonization process (increased aromaticity and decreased polarity). The evaluation of sludge's physical properties assigns that the AS-BC material would experience a better ability to sequester metal species from aqueous solutions than AS. The total contents of Al, Si, S, and Ca in the anaerobic sludge increased after pyrolysis, probably due to the thermal decomposition of organic matter and gradual loss of C, H, N, and O [13]. Moreover, the oxides of these elements (Al, Si, and Ca) are not volatile, except for the S-containing compounds that could be degraded to volatile SO_3 [17]. Increasing the cationic elements, e.g., Mg^{2+}, K^+, and Ca^{2+}, supports the application of biochar for soil deacidification and ion exchange with pollutants. Accordingly, most of the inorganic constituents and minerals in the sludge were enriched after the pyrolysis process, agreeing with the features of sludge-derived biochar reported previously [8, 26].

3.2.2 SEM-EDX

The surface morphology of sludge was also modified after pyrolysis (Fig. 3). The As material had a relatively plain and smooth surface with plate-like layer construction (Fig. 3a). However, a coarser and more porous surface with voids was observed for AS-BC (Fig. 3b), probably due to releasing the thermally unstable compounds from the biochar matrix. These findings complied with the volatilization of hydrocarbon compounds and the crystallization of carbon after sludge pyrolysis, as reported previously [14]. The AS and AS-BC samples had C (43.93 and 40.32 wt%), and O (25.34 and 19.79 wt%), equivalent to O/C= 0.53 and 0.49, respectively. Apparently, the continuous decomposition of volatile matter in the AS samples during pyrolysis was accompanied by the C, N, and O losses. Similarly, textile dyeing sludge had C (20.22 wt%), N (2.26 wt%), and O (18.36 wt%), which dropped to 12.28, 0.12, and 1.92 wt% after pyrolysis, respectively [15].

3.2.3 XRD and FTIR

The results of XRD complied with the SEM/EDX characterization for both AS and AS-BC material (Fig. 4a). The presence of more and sharper peaks in the AS-BC sample indicated that the pyrolysis process enhanced the crystallinity structure of sludge [20]. In particular, different species and elements released during the thermal breakdown of sludge at 500 °C tend to aggregate and alter the initial crystal feature. Similarly, phloroglucinol hydrate ($C_6H_6O_3{\cdot}2H_2O$, PDF#00-023-1822) and Fumaric acid ($C_4H_4O_4$, PDF#00-015-1187) in AS were not detected after pyrolysis. The Si-associated compounds (e.g., aluminum silicate) were detected in the XRD pattern due to the abundance of silicon as one of the primary inorganic elements in sludge [26]. The XRD pattern of AS shows a broad peak at $2\Theta \approx 21.3°$, corresponding to the (100) phase reflection of carbon. Moreover, the defined peaks at $2\Theta \approx 26.8°$ and 29.3° could be ascribed to calcium silicate (Ca_2SiO_4, PDF#00-031-0302) and silicon

