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Improved methane production and energy recovery of post-hydrothermal liquefaction waste water via integration of zeolite adsorption and anaerobic digestion

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Abstract:

Hydrothermal liquefaction (HTL) is a promising technology for converting organic wastes into bio-crude oil, with organic-rich post-hydrothermal liquefaction wastewater (PHWW) as by-product. In this study, zeolite adsorption and anaerobic digestion (AD) were integrated to improve the methane production and energy recovery of PHWW from *Chlorella* 1067. A statistical design for maximum toxicants removal by zeolite was applied before AD process. Zeolite could mitigate the inhibition associated to compounds such as ammonia, N-heterocyclic compounds, etc. in PHWW and thereby shortening the lag phase and increasing methane production by 32-117% compared with that without zeolite adsorption. Zeolite adsorption also increased energy recovery efficiency (up to 70.5%) for this integrated system. Integration of HTL and AD brought higher energetic return from feedstock via oil and biomethane production, which may offer insight into industrial application of microalgae biomass in the circular economy. In addition, carbon and nitrogen flow for the integrated process was determined.

Key words: Post-hydrothermal liquefaction wastewater; Zeolite; Anaerobic digestion; Energy recovery; Microalgae

1. Introduction

Algae are promising for developing renewable biofuels due to its high growth rate as well as no farmland occupation (Demirbas, 2010; Yang et al., 2014). Hydrothermal liquefaction (HTL) is a thermochemical process that could convert various biomass such as algae into renewable and sustainable energy alternatives to fossil fuels (Leng et al., 2018; Li et al., 2018; Patel et al., 2016; Vardon et al., 2011). However, HTL process cannot convert all the organics in feedstock into bio-crude oil, leaving the residual organics in the liquid as post-hydrothermal liquefaction wastewater (PHWW), rich in multiple valuable nutrients (Yu et al., 2011). For instance, about 20% of the carbon was transferred into PHWW, mainly in forms of monosaccharides, oligosaccharides and short chain organic acids (i.e., acetic acids) (Barreiro et al., 2015; Elliott et al., 2013; Lu et al., 2017; Toor et al., 2011; Zhou et al., 2013). Thus, downstream technologies that can further recover these dissolved organic carbons from PHWW by converting them into higher value products should be pursued as an essential step to promote the overall economic viability and economic feasibility of HTL (Si et al., 2018).

Anaerobic digestion (AD) was regarded as a potential complementary process that may allow future processing and concomitant energy and resource recover from PHWW (Posmanik et al., 2017). The organics in PHWW could serve as an ideal carbon source for AD process to produce biogas (a mixture of CH_4 and CO_2), and thereby permitting the usability (or exploitation) of PHWW. Therefore, synergistic integration of HTL with AD could significantly facilitate the recovery efficiency of resource and energy, and

thereby achieving maximum bioenergy production from waste streams. Nevertheless, there are also several potential challenges that need to be addressed in order to achieve a cost-effective and efficient integration. For instance, over 50% of the nitrogen in feedstock were found to be retained in PHWW, resulting in the accumulation of ammonia/ammonium and nitrogenous heterocycles that inhibit anaerobic digestion (Leng et al., 2018; Pham et al., 2013). Chen et al. (2008) reported a wide range of inhibiting ammonia concentration from 1700 to 14000 mg/L for AD. The inhibition was related to suppress activities of enzymes during methane formation (Li et al., 2017a; Li et al., 2017b). A synergistic cytotoxicity effect among the nitrogenous compounds was also identified (Sun et al., 2011; Vardon et al., 2011). Thus, the complicated wastewater must be treated properly whether it was released or reutilized (Eljamal et al., 2009). Pre-treatment for PHWW before AD process was necessary since these toxicants were likely to inhibit the microbes in the reactor.

Adsorption is an efficient and economically feasible detoxification method for wastewater treatment (Eljamal et al., 2011). Activated carbon and zeolite have a high degree of porosity, showing a great capacity for pollutant adsorption. Improved conversion efficiency of the PHWW from *Spirulina* sp. was obtained after activated carbon adsorption (Zhou et al., 2015). Tommaso et al. (2014) also declared enhanced methane production of the pre-treated PHWW derived from swine manure through activated carbon adsorption. Zeolite is a non-cytotoxic mineral composed of silica, aluminum and oxygen and it is distinguished by its systematic structure that consists of

plenty of channel and pore cavities (Amen et al., 2017). It is another commonly used adsorbent because of its unique porous structure and enhanced adsorption, ion-exchange, and catalytic properties. Kotsopoulos et al. (2008), Lin et al. (2013) and Zheng et al. (2017) observed ammonia adsorption as well as enhanced methane yield in the presence of zeolite during AD of different substrates. It's worth mentioning that the main advantage of natural zeolites was that it was low-cost minerals and widespread in terrestrial environments, which made zeolite a more cost-effective choice for wastewater treatment (Ariyanto, 2009). However, zeolite adsorption has not been fully explored. Ammonia adsorption and biogas enhancement have been studied the most, while there is a lack of information regarding the nitrogenous toxicants removal as well as energetic return viability of PHWW.

