Journal of Environmental Chemical Engineering 3 (2015) 2631–2636

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Characterization of organic matter in the thermal hydrolysis pretreated anaerobic digestion return liquor

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ARTICLE INFO

Article history:
Received 28 April 2015
Accepted 30 July 2015
Available online 3 August 2015

Keywords:
Return liquor treatment
Hydrophobic–hydrophilic fractions
Molecular weight distribution
Organic nitrogen
UV quenching

ABSTRACT

Disposal and treatment of the return liquor produced by the dewatering of the thermal hydrolysis pretreated anaerobic digestion biosolids is a major concern for treatment plants because the presence of UV quenching substances in the return liquor might interfere with UV disinfection. Also, with the lowering of effluent nitrogen standards in some locations, development of treatment techniques for nitrogen-containing organics in the return liquor is required. In this study, the molecular weight (MW) and chemical nature based fractions were characterized by their total organic carbon, UV absorbance, organic nitrogen and protein content. The humic acids and the hydrophilic fraction were found to be the major contributors to the organic matter and organic nitrogen in the return liquor, whereas the humic substances (humic and fulvic acids) were found to be mainly responsible for the UV_{254} quenching. Humic substances were observed to be the larger molecular weight (mainly >1 kDa) fractions and could not be efficiently removed by aerobic biological treatment.

Introduction

Wastewater treatment plants generate solids as a by-product. These solids are a combination of settled sewage and excess biomass produced during secondary treatment. These solids are processed to reduce vector attraction and to inactivate pathogens prior to reuse or disposal. For this purpose, anaerobic digestion (AD) has been the most popular option because it is a relatively simple and stable process that also yields methane gas. AD is usually carried out under mesophilic temperature conditions with hydraulic retention times (HRTs) of 15 days or more to provide stability and a consistent performance [1].

Thermal hydrolysis process (THP) is a wastewater organic residues pretreatment technique that uses high temperature and pressure prior to mesophilic AD to improve sludge digestion and dewatering. It results in increased biogas production, enhanced volatile solids destruction, doubling of digester loadings, production of stabilized and pathogen-free biosolids [2,3]. Since 1995, 20 TH plants have been built or are under construction [4].

The dewatering sidestream from the THP can contain up to double the amount of ammonium-N from a conventional AD system [5]. This occurs due to the improvement of biological accessibility of compounds and more nitrogen getting released in form of ammonium nitrogen by degradation of N-containing organic matter during the THP [6]. This reject water stream can also significantly impact the performance of secondary treatment systems for nitrification and total nitrogen removal [7].

Most of the focus for the nitrogen removal processes is with the removal of inorganic nitrogen from the return liquor. The return liquor from the THP typically comprises about 1–5% of the total plant flow volume, but can significantly increase the organic nitrogen (ON) in the effluent and thus can be a major contributor to the plant's effluent nitrogen [8,9]. During THP, low concentrations of soluble inert organics containing dissolved organic nitrogen are formed which are responsible for the increased ON loading [10]. Also, the bioconvertibility of individual nitrogen compounds decreases due to conversion of biodegradable organics to refractory ones [11]. With the integration of nitrification and denitrification systems into many of the publicly owned treatment works (POTWs), the ON fraction can account for 20–80% of the total nitrogen in POTW effluents [12,13] and with the introduction of the THP into the conventional POTWs, the ON loading will further grow due to the high ON content of the THP return liquor. With the permitted annual loads for plant effluent total nitrogen being lowered, several separate sidestream treatment techniques for the removal of nitrogen in the return liquor from THP are being explored [14].

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http://dx.doi.org/10.1016/j.jece.2015.07.029
2213-3437/

UV disinfection has become quite popular in wastewater treatment because it can eliminate the formation of regulated disinfection by-products (DBPs) [15]. In practice, for their disinfection systems, POTWs utilize $\lambda = 254$ nm because it can be readily generated by mercury lamps [16]. The POTWs generally require that the UV_{254} transmittance in a wastewater stream be 60–65% in regions where a minimum is regulated to ensure that UV_{254} disinfection can work properly [17].

However, the presence of UV_{254} quenching substances in the return liquor can lead to a significant decrease in the efficiency of the UV_{254} disinfection [8,18]. The UV quenching is mainly due to refractory dissolved organic compounds like larger molecular weight (>100 kDa) melanoidins formed during TH [8,11].

A study by Dwyer et al. [8] showed that as the return liquor increased, the effluent UV absorbance decreased and the effluent ON increased. The study also showed that a large proportion of the UV absorbance and ON from the TH return liquor was from the larger molecular weight (>10 kDa) compounds which showed characteristics similar to humic substances.

There is limited comprehensive literature available on the characterization of TH return liquor. Hence, this study aims at characterizing a TH–AD sludge return liquor by its UV absorbing behavior, organic matter, nitrogen species and protein occurrence, then investigate the potential impact on the receiving mainstream treatment process. Particularly. Molecular weight based and hydrophobic–hydrophilic fractionations were employed in conjunction with TOC, UV absorbance, nitrogen species and protein measurements for the sludge return liquor before and after an aerobic biological treatment, therefore the treatment efficiency was evaluated. The study can provide us with the valuable information on the characteristics of the return liquor required for the development of effective treatment techniques for return liquors from TH/AD systems.

Materials and methods

Return liquor collection, sampling and aerobic biological treatment

The return liquor sample investigated in this study was obtained by dewatering the TH pretreated AD sludge at the Anglian Water Cotton Valley sludge treatment center which is located at the Milton Keynes wastewater treatment works in Buckinghamshire, United Kingdom. The samples packed in ice were shipped directly from the facility to our laboratory at Virginia Tech, USA in plastic buckets and then stored at 4 °C in the dark to reduce the microbial activity. Before sampling and analysis, containers were shaken well to resuspend settled particles.