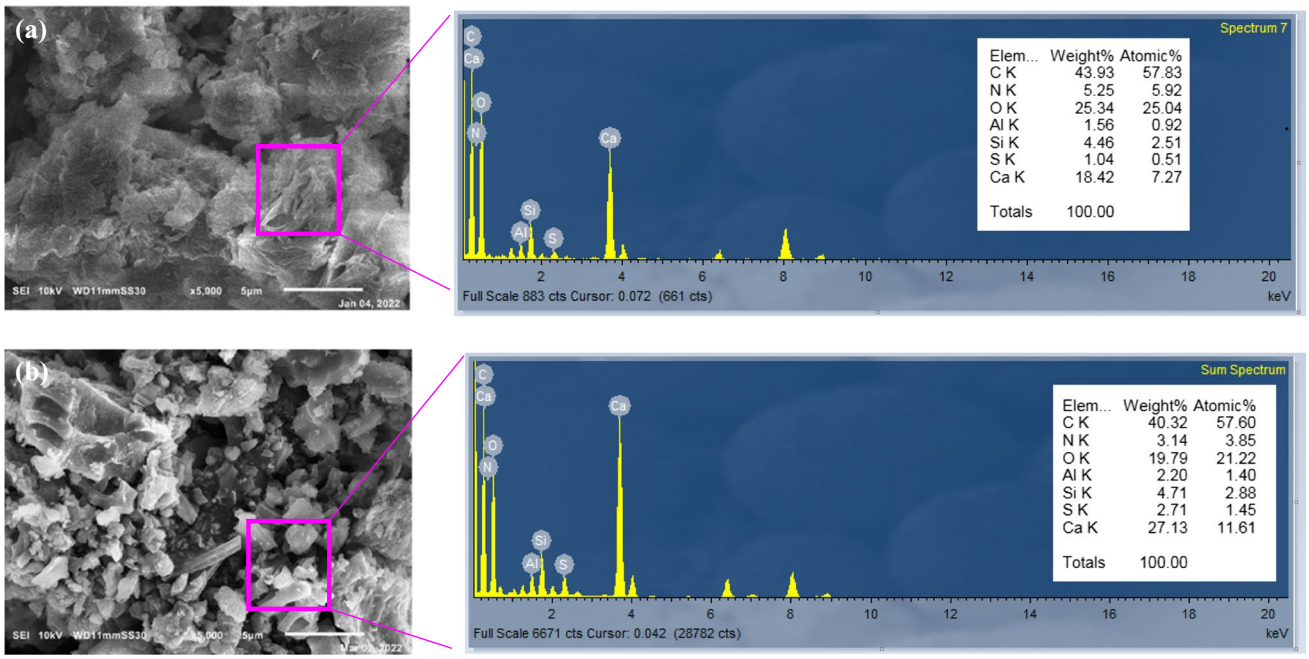

Fig. 3 SEM/EDX characterization of (**a**) anaerobic sludge (AS) and (**b**) biochar-based sludge (AS-BC)

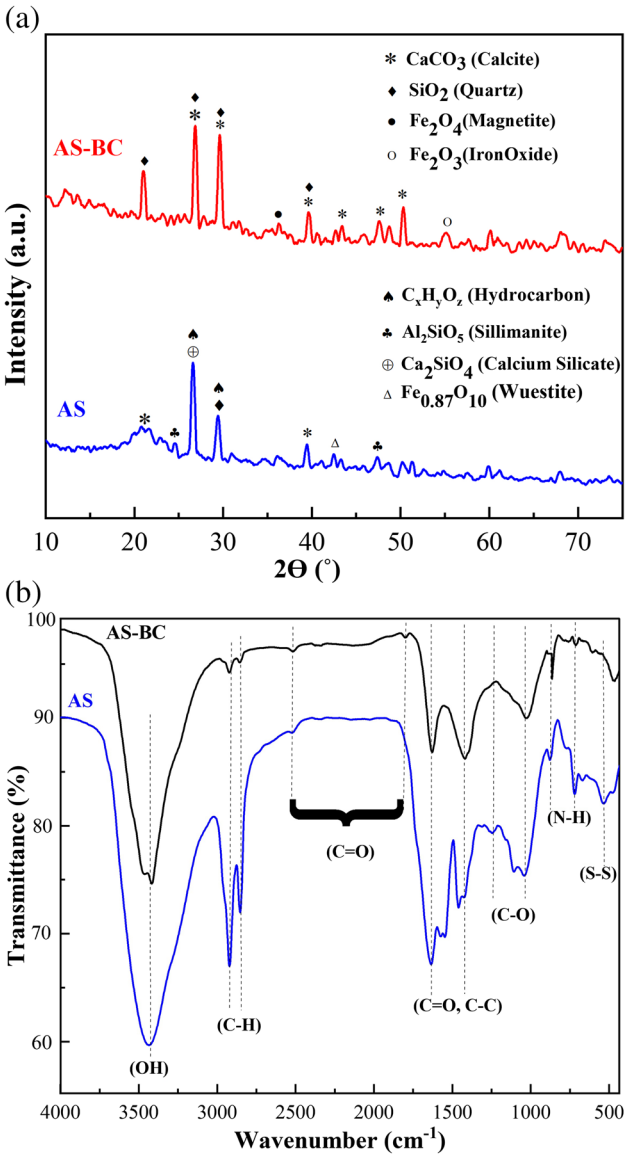

Fig. 4 Characterization of AS and AS-BC using (**a**) XRD and (**b**) FTIR

oxide (SiO_2, PDF#01-079-0446), respectively. These two peaks were elongated after pyrolysis to form a graphite-like carbon structure in AS-BC due to the occurrence of calcite ($CaCO_3$, PDF#01-086-2339).