This study introduces a statistical design for PHWW adsorption as well as energy quantitative analysis along the integrated HTL and AD system. The objective of this study is to: (1) apply a statistical design for maximum ammonia and toxicants removal from PHWW; (2) investigate the effect of zeolite adsorption on biomethanation of PHWW derived from *Chlorella* 1067; (3) overlook the energy recovery in the integrated system; (4) track footprint of carbon and nitrogen along the integrated system.

2. Materials and methods

2.1 Feedstock

The HTL process was conducted in a stainless steel cylinder reactor of 1 L in a batch mode (Parr 4574, Parr Instrument Co., USA) under 300 °C and 2 MPa for 30 min with a

rotate speed of 400 r/min. *Chlorella* 1067 slurry with a solid content of 15% by weight was put into the reactor.

The natural zeolite used in this study was obtained from Miaoyuan Co. located in Henan, China. The chemical composition of the zeolite was given in Table 1.

The inoculum sludge was taken from an upflow anaerobic sludge blanket (UASB) reactor operated stably for years treating different PHWW derived from various HTL feedstock.

2.2 Characterization Analysis of feedstock and products

Elemental contents of C, N and H of feedstock, oil and solid residue were determined using an elemental analyzer (Vario Micro Cube, Elementar Analysensystem GmbH, Germany), and the content of O was calculated by difference (Tian et al., 2015). The total carbon (TC) and total organic carbon (TOC) content of the aqueous phase were measured using a TOC analyzer (TOC-Cvpn, Shimadzu, Japan). The total nitrogen (TN) and total ammonia nitrogen (TAN) content were analyzed using ultraviolet spectrophotometer (UV-1800, Meipuda, China) according to Li et al. (2017a). The chemical oxygen demand (COD) was determined using a COD analyzer (DR-2800, HACHI, USA). The concentration of ions (i.e., NO_3^- , NO_2^- , H_2PO_4^- and SO_4^{2-}) was detected via an ion chromatograph (ICS-90, DIONEX, USA). The higher heating value (HHV, MJ/kg) of feedstock was analyzed using an oxygen bomb calorimeter (Parr 6200, Parr Instrument Co., USA).

2.3 Adsorption Experiments Design

The adsorbing experiment was carried out in 100 mL flasks with 30 mL of working volume. All the reactors were incubated in a time-controlled air-bath. Software Design Expert 8.0.6 was employed for process optimization and statistical analysis. In this study, TAN was used as a response value to establish a sequence of experiments. Based on the single factor experiments, zeolite size (A), treating temperature (B) and zeolite dosage (C) were selected as the most significant factors, which were then centrally compositely designed as presented in **Supplementary materials**. The adsorption time was 6 hours when there was no TAN decrease for PHWW.

2.4 Gas Chromatography-Mass Spectrometer (GC-MS) analysis

The PHWW components were firstly extracted using diethyl ether ($V_{\text{aqueous phase}}: V_{\text{diethyl ether}} = 1:9$) and then analyzed using a gas chromatograph-mass spectrometer (GC-MS) (Shimadzu QP2010, Kyoto, Japan). The GC-MS analysis was used to quantify the chemical compositions of PHWW and conducted under injection temperature 250 °C, interface 250 °C and ion source 200 °C with a 30 m DB-5 column. The oven temperature was set at 35 °C for 5 minutes, 130 °C for 4 minutes, 240 °C for 4 minutes and 280 °C for 7 minutes. All the temperatures increased at a speed of 25 °C /min. Helium gas was used as the carrier gas with the flow rate of 1.6 mL/min.

2.5 Biomethane potential (BMP) assays

The AD process of PHWW before and after adsorption was compared in batch experiment in order to determine the effect of zeolite pre-treatment. The gradient dilutions of 2, 3, 4, 5 and 7 g/L for both the original and pre-treated PHWW were performed using

the basal medium prepared according to the method described previously (Angelidaki et al., 2009), which contained macro- and micronutrients for microbes. The proportion of inoculation to PHWW was 1 g (VS)/ 1 g (COD). The experiment was assembled in 250 mL flasks with a working volume of 100 mL, which were incubated at 35 ± 1 °C in an incubator chamber. An air pocket assembled in each flask was used to collect the biogas generated and was replaced every time when sampling. All batch tests were conducted in triplicates.

Methane production potential ($P_{\max}$), methane production rate (R) and lag phase (λ) were fitted by the modified Gompertz equation (Chen et al., 2006) (Eq. (1)):

$$P(t) = \mu + (P_{\max} - \mu) \times \exp\{-\exp[R \times e \times (\lambda - t) / (P_{\max} - \mu) + 1]\} \quad \text{Eq. (1)}$$

Where $P(t)$ is the cumulative specific methane production (mmol/(g COD)) for an given time t (d). $P_{\max}$ is the specific methane production potential (mmol/(g COD)). R is the specific methane production rate (mmol/(g COD·d)). μ is the cumulative specific methane production for the control (mmol/(g COD)). λ is the lag phase (d) and e is the constant 2.71828.

