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Research article

Visible light photocatalytic disintegration of waste activated sludge for enhancing biogas production

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ABSTRACT

Biogas production using waste activated sludge (WAS) is one of the most demanding technologies for sludge treatment and generating energy in sustainable manner. The present study deals with the photocatalytic pretreatment of WAS using ZnO-ZnS@polyaniline (ZnO-ZnS@PANI) nanocomposite as means for increasing its degradability for improved biogas production by anaerobic digestion (AD). Photocatalysis accelerated the hydrolysis of WAS and increased the sCOD by 6.7 folds after 6 h and transform tCOD into bioavailable sCOD. After the AD of WAS, a removal of organic matter (60.6%) and tCOD (69.3%) was achieved in photocatalytic pretreated sludge. The biogas production was 1.6 folds higher in photocatalytic sludge with accumulative biogas up to 1645.1 ml L^{-1}vs after 45 days compared with the raw sludge (1022.4 ml $L^{-1}{}_{VS}$). Moreover, the photocatalysis decrease the onset of methanogenesis from 25 to 12 days while achieve the maximum conversion rate of reducing sugars into organic acids at that time. These results suggested that photocatalysis is an efficient pretreatment method and ZnO-ZnS@PANI can degrade sludge efficiently for enhance biogas production in anaerobic digestion process.

1. Introduction

With rapid industrialization and economical growth, reasonable numbers of wastewater treatment plants have been established, producing a huge amount of waste activated sludge (WAS) (Liu et al., 2016). Industrial sector in Saudi Arabia, has made momentous progress during last four decades where the number of operating units has increased from 198 to 7007 between 1974 and 2015 (SIDF, 2016). Industries are using enormous amount of fresh water $\approx 7.1 \times 10^8$ m^3/year, and generating an excess of wastewater ≈ 1238 tons of WAS/day from treatment plants. The WAS from secondary treatment of wastewater exerts a significant to its disposal and stabilization (Nazari et al., 2017). Sludge processing and disposal entails high expenditure that accounts 50% of the total operating cost of wastewater treatment plant (Appels et al., 2010; Nazari et al., 2017) (see Table 1).

Anaerobic digestion (AD) is a most promising technology used for stabilization and safe disposal of WAS. AD is highly favorable due to its capacity of energy recovery by conversion of volatile solid into biogas (CH_4, CO_2) odors reduction, elimination of pathogens and mass reduction of solids (Cao and Pawłowski, 2012; Liu et al., 2016; Nazari et al., 2017). AD process entails of four progressive phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Kim et al., 2015; Nazari et al., 2017). However, the initial phase (hydrolysis) is rate-limiting step that restricts its degradation capability (Chen et al., 2013; Kavitha et al., 2016). Due to the particulate nature and low biodegradability of WAS, anaerobic digestion is always limited with low methane potential and long retention time (Liu et al., 2016).

WAS is a complex heterogeneous material containing of microbial flocs, hard cell walls consists of lignin, cellulose and hemicellulose, colloids and polymeric substances (Yu et al., 2008; Liu et al., 2012; Abelleira-Pereira et al., 2015). These components are highly recalcitrant and resistant to degrade by anaerobic bacteria, thus increase the overall retention time and lowering biogas

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production. The major fraction of the organic contents in WAS is bounded in a network of aggregated polymers known as extracellular polymeric substances (EPS) (Nielsen et al., 2011; Dhar et al., 2012; Nazari et al., 2017; Anjum et al., 2016a). These EPS are highly hydrated structures and play an important role in bioflocculation and settling WAS. Reportedly, up to 80% of EPS in WAS are attributed to carbohydrates and proteins (Neyens et al., 2004). The EPS network should be fragmented to make the organic materials and cell contents available to anaerobic bacteria (Nazari et al., 2017) for efficient AD process.

To improve the biodegradability of WAS, a pretreatment step before AD is therefore required to solubilize the complex organic contents (Liu et al., 2016; Sharmila et al., 2015; Kavitha et al., 2016). Various solubilization methods (chemical, biological, and mechanical, chemo mechanical and thermal) either alone or in combination have been reported for pretreatment of WAS (González et al., 2013; Kavitha et al., 2016). The pretreatment methods such as thermal microwave (Liu et al., 2015), ozone, H_2O_2 (Pilli et al., 2015), ultrasonic (Houtmeyers et al., 2014) and Fenton are widely applied, but these pretreatment demands input of high energy, cost and long treatment time. Therefore, the overall profitability of the process becomes limited due to more energy consumption and loss of organic matter during long treatment duration that may decrease the methane yield in subsequent AD (Kannah et al., 2017). Among various solubilization technologies, photocatalysis is the promising technique for the pretreatment of WAS. Previously, photocatalysis has been proved to be an effective method for the degradation of toxic organic pollutants from domestic and industrial wastewater (Miranda-Garcia et al., 2011). However, the use of photocatalysis as a pretreatment method for sludge (solubilization) is a novel area of research. Limited literature is available regarding the use of photocatalysis for sludge pretreatment; therefore, there is a need to focus its properties in this respect. Photocatalysis is considering as cost effective pretreatment method with respect to energy consumption (Liu et al., 2014). The process can be activated under solar light (visible light fraction) which is available as inexhaustible sources of energy in nature. The photocatalysis using nano-ZnO may cause inhibition in methane production (Mu et al., 2011), however, using modified photocatalyst with other metal oxides and polymers could reduce this problem.

