Science of the Total Environment 651 (2019) 61–69

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

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

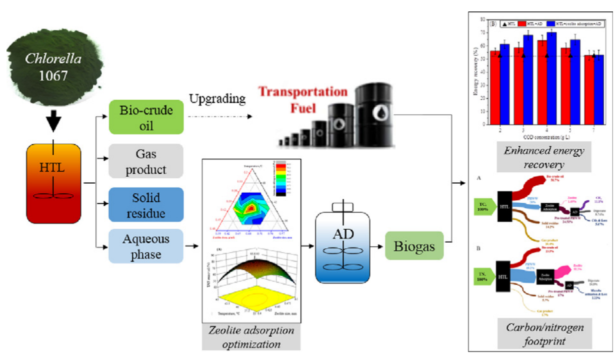
Ruirui Li [a], Dianlei Liu [b], Yifeng Zhang [c], Na Duan [a,*], Jialiang Zhou [a], Zhidan Liu [a], Yuanhui Zhang [a,d]

[a] College of Water Resources and Civil Engineering, China Agricultural University, Beijing 100083, China
[b] School of Biological Science and Medical Engineering, Beihang University, Beijing 100191, China
[c] Department of Environmental Engineering, Technical University of Denmark, Kgs. Lyngby DK-2800, Denmark
[d] Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

HIGHLIGHTS

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

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2018
Received in revised form 12 September 2018
Accepted 13 September 2018
Available online 14 September 2018

Editor: Zhen (Jason) He

Keywords:
Post-hydrothermal liquefaction wastewater
Zeolite
Anaerobic digestion
Energy recovery
Microalgae

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.

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

* Corresponding author.
E-mail address: duanna@cau.edu.cn (N. Duan).

https://doi.org/10.1016/j.scitotenv.2018.09.175

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 was 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 14,000 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 Analysensysteme 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 h 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 ($V_{aqueous\ phase}$: $V_{diethyl\ ether}$ = 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

Table 1
Chemical composition of the natural zeolite used in this study.

Composition	Weight, %
SiO_2	69.82
Al_2O_3	12.09
K_2O	2.55
Na_2O	1.85
Fe_2O_3	0.75
MgO	0.41
TiO_2	0.05
MnO_2	0.02
Others	12.46