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Anaerobic digestion for solids reduction and detoxification of refinery waste streams

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ABSTRACT

Lab scale studies were conducted to test the anaerobic digestibility of two waste streams acquired from a petrochemical refinery. The waste streams comprised float from the dissolved air flotation (DAF) unit and waste activated sludge (WAS) from the biological treatment unit. Three semi continuous anaerobic digesters (AD) examined mono and co-digestion of the substrates. Mono-digestion of WAS yielded the highest reductions in organics whereas substrates with portions of DAF float showed inhibition. Prior to AD, batch bioassays were used as a preliminary tool to determine the toxicity profiles and the biodegradability of the samples. Pretreatment of the feeds by ozonation exhibited improvement in the digestion of DAF float with a higher digester hydraulic retention time (HRT), indicated by increased solids removal. Ozonation also resulted in enhanced removal of toxic organic compounds found in DAF float.

1. Introduction

High strength organic wastes from industries can be treated by anaerobic digestion (AD) for mass reduction and recovery of organic carbon as biogas. It is often used as a first treatment step to reduce high chemical oxygen demand (COD) in a concentrated organic-rich waste stream for subsequent aerobic treatment. AD is widely used for sludge stabilization and to reduce mass of solids for final disposal during municipal wastewater sludge treatment. Biogas generated in the AD process is a valuable energy source that benefits renewable energy utilization. AD is used extensively in the food and related industries for concentrated waste treatment [1]. However, its application to other industrial wastes is limited. For example, use of AD to reduce organic matter content in petrochemical and refinery waste sludges has been the subject of limited research, with preliminary results indicating some such streams may be effective in co-digestion with other industrial wastes or in mono-digestion of soluble fractions [2]. Hence, this paper investigates two waste streams from an oil refinery as substrates for AD in order to reduce the quantity of waste and recovery of biogas as a resource.

Petrochemical/refinery industries utilize a complex system of processing operations generating wastes of varying physical/chemical properties. The complexity of a refining process dictates the composition of refinery wastewater being generated. The floating materials (oils) and settleable solids in the refinery wastewater are removed/recovered by either gravity separation or by flotation. The oily matter is treated by dissolved air flotation (DAF) units for oil/water separation [3]. The float from the DAF process is the sludge material and the underflow is the wastewater for further treatment. The wastewater is further treated in a typical activated sludge process where soluble and colloidal organic matter is converted into biological sludge or also known as waste activated sludge (WAS). Both DAF float and WAS contain a high amount of organic content and could be suitable for AD. Studies have indicated the success of microbial cultures at degrading petroleum contaminated soils including toxic and carcinogenic components such as polycyclic aromatic hydrocarbons (PAH), and polychlorinated biphenyls [4]. Application of AD to DAF float and WAS from a petrochemical refinery could be an alternative means to reduce waste that must otherwise be disposed of in a landfill or landfarm [5]. Additionally, the costs of operating AD for sludge stabilization and solids reduction may offer considerable savings when disposal costs are exacerbated by limited land availability and incineration requirements [6].

There is a very limited and narrow description of the physical chemical state of DAF float. Researchers have shown that DAF float contains high concentrations of PAH, aliphatic hydrocarbons and inorganics such as heavy metals [7,8]. The diverse composition and high variability refinery waste sludge streams such as DAF float, is largely due to origin and quality of the crude oil, dif-

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ferences in refinery processes used for oil-water separation, and treatment complications [7]. DAF float has an amorphous and variable nature which adds uncertainty to its contents, particularly organic toxicants or inorganics which are inhibitory to the anaerobic process [9,10]. The float generated from DAF in an oil refinery's wastewater treatment plant is designated as hazardous under the Resource Conservation and Recovery Act (RCRA) [11]. This designation creates a significant cost and ecological incentive for the development of new and improved treatment processes of such waste streams. However, several toxicants expected to occur in DAF float are inhibitory to microorganisms even at low concentrations and may thus hinder the anaerobic mechanisms in AD [12]. Past studies show that such a complex mixture of hydrocarbons can also be metabolized by anaerobic microorganisms under specific treatment conditions [13–15].

Treatment of complex waste streams through AD is a challenge since methanogens are sensitive to environmental changes such as dramatic swings in organic loading or volatile fatty acids in the feed. Thus, stable operating conditions and minimal variation in the feedstock quality and quantity are required. An organic waste sludge with moderate strength plays a crucial role in the overall design of an anaerobic setup for treatment. In the case of complex sludge streams with high solids content, a dilute and defined waste stream (such as WAS) can be a co-substrate in AD. Co-digestion in this manner can result in better digestibility than either waste may exhibit on its own [16]. An added advantage of co-digestion in AD is the amalgamation of two waste streams of different properties leading to higher treatment and biogas production. This technique has been extremely successful with municipal solid waste (MSW) acting as an AD co-substrate to municipal, food, industrial or agricultural wastes [16–18]. The WAS generated from the refinery wastewater treatment contains biomass and can be used as co-substrate for AD with DAF float.