The return liquor was treated in a closed system batch bioreactor kept in a fume hood at a constant temperature of 25 °C. The 10-L bioreactor had a continuous supply of air using porous ceramic air diffusers connected to the air supply gas cock of the fume hood. The return liquor was continuously aerated until equilibrium was reached, i.e. a point after which there was little additional biological degradation in terms of loss in TOC content. The steady-state was achieved in 28 days. Since, the return liquor contained microorganisms from AD, no external seed was added. Biological flocs similar to activated sludge flocs, in terms of texture, were observed during the process. pH of the bioreactor effluent was around 7–8 during the operation. Distilled water was added to compensate for water lost due to evaporation. The characteristics of the untreated and biologically treated return liquor are listed in Table 1.

Table 1
Characteristics of the thermal hydrolysis/anaerobic digestion return liquor.

Parameter	Unit	Untreated	Biologically treated
TOC	$mg\,L^{-1}$	2431.5 ± 55.3	1592.7 ± 41.2
COD	$mg\,L^{-1}$	7225 ± 70	5250 ± 45
TSS	$mg\,L^{-1}$	1352 ± 46	769 ± 32
UV_{254} absorbance	cm^{-1}	37.7 ± 1.7	32.6 ± 2.8
Total nitrogen	$mg\,N\,L^{-1}$	2203.3 ± 102.1	537.4 ± 63.3
NO_2	$mg\,N\,L^{-1}$	7.7 ± 0.5	ND[a]
NO_3	$mg\,N\,L^{-1}$	20.1 ± 3.7	27.1 ± 1.4
NH_3	$mg\,N\,L^{-1}$	1895.5 ± 168.7	280.3 ± 53.4
pH	–	7.7	7.3
Color	ADMI	14904 ± 134	12420 ± 256
PO_4	$mg\,P\,L^{-1}$	115.4 ± 6.4	136.1 ± 13.5
SO_4	$mg\,L^{-1}$	23.0 ± 8.8	55.1 ± 13.1
Na	$mg\,L^{-1}$	121.8 ± 25.7	133.5 ± 4.3
Mg	$mg\,L^{-1}$	2.7	5.0 ± 0.2
Si	$mg\,L^{-1}$	37.3 ± 2.3	33.7 ± 0.5
Cl	$mg\,L^{-1}$	180.7 ± 6.3	219.2 ± 21.7
K	$mg\,L^{-1}$	212.7 ± 17.9	200.8 ± 6.5
P	$mg\,L^{-1}$	174.5 ± 5.7	161.5 ± 2.9
Ca	$mg\,L^{-1}$	40.5 ± 0.7	26.2 ± 0.7
Cr	$\mu g\,L^{-1}$	64.9	51.9 ± 0.4
Mn	$\mu g\,L^{-1}$	27.7 ± 5.7	12.7 ± 0.7
Zn	$mg\,L^{-1}$	0.1	0.1

[a] Non-detectable.

Hydrophobic–hydrophilic and molecular weight based fractionations

Return liquor samples were fractionated into humic acids (HA), fulvic acids (FA) and a hydrophilic (Hpi) fraction based on their hydrophobic–hydrophilic nature and solubility. Methods developed by Thurman and Malcolm [19] and Leenheer [20] were used in this study.

The XAD-8 resin (currently Supelite DAX-8 resin, Sigma Aldrich, St. Louis, MO) was packed and cleaned following the method described by Leenheer [20]. Approximately 3.5–4.5 mL of cleaned XAD-8 resin slurry was packed in a borosilicate glass column (1.0 cm × 10 cm, Thomas Scientific, Swedesboro, NJ). Leachate samples were first filtered with a 1.5 μm micro glass fiber filter and then acidified to pH 2 using concentrated HCl. The HAs precipitated and were separated with 0.45 μm cellulose nitrate membrane (47 mm, Sartorius Stedim Biotech, France). The HAs collected on the glass fiber filter were re-dissolved into a 0.1 M NaOH solution. The re-dissolved HA solution was used for analysis. The supernatant containing FAs and the Hpi organics was then passed through the XAD-8 resin column at a flow rate of 10–15 bed volumes/h. FAs were sorbed and retained onto the resin column. Then 0.1 M NaOH was used to elute the FAs and this eluent was used for characterization of the FA fraction. The residual portion not sorbed by the resin is called the Hpi fraction.

The molecular weight (MW) based fractionation apparatus consisted of 200 mL stirred ultrafiltration cells (Amicon model # 8200), a nitrogen gas tank (pressure: 120 kPa) and membrane disks (Millipore, Billerica, MA) with a range of MW cut offs (MWCO). Details can be found in Zhao et al. [21].

Analysis

TOC was analyzed by a high temperature combustion TOC analyzer (Shimadzu TOC-5000A, Japan). The chemical oxygen demand (COD) analysis was executed by the closed reflux, titrimetric method per Standard Method 5220-D. The color analysis was carried out by the ADMI tristimulus filter Method 2120-E [22]. The UV absorbance at 254 nm (UV_{254} absorbance) was measured with a spectrophotometer (Beckman Coulter, Brea, CA). The samples were diluted at multiple dilution levels if the absorbance values were above the detection limited for the instrument. For a particular sample, UV_{254} values were multiplied by the corresponding dilution factors and an average was taken to give the effective UV_{254} absorbance [21].