Figure 4(b) shows the locations of the FTIR peaks for both AS and AS-BC, along with the variations in the transmittance intensities. The AS-related FTIR showed a strong peak at 3463 1/cm mainly attributed to the hydroxyl (-OH) group [27]. The intensity of this peak was reduced for AS-BC, probably due to the decomposition of the hydroxyl bonds at the 500 °C pyrolysis temperature. The intensities of some peaks around 2929 and 2862 1/cm for C-H groups in AS were reduced after pyrolysis, assigning to the thermal decomposition of hydrocarbons and volatile constituents [14]. The detection of a band around 2526 1/cm implied the presence of organic sulfur in the samples. A strong peak appeared at the 1649 1/cm, followed by smaller peaks at 1545, 1467, and 1440 1/cm due to the presence of C=O vibrations and C-C aromatic rings in the sludge samples. These peaks complied with the carbonyl group (at 1687 1/cm) of terephthalic acid observed previously [28]. Hence, a portion of terephthalic acid could be eliminated by adsorption onto the anaerobic sludge. Additional smaller peaks between 1545 and 1440 1/cm were bonded into two strong peaks at 1631 and 1413 1/cm after pyrolysis, probably because multiple oxides combined with the adjacent carbon elements to form a single carbon-oxygen bond [18]. Other peaks at 1120 and 1051 1/cm revealed the presence of Si-O stretching and siloxanes. The N-H peaks at 864 and 711 1/cm disappeared after pyrolysis, mainly due to the separation of nitrogen-containing compounds by thermal decomposition. The observations of C bonds and Si-O stretching in the FTIR spectra agree with the detection of both calcite and quartz in XRD (see Fig. 4a).

3.3 Economic evaluation of dual biogas/biochar production

The economic feasibility of the dual biogas/biochar production from PCW treatment and AS pyrolysis was performed, following [8, 29]. Table 4 lists detailed results of the capital cost for the installation of an anaerobic system receiving 30 m^3/day followed by sludge thermal treatment. The construction of an anaerobic digestion unit accounted for 4200 USD for frame structure and 3800 USD for the pyrolysis (thermal) reactor. The construction of other tanks, i.e., receiving and balancing tank, treated water tank, and sludge tank, represented 26.6% of the total capital cost. Electrical energy demands retained 87.04% (i.e., the majority) of the operational cost of the anaerobic/pyrolysis system. The prices of chemical addition (for pH adjustment) and sludge handling were 4.5% and 4.0% of the operational costs, respectively. The manpower cost was neglectable because the anaerobic unit was operated automatically with no need for close supervision. As a result, the overall operational cost of the biogas/biochar producing system was 10.11 USD/day, equivalent to 0.34 USD for 1 m^3 of treated wastewater or recycled water. The profitability scenario was performed based on selling the biogas and biochar. The highest income from energy was reported in 1:0 (PCW:DW), equivalent to 9.15 USD/day (biogas= 9.38 m^3/day using the COD mass balance of the experimental assays). The selling of biochar increased for the 0:1 (PCW:DW) condition, due to the generated sludge of 7.51 kg/day (estimated from 13.3% of influent COD and biochar yield of 0.6 g/g dry sludge). An additional benefit was obtained from pollution reduction, corresponding to 0.22 USD per kg $COD_{removed}$ [6, 11]. In particular, the proposed system tends to avoid the negative impact of PCW on human health and the aquatic culture, further limiting environmental

Table 4 Profitability scenario of dual biogas/biochar production from PCW treatment

Capital cost (USD)		Operational cost (USD/d)		Profits and payback period					
Item	Cost	Item	Cost	Item	PCW:DW				
					0:1	1:2	1:1	2:1	1:0
Parabolic fine screen	1200	Electrical consumption 55 kW per day	8.80	Energy content of biogas (kWh/d)	44.93	45.53	50.63	56.11	57.19
Tanks (receiving and balancing, treated effluent, and sludge)	2350	Chemicals for pH adaptation	0.45	Income from energy (USD/d)	7.19	7.28	8.10	8.98	9.15
Anaerobic unit	4200	Water utilization	0.20	Biochar (kg/d)	1.35	1.15	1.10	1.10	1.05
Heating unit	3800	Sludge disposal every 3 months	0.40	Biochar selling (USD/d)	0.68	0.58	0.55	0.55	0.53
Pumps (lifting and sludge)	2000	Salaries	0.08	Pollution reduction (USD/d)	5.29	5.45	6.48	7.44	7.72
Miscellaneous (valves, pipes, and cabling)	750	Maintenance	0.18	Total profit (USD/d)	13.16	13.31	15.13	16.97	17.40
Total capital cost (USD)	14300	Total operational cost (USD/d)	10.11	Payback period (year)	12.86	12.24	7.80	5.71	5.38

deterioration. Based on this estimation, the capital cost was 14,300 USD and the net profit reached 2660 USD/year; thus, the payback period was approximately 5.4 years. This time was shorter than 12.9 years for the 0:1 (PCW:DW) case that had an insufficient revenue of biogas production. Apparently, the 1:0 (PCW:DW) scenario contained a higher concentration of COD, which could obtain beneficial products under the anaerobic treatment condition. Hence, the dual biogas/biochar production from PCW is considered an economically beneficial process. Although this economic evaluation showed a short payback period (smaller than the project lifetime), it should be expanded to cover other items such as the cost of a post-treatment system, labor, maintenance, and the penalty fee due to the discharge of the untreated wastewater in the main sewage system.