Pretreatment of any waste generally increases its digestibility by modifying the overall physical, chemical or biological properties. Ozonation has been effectively utilized for pretreatment of WAS, leading to solubilization of solids, improved settling, and lower viscosity [19,20]. Studies have shown that ozonation is also successful in converting the higher molecular weight organics into lower molecular weight organics commonly associated with petrochemical wastes [4,21]. A strong oxidant like ozone reacts with the complex organics present in the DAF float and produce simpler organic compounds that are more amenable to AD. Therefore, use of ozonation as a pretreatment step could lead to increased biogas production, reduced substrate toxicity, and potential for AD operation with higher loading and shorter hydraulic retention time (HRT).

In this paper, the anaerobic digestibility of DAF float and WAS acquired from a refinery wastewater treatment plant are investigated. A total of six scenarios are applied, involving AD with and without ozonation of the substrates. The goal is to observe if AD is an efficient treatment process for reducing solids content, especially organic matter removal, reduction in potential toxicant concentration, and energy recovery through biogas production. Lab scale AD studies were conducted using actual waste streams from a refinery to investigate this goal.

2. Materials and methods

2.1. Refinery waste streams

DAF float and WAS were collected from a refinery wastewater treatment plant twice throughout the duration of the experiment. Subsequent to collection, samples were transported on ice. Characterizations were carried out on the same day to minimize degradation. Remaining samples were mixed according to digester influent specifications and stored as weekly batches at 4 °C. Influent mixtures were warmed to room temperature and homogenized in an industrial blender prior to testing and use; this ensured representative sampling and some de-emulsification of oils in the DAF float.

Characterization of samples was carried out in two phases. First, parameters relevant to AD were examined. Test methods varied by sample to some degree: Total Solids (TS) and Volatile Solids (VS) were conducted according to Standard Methods 2540 B and 2540 E, respectively; pH by Standard Methods E9045 D for DAF float and E9040C for WAS [21]; Total Nitrogen (TN), Total Phosphorus (TP), soluble and total COD (SCOD and COD, respectively) were tested using HACH methods 8190, 10071, and 8000 using DR2000 spectrophotometer, respectively (HACH, Loveland, CO). Measurement of COD required dilution due to high organic content and test range limitations. Dilution ratios were selected and sampling performed to ensure minimal sample handling and rapid sample preparation. The process of dilution is not desirable for analysis with oil-containing samples due to errors and increased potential for unrepresentative sampling as a result of the sample volatility and physical-chemical properties such as hydrophobia and surface tension [23]. Similarly, SCOD is not a reliable measure for oil-containing samples because methods to extract only the soluble fraction of COD in oil-containing samples can result in uncontrolled chemical loss or change; thus, SCOD was not used as a parameter to examine digestion efficiency. The methodology proposed by Singer et al. [23] to measure the water accommodated fraction of COD (WAF-COD) was selected to examine the impacts of ozonation on DAF containing influents. This protocol is appropriate to indicate the solubilization of COD in samples containing oil with less risk of altering sample composition. Alkalinity and volatile fatty acid (VFA) concentrations were measured following the methods 8221 (USEPA) and 8196 (HACH), respectively. Oil emulsions also resulted in problematic measurements for these colorimetric methods. Thus, for sample treatments containing DAF float, effluent VFA and alkalinity measurements were taken only of the aqueous portion of the sample. Previous research has shown that light aliphatic and light aromatic compounds are relatively soluble in crude oil whereas fluoranthene and phenanthrene have low solubility and may have been omitted in the WAF-COD method [23,24].

The second phase of analysis involved influent and effluent samples characterization of several organic compounds of interest at an external commercial laboratory. DAF float influent as well as effluent from digesters subsisting on DAF float were analyzed for volatile organic compounds (VOC) and semi volatile organic compounds (SVOC) as listed in Title 40: Protection of Environment, Part 268 for Land Disposal Restriction, Subpart D – Treatment System [11]. Standard EPA protocols (8260 B and 8270 D) utilizing GC/MS were followed for VOC and SVOC analysis. The goal of this analysis was to determine if concentrations of VOCs and SVOCs of interest were reduced by AD treatment of the DAF float with and without ozone pretreatment.

2.2. Inoculum

Inoculum used for the lab scale AD studies was obtained from a full scale mesophilic AD at a municipal wastewater treatment plant. The inoculum was degassed under mesophilic anaerobic conditions for three to five days prior to use in the lab scale ADs. This allowed for degradation of most residual organic matter present in the inoculum sludge from the municipal wastewater treatment plant.