2.6 Energy calculation

The HHV of the crude oil was estimated using the modified Dulong's formula based on its elemental composition (Chen et al., 2014; Theegala and Midgett, 2012):

$$HHV = 0.338 \times C + 1.428 \times (H - O/8), \quad \text{Eq. (2)}$$

where C , H and O are the mass percentage of carbon, hydrogen and oxygen (% , w/w).

The HHV of methane was determined as 55 MJ/kg (Posmanik et al., 2017). Thus

gross energy recovery for each scenario was calculated as given in Eq. (3):

$$GER(\%) = \sum \frac{Y_i \times HHV_i}{Y \times HHV_{\text{feed}}}, \quad \text{Eq. (3)}$$

where GER is the gross energy recovery (%), i is the energy product (oil or methane), Y_i and HHV_i are the yield (kg) and higher heating value (MJ/kg) for each product, Y and HHV_{feed} are the mass (kg) and higher heating value (MJ/kg) for feedstock.

3 Results and discussion

3.1 Statistical Adsorption Experiment

As shown in Fig. 1, the ternary relation between the three factors selected for central composite design was illustrated. Zeolite size and adsorbing temperature presented negative effect on TAN adsorption, while zeolite dosage exhibited positive effect. The maximum TAN adsorption (up to 83.81%) occurred when zeolite size, treating temperature and zeolite dosage were 0.44 mm, 39.4 °C and 0.36 g/mL, respectively. Scanning electron micrographs were obtained for zeolite samples before and after adsorption. Before adsorption, a well-formed cubic-like crystals indicated a typical morphology of clinoptilolite. Evidently, the surface has been constituted by aggregated irregular molecules which should be adsorbed from the aqueous phase (**Supplementary materials**).

Fig. 2A showed the combined effect of zeolite size and temperature on TAN adsorption. It was predicted that the maximum adsorption value occurred at 39.4 °C with zeolite size of 0.44 mm. Considering the effect of adsorption temperature, the ion exchange interaction between zeolite and ammonium could be enhanced as the

temperature increased from 35 to 39.4 °C. This may be due to the reduced resistance for mass transfer in the aqueous phase. Nevertheless, when the temperature was further increased to 45 °C, the adsorbed ammonium began to descend, indicating desorption from zeolite. In addition, there was a notable rise of TAN adsorption when zeolite dose ranged from 0.30 to 0.36 g/mL, but it decreased when more adsorbent was used (Fig. 2B). This may be related to the reduced available surface of zeolite as results of aggregation of adsorption sites and increased diffusion path length (Tavlieva et al., 2013). It has been demonstrated that the decrease in adsorbent capacity with increasing of adsorbent mass was attributed to the split in the concentration gradient between the solute concentration in the solution and on the surface of zeolite (Vadivelan and Kumar, 2005; Yagub et al., 2012).

The adsorbed PHWW mentioned below (hereinafter referred as pre-treated PHWW) was processed under the optimal condition selected above, except where noted.

3.2 Biochemical properties

The TOC value in PHWW was 31.1 g/L which was consistent with that reported in previous study, where TOC values for the aqueous phase produced from hydrothermal treatment of microalgae were found being widely distributed (3-80 g/L), but mainly in the range of 10-30 g/L (Leng et al., 2018). Zeolite adsorption did slight reduction of TOC and COD followed the similar trend as TOC. Nitrogen content in the PHWW highly depended on the protein content of feedstock used in HTL. As presented in Table 2, ammonia nitrogen accounted for a large proportion of the TN (more than 50%). The toxic

effect of ammonium on AD was mainly from the non-ionized form NH_3 , which can easily penetrate the microbial cell membrane and change the intracellular pH (Li et al., 2017b). Zeolite exhibited efficient adsorptive selectivity for ammonium due to its porous property and ion exchange capacity, which made the pre-treated PHWW suitable for AD. In anaerobic condition, sulfate could be reduced to sulfide through employing organic matters or H_2 as electron donors by sulfate-reducing bacteria, resulting in declined biogas production. In addition, as a reduction product, H_2S is also toxic to methanogens (Li et al., 2015). Beside ammonium, zeolite could effectively remove sulfate, and thereby reducing competition for carbon source between sulfate-reducing bacteria and methane-producing archaea. There was no obvious decrease of H_2PO_4^- and Cl^- compared with the initial concentration right after zeolite adsorption.

3.3 Organic compounds of PHWW

The GC-MS analysis revealed the organic compounds distribution in the PHWW. It is noticed that the composition of PHWW was fairly complicated. N-heterocyclic compounds, ketones, alcohols and phenols were the major components accounting for about 76 % in the ether extracted PHWW (Fig. 3). Phenol and nitrophenols (Borja et al., 1997), alcohols (Demirer and Speece, 1998), pyridine and its derivations (Speece, 1996) have proved to be toxic to AD process and therefore were undesirable in this case. Pham et al. (2013) also demonstrated that PHWW presented toxic or inhibitory influences on the anaerobic consortium. The toxicity could be influenced by many factors including specific toxicant concentrations, biomass concentration, acclimation and cell age (Chen

et al., 2008). In this study, some compounds such as butylated hydroxytoluene and N-[2-Hydroxyethyl] succinimide were completely removed after zeolite absorption (Fig. 3, Table 3). Comparatively, the average removal rate of all the other nitrogenous compounds detected appropriately reached 50%. The reduction may be related to the adsorption of toxic compounds where zeolite served as a physic-chemical sink. It probably could promote the AD process for PHWW treatment. This was justified by a previous study which observed positive effect of activated carbon for anaerobic stabilization of PHWW obtained from swine manure through HTL (Zhou et al., 2015).