3.4 Meeting SDGs from PCW co-digestion via delivering beneficial by-products

Figure 5 shows the potential contribution of the current study objectives and findings for meeting several SDGs [30]. Biogas production affords a versatile carrier of renewable energy, in which it can be generated from various bio-wastes such as food and animal residuals, livestock manure, and some domestic and industrial by-products [3]. Biogas could replace fossil fuels in some heat- and power-required applications, minimizing the negative impact of carbon emissions on the atmosphere [23]. The technology of biogas production using the bacterial conversion of organic matter is considered cheap and simple; hence, it would fulfill the targets of SDG 7 "Affordable and Clean Energy" and SDG 13 "Climate Action." The current study also highlighted the role of anaerobic treatment to reduce COD pollution from PCW before reaching the aquatic environment. Moreover, biochar generation from the sludge of this anaerobic process is considered a beneficial pathway for avoiding a further uncontrolled disposal and burning of solid wastes. This objective would meet the targets of SDG 3 "Good Health and Well-being" and SDG 14 "Life Below Water." The generated biochar, with suitable elemental composition, functional groups, ion exchange capacity, and surface feature, maintains a long-term sludge recycling strategy. Similar biochars have been employed for removing metal ions from industrial effluents (as ion exchangers), modifying soil properties (as soil amendment), and producing energy (as feedstock). These advantages comply with the targets of SDG 2 "Zero Hunger" by improving the soil quality of farmlands and SDG 6 "Clean Water and Sanitation" by eliminating heavy metals and dyes from the wastewater industries. Accordingly, the present study revealed the applicability of PCW to acquire dual biogas and biochar, with a positive contribution to economic and sustainable development.

3.5 Research gaps in PCW-related studies

Recently, the anaerobic degradation of PCW has been adopted to reduce the COD concentrations, with a tangential benefit of biogas production (Table 5). The generation of both CH_4 (165 mL/gCOD$_{add}$) and H_2 (102 mL/gCOD$_{add}$) gasses from PCW treatment has also been reported [1]. Moreover, a payback period of 7.13 years was achieved from the anaerobic fermentation of PCW, regarding profits of bioenergy recovery and COD removal [7]. The anaerobic co-digestion of PCW and manure was a positive strategy to achieve 98.6% COD removal, with energy recovery and agricultural irrigation and fertilization, giving a payback period of 3.75 years [12]. Based on the literature survey and the results obtained from the current study, other types of organic wastes (co-substrates) could be added to PCW for maximizing biogas recovery (Table 5). Moreover, an economical and efficient post-treatment step is necessary to ensure the safe disposal of PCW. Furthermore, mathematical models and computational techniques