'Solubilization' is an indicator representing pretreatment efficiency of sludge (Kim et al., 2013; Kavitha et al., 2016). The aim of the present study is to increase the solubilization of WAS using visible light photocatalysis to enhance subsequent AD and biogas production. Visible light active ZnO-ZnS@polyaniline (ZnO-ZnS@PANI) catalyst was used in photocatalytic pretreatment of WAS. The pretreated sludge was anaerobically digested to estimate the biogas production potential.

2. Materials and methods

2.1. Sampling and physio-chemical analysis of WAS

The real WAS sample was collected from Industrial City wastewater treatment plant, located at South of Jeddah (21° 23′ 59″ N, 39° 13′ 40″ E), Kingdom of Saudi Arabia. The wastewater treatment plant received water from more than 550 industries and handled 25,000 m^3 of daily water flow. WAS samples were taken in polyethylene bags and stored in refrigerator at 4 °C for about one week of duration of experimental preparation. The samples was analyzed for its physio-chemical properties such as Carbon, nitrogen, soluble chemical oxidation demand (sCOD), total chemical oxygen demand (tCOD), volatile solids (VS), total solids (TS), pH and electrical conductivity (EC).

2.2. Synthesis and characterization of photocatalyst

The photocatalyst ZnO-ZnS@PANI used in the present study was synthesized by the method as described in our previous study (Anjum et al., 2017). The characteristics of ZnO-ZnS@PANI was performed using various techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, energy disperse X-ray, UV–visible absorbance spectroscopy, Fourier transforms infrared and Raman spectroscopy. The photocatalytic property of ZnO-ZnS@PANI nanocomposite was investigated on 2-chlorophenol (Anjum et al., 2017).

2.3. Experimental setup

A two-step sequential experiment was setup including photocatalytic solubilization of WAS, followed by anaerobic digestion of photocatalytic solubilized sludge. The model of the experimental setup is illustrated in Fig. 1 and explained as follows.

2.3.1. Photocatalytic solubilization of WAS

The photocatalytic solubilization of WAS was carried out in a three neck photochemical column reactor equipped with a continuous stirring, pH probe and aeration system (Fig. 1). A visible light lamp (150 W) was installed in the center position that was covered by a cylindrical glass having a continuous water circulation system to keep the system under normal temperature. The reactor was filled with one liter volume of WAS (2% w/v) and 0.25 g ZnO-ZnS@PANI was added. The WAS concentration as 2% w/v was fixed for the purpose of better penetration of light and high photocatalytic activity. The photocatalytic pretreatment was carried out for 6 h and the initial pH of the sludge solution was adjusted in the range of 3.0–5.0. Similar photolysis experiment was also performed without addition of catalyst under illumination of light only to find the role of photolysis on pretreatment and to specify the role of catalyst in photocatalysis solubilization. The sludge sample was collected every hour during pretreatment process and analyzed for sCOD, solubilization rate and VS degradation.

2.3.2. Anaerobic digestion of pretreated WAS

2.3.2.1. Inoculum preparation. The inoculum was prepared using cow manure as source of anaerobic methanogenic bacteria. The samples of cow manure were collected from the livestock farm of King Abdulaziz University located at agricultural research station Hada Al-Sham, Saudi Arabia. The culture media was prepared using recipe no. 195 (DSMZ, 2015) with little modifications depending upon availability and supply of chemicals in the region. The composition of the media for preparation of 1 L of inoculum was KH_2PO_4 (0.50 g), $MgSO_4{\cdot}7H_2O$ (0.40 g), NaCl (0.40 g), NH_4Cl (0.40 g), $CaCl_2{\cdot}2H_2O$ (0.05 g), $FeSO_4.7\ H_2O$ (0.1% w/v in 0.1 N H_2SO_4, 2 ml), trace element solution (1 ml), Yeast extract (1.00 g), Na-acetate (1 g), Na-formate (2.00 g), Fatty acid mixture (20 ml), Na-

Table 1
Physio-chemical characteristics of sludge.

Parameters	Values	SD
TS (%)	24	1.6
VS/TS (%)	89	0.6
FS/TS (%)	11	0.6
C (g L^{-1})	496	14.2
sCOD (mg/L^{-1})	405	17.3
tCOD (mg/L^{-1})	13243	56.4
pH	5.5	0.2
EC (μS)	574	13.0
Moisture (%)	76	1.7