3.4 BMP assays

This study compared the specific methane production from original PHWW and pre-treated PHWW. Fig. 4A depicted the cumulative methane production from AD of PHWW with gradient COD concentrations ranging from 2 to 7 g/L. For the low COD concentrations (2, 3, 4 and 5 g/L), methane was generated after a relatively long lag phase of about 10 days, indicating the ability of anaerobic microbial to adapt to and acclimate the toxicant in PHWW. It should be noted that the ultimate methane accumulation was far less than the theoretical potential of about 0.395 L/(g COD), approximately equating to 17.6 mmol/(g COD) under standard atmospheric pressure (Speece, 1996). As presented in Fig. 4A, the AD process with a higher COD concentration of 7 g/L has been severely inhibited leading to an extremely low methane production. This must be significantly caused by the high content of toxic compounds observed in PHWW. Besides, the synergistic effect of the multi inhibitors may also potentially contribute to the inhibition.

For instance, pyridine degradation would somehow be inhibited when phenol concentration was higher than 400 mg/L (Tommaso et al., 2015). Pham et al. (2013) also verified that the nontoxic nitrogen-containing molecules in PHWW derived from *Spirulina* proved to be synergistically cytotoxic in the mixture.

Under relatively low COD concentrations (2-5 g/L), zeolite adsorption significantly mitigated the inhibition to AD process because no obvious inhibition effect was observed in terms of short lag phases prior to methane production (Fig. 4B). The shortened lag phase is very important for practical applications (Zhou et al., 2015). For instance, original PHWW incurred an 8.8-day lag phase prior to methane production at 4 g/L (Table 4); while steady methane production has already been underway at the moment for the AD of pre-treated PHWW (Fig. 4B). According to Moreno and Buitron (2004), the well treated sludge inoculated in this study may also contributed to the shortened lag phase. At a medium COD concentration of 4 g/L, the actual methane production of original PHWW was 10.95 mmol/(g COD); while the zeolite pre-treatment promoted it to 14.79 mmol/(g COD) (Fig. 4). Zeolite pre-treatment achieved an increase of methane yield by 32-117% for PHWW with concentrations ranging from 2 to 7 g/L. The values were comparable with those in previous studies approximately ranging from 3 to 16 mmol/(g COD) (Table 5). The differences in methane yield may be due to the different feedstock and HTL conditions which resulted in different PHWW characteristics and digestibility.

However, zeolite adsorption was not able to induce successful AD during the 45-day experiment for the highest COD concentration of 7 g/L. This may be related to the high

inhibitions beyond the tolerable capacity of microbes even after zeolite adsorption.

3.5 Energy recovery calculation

AD has been proposed as an effective method to simultaneously treat PHWW and enhance the energy recovery efficiency. In this study, combining HTL and AD yielded a higher energetic return by converting the feedstock into oil and biomethane (Fig. 5). It was observed that the zeolite adsorption additionally increased the energy recovery efficiency (from 53.2% to 70.5%) compared to the condition without zeolite (from 52.9% to 64.1%). This is because zeolite adsorption could improve the quantity of biomethane produced, according to the experimental result (Fig. 5). As illustrated in Fig. 5B, with the COD concentration of 4 g/L, zeolite adsorption brought the highest energy recovery of 70.5%, which was significantly higher than that of the sole HTL process (rarely 52.3%). This energy evaluation also gives a perspective on the residual energy from each process (i.e., AD). Beyond the energy recovery from the integrated HTL and AD system, there may be a potential for production of biomass through recycling the digestate for microalgae cultivation (Vardon et al., 2011).

3.6 TC and TN balance

The overall TC and TN flows obtained from the integration of HTL and AD for treating *Chlorella* 1067 were emphasized by the Sankey diagram (Fig. 6). Fig. 6 presented a typical integration of HTL and AD of PHWW at 4 g/L which has been proved the optimal concentration for methane production. The elemental transfer from feedstock (*Chlorella* 1067) to products during HTL process was presented in **Supplementary**

materials. As presented, 26% of the carbon and 69.2% of the nitrogen in the feed were transferred into PHWW, mainly in forms of short-chain acids (such as acetic acid) and ammonia/ammonium/nitrogenous heterocyclic compounds, respectively. High content of ammonia/ammonium/nitrogenous heterocyclic compounds was undesired for AD which was related to suppressing specific enzyme reactions during methane formation (Li et al., 2017a; Li et al., 2017b). After zeolite treatment, only 5.73% of the carbon in PHWW was adsorbed, while 75.4% of the nitrogen was removed, which indicated that AD of the pre-treated PHWW could make technical and economic senses. More than 60% of the carbon in PHWW was reutilized after AD, which was consist with the corresponding COD removal rate of 60.3%. While AD did little in nitrogen reduction (rarely about 13%). This analysis was essential as a design tool for any future process integration as it could provide a good estimation for resource recovery based on the final product.