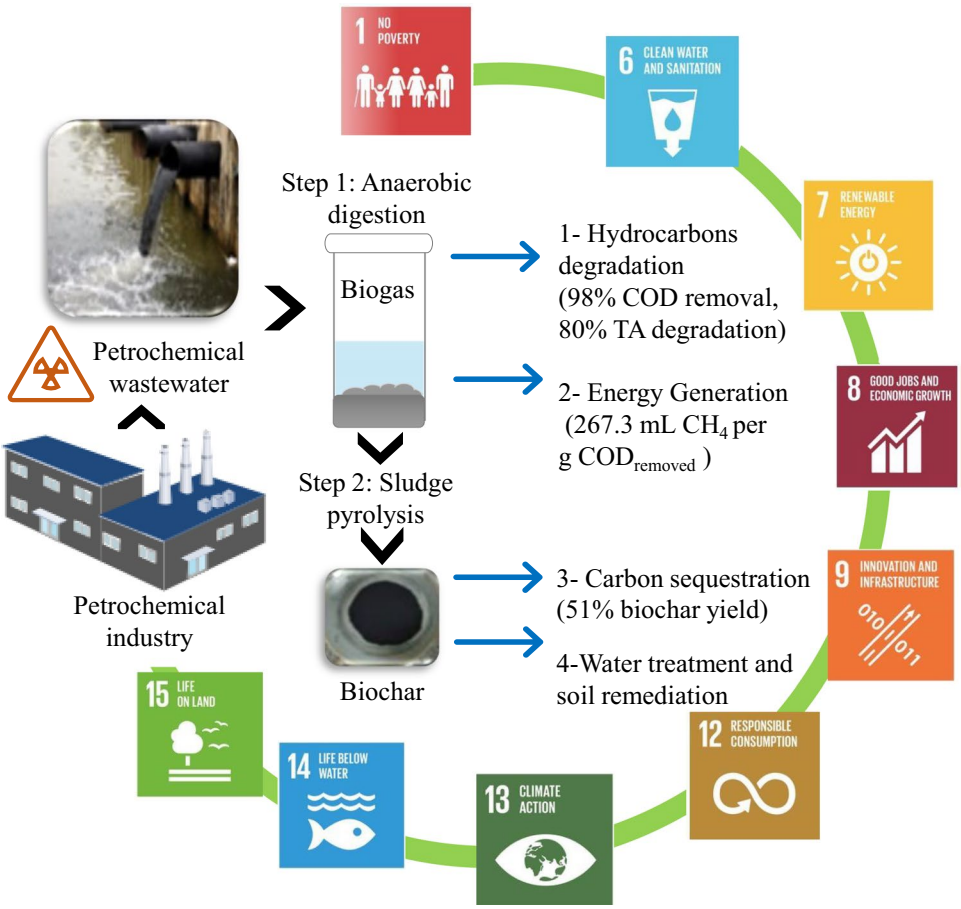

Fig. 5 Fulfillment of SDGs via dual biogas/biochar production from PCW waste

Table 5 Techno-economic feasibility of petrochemical wastewater (PCW) treatment

Process	Outputs	COD removal (%)	Profit criterion	Reference
Anaerobic digestion and pyrolysis	267.3 mL CH_4/g COD removed; 0.6 g biochar/g dry sludge	43.0	Payback period 5.38 years	This study
Anaerobic digestion and fermentation	165 mL CH_4/g COD add; 102 mL H_2/g COD add	65.0	Payback period 5.27 years	Ali et al. [1]
Anaerobic fermentation	189 mL H_2/g MEG initial	36	Payback period 7.13 years	Elreedy et al. [7]
Anaerobic digestion	11.1 m^3 biogas/d; 80 % CH_4; 0.85 m^3 irrigation water/m^3 substrate; 0.08 m^3 agricultural supplement/m^3 substrate	98.6	Payback period 3.75 years	Siddique et al. [12]
Adsorption	79.1% Toluene removal; 86.6% Xylene removal	-	Payback period 6.86 years	Kumi et al. [4]
Two-phase anaerobic digestion system	152 mL CH_4/g COD initial; 22.27 mL H_2/g COD initial	80.02	Net profit= 139,996 USD/year	Elreedy et al. [5]

should be developed to illustrate the relationship between PCW quantities and biogas/sludge yields. Additionally, the real application of AS-BC for lowering atmospheric GHG concentrations by sequestering carbon, with unifying the market value of biochar internationally, should be investigated. The government and policymakers should develop strategies that make the commercialization of biochar and methane-rich biogas more profitable.

4 Conclusions

This study focused on increasing the amount of biogas production from PCW by investigating the addition of several proportions of DW. Varying the PCW:DW fractions significantly affected the organic mass balance distribution, where a higher portion of the initial COD_{total} was

converted to biogas and sludge productions with increasing the DW content. The yields of biogas (mL/g $COD_{removed}$) and sludge (g /g COD_{total}) were 301.5±12.2 and 0.16±0.01 at 1:2 (PCW:DW), which reduced to 267.3±10.3 and 0.07±0.00 at 1:0 (PCW:DW). After PCW treatment, the anaerobic sludge was thermally treated for biochar synthesis, showing appropriate SEM/EDX elemental composition, BET surface area, and FTIR functional groups. The economic feasibility of the anaerobic digestion and pyrolysis processes was performed, regarding the profits of biogas and biochar productions and COD removal. After validating the COD mass balance (84–94%), the use of 1:0 (PCW:DW) revealed a profitability scenario with a payback period of 5.38 years. The study concluded that the dual biogas/biochar production from the PCW treatment could be an economically feasible pathway, recovering the investment cost within a short time-span. The study outputs revealed the fulfillment of several SDGs, regarding energy generation, pollution reduction, and a carbon-rich material synthesis.

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Availability of data and material The data that support the findings of this study are available within the article (and/or) its supplementary materials.

Declarations

Ethics approval Not applicable.'

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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