4 Conclusion

This study investigated the feasibility of recovering energy and carbon/nitrogen from PHWW through zeolite adsorption and AD. Results showed a good AD performance with methane production of 14.79 mmol/(g COD) at a moderate COD concentration of 4 g/L. Zeolite mitigated the inhibition in PHWW by shortening the lag phase and allowed AD to acquire higher methane production with an increase of 32-117%. The addition of zeolite increased the energy recovery efficiency (up to 70.5%) for the integrated system. Carbon and nitrogen migration from feedstock to products was also demonstrated, which provides assessment for nutrients recovery based on the final products.

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References

- Amen TWM, Eljamal O, Khalil AME, Matsunaga N. Biochemical methane potential enhancement of domestic sludge digestion by adding pristine iron nanoparticles and iron nanoparticles coated zeolite compositions. *JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING* 2017; 5: 5002-5013.
- Angelidaki I, Alves M, Bolzonella D, Borzacconi L, Campos JL, Guwy AJ, et al. Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays. *WATER SCIENCE AND TECHNOLOGY* 2009; 59: 927-934.
- Ariyanto, E. Adsorption malchite green on natural zeolite. *Reaktor* 200), 12: 161–165.
- Barreiro DL, Riede S, Hornung U, Kruse A, Prins W. Hydrothermal liquefaction of microalgae: Effect on the product yields of the addition of an organic solvent to separate the aqueous phase and the biocrude oil. *ALGAL RESEARCH-BIOMASS BIOFUELS AND BIOPRODUCTS* 2015; 12: 206-212.
- Borja R, Alba J, Banks CJ. Impact of the main phenolic compounds of olive mill wastewater (OMW) on the kinetics of acetoclastic methanogenesis. *PROCESS BIOCHEMISTRY* 1997; 32: 121-133.
- Chen H, Zhang C, Rao Y, Jing Y, Luo G, Zhang S. Methane potentials of wastewater generated from hydrothermal liquefaction of rice straw: focusing on the wastewater characteristics and microbial community compositions. *BIOTECHNOLOGY FOR BIOFUELS* 2017; 10.
- Chen W, Chen S, Khanal SK, Sung S. Kinetic study of biological hydrogen production by anaerobic fermentation. *INTERNATIONAL JOURNAL OF HYDROGEN ENERGY* 2006; 31: 2170-2178.
- Chen W, Zhang Y, Zhang J, Schideman L, Yu G, Zhang P, et al. Co-liquefaction of swine manure and

- mixed-culture algal biomass from a wastewater treatment system to produce bio-crude oil. *APPLIED ENERGY* 2014; 128: 209-216.
- Chen Y, Cheng JJ, Creamer KS. Inhibition of anaerobic digestion process: A review. *BIORESOURCE TECHNOLOGY* 2008; 99: 4044-4064.
- Demirbas A. Use of algae as biofuel sources. *ENERGY CONVERSION AND MANAGEMENT* 2010; 51: 2738-2749.
- Demirer GN, Speece RE. Anaerobic biotransformation of four 3-carbon compounds (acrolein, acrylic acid, allyl alcohol and n-propanol) in UASB reactors. *WATER RESEARCH* 1998; 32: 747-759.
- Eljamal O, Sasaki K, Tsuruyama S, Hirajima T. Kinetic Model of Arsenic Sorption onto Zero-Valent Iron (ZVI). *WATER QUALITY EXPOSURE AND HEALTH* 2011; 2: 125-132.
- Eljamal O, Jinno K, Hosokawa T. Modeling of solute transport and biological sulfate reduction using low cost electron donor. *ENVIRONMENTAL GEOLOGY* 2009; 56: 1605-1613.
- Elliott DC, Hart TR, Schmidt AJ, Neuenschwander GG, Rotness LJ, Olarte MV, et al. Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. *ALGAL RESEARCH-BIOMASS BIOFUELS AND BIOPRODUCTS* 2013; 2: 445-454.
- Fernandez S, Srinivas K, Schmidt AJ, Swita MS, Ahring BK. Anaerobic digestion of organic fraction from hydrothermal liquefied algae wastewater byproduct. *BIORESOURCE TECHNOLOGY* 2018; 247: 250-258.
- Kotsopoulos TA, Karamanlis X, Dotas D, Martzopoulos GG. The impact of different natural zeolite concentrations on the methane production in thermophilic anaerobic digestion of pig waste. *BIOSYSTEMS ENGINEERING* 2008; 99: 105-111.
- Leng L, Li J, Wen Z, Zhou W. Use of microalgae to recycle nutrients in aqueous phase derived from hydrothermal liquefaction process. *BIORESOURCE TECHNOLOGY* 2018; 256: 529-542.
- Li H, Wang M, Wang X, Zhang Y, Lu H, Duan N, et al. Biogas liquid digestate grown *Chlorella* sp for biocrude oil production via hydrothermal liquefaction. *SCIENCE OF THE TOTAL ENVIRONMENT* 2018; 635: 70-77.
- Li R, Duan N, Zhang Y, Liu Z, Li B, Zhang D, et al. Anaerobic co-digestion of chicken manure and microalgae *Chlorella* sp.: Methane potential, microbial diversity and synergistic impact evaluation.

WASTE MANAGEMENT 2017a; 68: 120-127.

Li R, Duan N, Zhang Y, Liu Z, Li B, Zhang D, et al. Co-digestion of chicken manure and microalgae *Chlorella* 1067 grown in the recycled digestate: Nutrients reuse and biogas enhancement. WASTE MANAGEMENT 2017b; 70: 247-254.

Li W, Niu Q, Zhang H, Tian Z, Zhang Y, Gao Y, et al. UASB treatment of chemical synthesis-based pharmaceutical wastewater containing rich organic sulfur compounds and sulfate and associated microbial characteristics. CHEMICAL ENGINEERING JOURNAL 2015; 260: 55-63.

Lin L, Wan C, Liu X, Lei Z, Lee D, Zhang Y, et al. Anaerobic digestion of swine manure under natural zeolite addition: VFA evolution, cation variation, and related microbial diversity. APPLIED MICROBIOLOGY AND BIOTECHNOLOGY 2013; 97: 10575-10583.

Lu J, Zhang J, Zhu Z, Zhang Y, Zhao Y, Li R, et al. Simultaneous production of biocrude oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction. ENERGY CONVERSION AND MANAGEMENT 2017; 134: 340-346.

Moreno G, Buitron G. Influence of the origin of the inoculum and the acclimation strategy on the degradation of 4-chlorophenol. BIORESOURCE TECHNOLOGY 2004; 94: 215-218.

Patel B, Guo M, Chong C, Sarudin SHM, Hellgardt K. Hydrothermal upgrading of algae paste: Inorganics and recycling potential in the aqueous phase. SCIENCE OF THE TOTAL ENVIRONMENT 2016; 568: 489-497.

Pham M, Schideman L, Scott J, Rajagopalan N, Plewa MJ. Chemical and Biological Characterization of Wastewater Generated from Hydrothermal Liquefaction of *Spirulina*. ENVIRONMENTAL SCIENCE & TECHNOLOGY 2013; 47: 2131-2138.

Posmanik R, Labatut RA, Kim AH, Usack JG, Tester JW, Angenent LT. Coupling hydrothermal liquefaction and anaerobic digestion for energy valorization from model biomass feedstocks. BIORESOURCE TECHNOLOGY 2017; 233: 134-143.

Speece, R.E. Anaerobic Biotechnology for Industrial Wastewater. ARCHAE PRESS, Nashville 1996; 394.

Si B, Li J, Zhu Z, Shen M, Lu J, Duan N, et al. Inhibitors degradation and microbial response during continuous anaerobic conversion of hydrothermal liquefaction wastewater. SCIENCE OF THE

TOTAL ENVIRONMENT 2018; 630: 1124-1132.

Sun J, Xu L, Tang Y, Chen F, Liu W, Wu X. Degradation of pyridine by one *Rhodococcus* strain in the presence of chromium (VI) or phenol. JOURNAL OF HAZARDOUS MATERIALS 2011; 191: 62-68.

Tavlieva MP, Genieva SD, Georgieva VG, Vlaev LT. Kinetic study of brilliant green adsorption from aqueous solution onto white rice husk ash. JOURNAL OF COLLOID AND INTERFACE SCIENCE 2013; 409: 112-122.

Theegala CS, Midgett JS. Hydrothermal liquefaction of separated dairy manure for production of bio-oils with simultaneous waste treatment. BIORESOURCE TECHNOLOGY 2012; 107: 456-463.

Tian C, Liu Z, Zhang Y, Li B, Cao W, Lu H, et al. Hydrothermal liquefaction of harvested high-ash low-lipid algal biomass from Dianchi Lake: Effects of operational parameters and relations of products. BIORESOURCE TECHNOLOGY 2015; 184: 336-343.

Tommaso, G, Chen, W, Li, P, Zhang, P, Zhou, Y, Zheng, M. Anaerobic digestion of the aqueous product from hydrothermal liquefaction of *Spirulina* algae. XI Simposio Latinoamericano de Digestión Anaerobia. 2014.

Tommaso G, Chen W, Li P, Schideman L, Zhang Y. Chemical characterization and anaerobic biodegradability of hydrothermal liquefaction aqueous products from mixed-culture wastewater algae. BIORESOURCE TECHNOLOGY 2015; 178: 139-146.

Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. ENERGY 2011; 36: 2328-2342.

Vadivelan V, Kumar KV. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. JOURNAL OF COLLOID AND INTERFACE SCIENCE 2005; 286: 90-100.

Vardon DR, Sharma BK, Scott J, Yu G, Wang Z, Schideman L, et al. Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge. BIORESOURCE TECHNOLOGY 2011; 102: 8295-8303.

Yagub MT, Sen TK, Ang HM. Equilibrium, Kinetics, and Thermodynamics of Methylene Blue Adsorption by Pine Tree Leaves. WATER AIR AND SOIL POLLUTION 2012; 223: 5267-5282.

- Yang W, Li X, Liu S, Feng L. Direct hydrothermal liquefaction of undried macroalgae *Enteromorpha prolifera* using acid catalysts. *ENERGY CONVERSION AND MANAGEMENT* 2014; 87: 938-945.
- Yu G, Zhang Y, Schideman L, Funk T, Wang Z. Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae. *ENERGY & ENVIRONMENTAL SCIENCE* 2011; 4: 4587-4595.
- Zheng M, Schideman LC, Tommaso G, Chen W, Zhou Y, Nair K, et al. Anaerobic digestion of wastewater generated from the hydrothermal liquefaction of *Spirulina*: Toxicity assessment and minimization. *ENERGY CONVERSION AND MANAGEMENT* 2017; 141: 420-428.
- Zhou Y, Schideman L, Yu G, Zhang Y. A synergistic combination of algal wastewater treatment and hydrothermal biofuel production maximized by nutrient and carbon recycling. *ENERGY & ENVIRONMENTAL SCIENCE* 2013; 6: 3765-3779.
- Zhou Y, Schideman L, Zheng M, Martin-Ryals A, Li P, Tommaso G, et al. Anaerobic digestion of post-hydrothermal liquefaction wastewater for improved energy efficiency of hydrothermal bioenergy processes. *WATER SCIENCE AND TECHNOLOGY* 2015; 72: 2139-2147.

Fig. 1 Ternary diagram for ammonia nitrogen removal based on the experimental design.

Fig. 2 (A) Three dimensional response surface of zeolite size and temperature effects on TAN removal efficiency; (B) Three dimensional response surface of zeolite size and zeolite dosage effects on TAN removal efficiency.

Fig. 3 Gas chromatography-mass spectrometer (GC-MS) chromatograms for PHWW and pre-treated PHWW.

Fig. 4 Effect of zeolite adsorption on the specific methane production from PHWW: (A) without zeolite adsorption; (B) with zeolite adsorption.

Fig. 5 (A) Global energy recovery diagram from PHWW treatment system integrated with HTL. (B) Energy recovery efficiency from different conditions. Values were calculated based on the yield and higher heating value of each energy product. ^a: The value was calculated based on 150 g of *Chlorella* 1067. Assuming no water loss, the total volume of PHWW from the 150 g biomass is 1 L according to the solid content of 15% for HTL process.

Fig. 6 Sankey diagrams showing total carbon (TC) (A) and total nitrogen (TN) (B) flows for the integrated HTL and AD system with zeolite adsorption. The widths of the bands are directly proportional to carbon production, utilization and losses.

Table 1

Chemical composition of the natural zeolite used in this study

Composition	Weight, %
SiO ₂	69.82
Al ₂ O ₃	12.09
K ₂ O	2.55
Na ₂ O	1.85
Fe ₂ O ₃	0.75
MgO	0.41
TiO ₂	0.05
MnO ₂	0.02
Others	12.46

Table 2

Biochemical characteristics of PHWW and pre-treated PHWW.

	PHWW	Pre-treated PHWW	Sludge
pH	7.82±0.35	7.78±0.18	7.57±0.32
TS, %	NA	NA	2.55±0.15
VS, %	NA	NA	75.7±3.44
TOC, g/L	31.1±0.4	30.5±3.7	NA
COD, g/L	75.5±5.9	70.8±5.5	NA
TN, g/L	20.2±3.3	7.93±1.25	2.89±0.55
TAN, g/L	10.22±2.03	1.65±0.25	0.35±0.06
SO ₄ ²⁻ , g/L	1.59±0.43	0.68±0.05	NA
H ₂ PO ₄ ⁻ , g/L	5.89±1.38	4.13±0.51	NA
Cl ⁻ , g/L	BDL	BDL	NA
NO ₃ ⁻ , g/L	BDL	BDL	NA
NO ₂ ⁻ , g/L			

*BDL: below detection limit; NA: not analyzed.

Table 3

Removal efficiencies of organic compounds in post-hydrothermal liquefaction wastewater (PHWW) after zeolite adsorption identified by GC/MS.

No.	Ret. time	Formula	Compound	Relative area ^a (%)	Remove efficiency ^b (%)
1	3.24	C ₄ H ₄ N ₂	Pyrazine	1.58	53.2
2	5.79	C ₅ H ₆ N ₂	Methyl- pyrazine	15.56	45.8
3	8.39	C ₆ H ₈ N ₂	2,5-dimethyl-pyrazine	11.98	52.1
4	8.48	C ₆ H ₈ N ₂	Ethyl-pyrazine	4	55.3
5	10.02	C ₆ H ₆ O	Phenol	1.8	55.8
6	10.43	C ₇ H ₁₀ N ₂	2-ethyl-6-methyl-pyrazine	4.02	49.2
7	10.51	C ₇ H ₁₀ N ₂	Trimethyl-pyrazine	4.28	53.1
8	10.96	C ₆ H ₁₃ NO	N-(2-methylpropyl)-acetamide	3.24	54.1
9	11.21	C ₇ H ₁₀ O	2,3-dimethyl-2-cyclopenten-1-one	1.08	19.0
10	12.06	C ₈ H ₁₂ N ₂	3-ethyl-2,5-dimethyl-pyrazine	2.17	31.9
11	12.64	C ₇ H ₁₄ N ₂ O	2-amino-5,6-dihydro-4,4,6-trimethyl-4H-1,3-oxazine	2.04	100.0
12	12.87	C ₉ H ₁₆ O	3,3,4,4-tetramethyl-cyclopentanone	3.03	45.5
13	12.96	C ₈ H ₁₇ NO	N-acetyl-2-ethylbutan-1-amine	2.77	35.2
14	13.02	C ₇ H ₁₅ NO	N-(3-methylbutyl) acetamide	6.57	43.0
15	13.48	C ₅ H ₁₂ O ₂	Neopentyl glycol	2.33	58.2
16	14.21	C ₈ H ₁₃ NO ₂	Alpha-Methyl-alpha propylsuccinimide	3.95	54.9
17	15.39	C ₆ H ₉ NO ₃	N-[2-Hydroxyethyl] succinimide	2.07	100.0
18	17.18	C ₇ H ₁₂ N ₂ O ₃	2,4-imidazolidinedione, 5-(4-hydroxybutyl)-	1.07	100.0
19	19.76	C ₁₅ H ₂₄ O	Butylated hydroxytoluene	2.45	100.0

^a The relative area of organic compounds in raw PHWW; ^b With respect to peak area.

Table 4

Removal efficiency and values predicted by the modified Gompertz model: specific methane production potential ($P_{\max}$), specific methane production rate (R) and duration of the lag phase (λ).

Total COD added, g/L	$P_{\max}$, mmol/(g COD)	R, mmol/(g COD)/d	λ , days	COD removal, %
PHWW				
2	4.93	0.32	12.22	36.13±3.04
3	7.93	0.55	9.53	38.22±3.89
4	10.95	0.71	8.80	49.49±4.03
5	8.38	0.66	8.73	33.72±2.32
7	2.64	0.14	11.86	12.02±2.02
Pre-treated PHWW				
2	10.70	0.84	0.70	56.82±3.09
3	12.77	0.98	0.72	61.07±4.90
4	14.79	1.57	1.03	60.33±2.98
5	13.10	0.96	0.90	46.77±4.34
7	3.48	0.38	9.91	14.39±0.89

Table 5

Methane potential of post-hydrothermal liquefaction wastewater (PHWW) from other anaerobic studies. The unit of methane in literatures was unified in the table where 1 mol equated to 22.4 L under standard atmospheric pressure.

H TL feedstock	Digestion type	AD temperature	PH WW loading	Digestion time	Adsorbent addition	Methane yield	References
Swine manure	Batch	37 °C	3.3%-6.7% (v/v)	65 days	None	4.91-14.29 mmol/(g COD)	Zhou et al., 2015.
Mixed-culture algae	Batch	35 °C	0.28 g COD/(g TVS)	45 days	None	8.94-16.30 mmol/(g SSV)	Tommaso et al., 2015.
Model compounds	Batch	37±2 °C	2.5-4 g COD/L	30 days	None	3.35-12.95 mmol/(g COD)	Posmanik et al., 2017.
Algae <i>Tetraselmis</i>	Semi-continuous	37 °C	0.827 g VS/(L·d)	89 days	None	13.98 mmol/(g COD)	Fernandez et al., 2018.
Algae <i>Chlorella</i>	Semi-continuous	37 °C	0.812 g VS/(L·d)	89 days	None	10.89 mmol/(g COD)	Fernandez et al., 2018.
Rice straw	Batch reactors	37 °C	0.75 g COD/L	30 days	None	9.69-14.02 mmol/(g COD)	Chen et al., 2017.
<i>Spirulina</i> sp.	Two-stage batch	Not mentioned	6.7% (v/v)	213 days	None	5.49 mmol/(g COD)	Zheng et al., 2017.
					Zeolite	6.07 mmol/(g COD)	

					GAC	7.54 mmol/(g COD)	
					PM	7.5 mmol/(g COD)	
<i>Chlorel la 1067</i>	Batch reactors	35±1 °C	2-5 g COD/L	50 days	None	4.93- 10.95 mmol/(g COD)	This study
				45 days	Zeolite	10.70- 14.79 mmol/(g COD)	

Highlights

1. Anaerobic digestion and adsorption were integrated for PHWW management.
2. Statistical design was applied to optimize toxicants removal from PHWW by zeolite.
3. About 5.73% of the carbon and 75.4% of the nitrogen in PHWW was adsorbed by zeolite.
4. Zeolite can shorten the lag phase with increase of methane production by 32-117%.

Figure 1

Figure 2

Figure 3

Figure 4

A

B

Figure 5

A

B

Figure 6