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Treatment of automotive industry wastewater using anaerobic batch reactors: The influence of substrate/inoculum and molasses/wastewater

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ABSTRACT

A study of the anaerobic treatment of an automotive-industry wastewater was conducted at mesophilic temperature in batch mode. In this study, molasses was used as a co-substrate. The experiments were carried out with samples prepared in 500 ml bottles using a shaker at 35 °C. The concentration of inoculum was prepared to be 5000 mg/L VSS. Substrate–inoculum ratios (SIR) were 0.75 and 1.0. Molasses–wastewater ratios (MWR) were 0.3, 1, and 3. All tests were carried out against controls of inoculum without substrate. A speed of 150 rpm was used for the sample bottles and they were examined daily for chemical oxygen demand (COD), pH, total solids, and total gas. The highest COD removal efficiency, 47%, was at SIR = 0.75 and MWR = 3. The highest total solid material removal efficiency was at SIR = 1 and MWR = 0.3. The best result in biogas production was at SIR = 1 and MWR = 0.3 and SIR = 0.75 and MWR = 3. Monod-, zero-, first-, and second-order kinetic models were used to calculate and define model constants for organic removal rates. Data show a close fit to the Monod kinetic model based on the verification constants (R^2) and other parameters (K_s, U_{max}, k_0, k_1, and k_2).

1. Introduction

Metal working fluids (MWF) are widely used as industrial lubricants and refrigerants to extend the life of tools, prevent corrosion, and improve productivity. These liquids enable the removal of swarf and metal parts. The global use of MWF is estimated at more than two million cubic meters (Muszyn'ski et al., 2007). Some 97% of the energy used in metal working operations is converted to heat, which can cause cutting tools to loose rigidity and make it difficult to produce workpieces within desired tolerances. Chips released during processing can conglutinate to parts and cause a loss of surface quality. Hence MWFs are very important in manufacturing (Hu et al., 2002, 2004; Hilal et al., 2004; Muszynski and Lebkowska, 2005; Bensadok et al., 2007; Busca et al., 2003; Cheng et al., 2005; Jagadevan et al., 2013; Rodriguez-Verde et al., 2014; Carvalhinha et al., 2010). MWFs are classified as lubricating oils (non-emulsified), emulsifiable oils, semi-synthetic MWFs, synthetic MWFs, alkali cleaners, and mineral solvent emulsion cleaners (Teli et al., 2014). The chemical structure and toxicity of MWFs are quite complex. Contact of MWFs with the skin, ingestion, or inhalation can have harmful effects on human health. The severity of the health problem depends on the type of fluid, the type and degree of contamination, and the duration and level of exposure (Teli et al., 2014). According to the National Institute for Occupational Safety and Health (NIOSH), the exposure to hazardous metal working fluids causes the healthy problems such as carcinoma of

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different organs including rectum, pancreas, larynx, scrotum, skin (Najiha et al., 2016).

There have been an increasing number studies on chemical (Zhong et al., 2003; Muszyn'ski et al., 2007; Jagadevan et al., 2011, 2013), physical (Karakulski et al., 1995; Hu et al., 2002; Busca et al., 2003; Chakrabarty et al., 2010), mechanical, and biological methods (Perez et al., 2006, 2007; Jeganathan et al., 2007; Carvalhinha et al., 2010, Rodriguez-Verde et al., 2014) to treat MWFs. They are mainly based on the initial separation of oil and water, after which each component is treated independently. Chemical, physico-chemical, mechanical, and thermal techniques are used in MWF treatment. In chemical and physico-chemical techniques, chemical pre-treatment is used first, to destabilize emulsions such as coagulation followed by gravity separation. Mechanical methods are based on gravity separation. Thermal methods are based on the thermal emulsion separation principle. Recently, membrane separation techniques (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) have been used because of their high output quality and efficiency in the treatment of oil emulsions. Although the complexity of MWFs affects the activity of bioreactors and stability of microbial structures, biological treatment is considered to be a potential solution for treating MWFs (Teli et al., 2014).

There are few studies on the anaerobic treatment of MWFs. Methods include membrane separation, aerobic treatment, and anaerobic and aerobic techniques that are often used in combination. As for biological treatments, Kim et al. (1989) achieved a 60% removal efficiency in an anaerobic fluidized bed process when the MWF inlet concentration was 3300 mg/L, using granular active carbon as carrier. Kim et al. (1992) reported a 68% removal efficiency using an anaerobic reactor with inlet chemical oxygen demand (COD) concentrations of 1029–5324 mg/L. Connolly et al. (2006) investigated the removal of metal-working wastewater using two synthetic polymers. In their studies, inlet COD concentrations of metal working wastewater were 13,500 mg/L with a cathode polymer and 9980 mg/L with an anode polymer, with 34% and 30% COD removal, respectively. Carvalhinha et al. (2010) used an anaerobic-sequencing batch reactor under mesophilic conditions with initial concentrations of 500, 1000, and 2000 mg COD/L and removal efficiencies of 87%, 86%, and 80%, respectively. Jagadevan et al. (2011) reported 65% COD removal following fenton processing of MWFs, and 92% COD removal with biological treatment following fenton processing. Rodriguez-Verde et al. (2014) published a 74% COD removal using pig manure as co-substrate in an anaerobic digester and biogas production of 0.26 L/L day at 0.7 g COD/L day OLR. Batch studies have tested kinetic models of anaerobic treatments in wastewaters from vinasse (Kobya and Demircioglu, 1993; Filik İşçen, 2006), textiles (Gnanapragasam et al., 2011), whey (Ergüder et al., 2000), sunflower meal (Raposo et al., 2009), apples (Kafle and Kim, 2013), corn (Raposo et al., 2006), slaughterhouses (Slimane et al., 2014), and dyes (Hosseini Koupaie, 2012). However, a few anaerobic batch studies related of oil emissions were found in the literature.

This study investigates batch anaerobic treatment of wastewater from the automobile industry. Molasses was used as co-substrate, and studies were conducted at various inoculum to substrate ratios (SIR) and molasses to wastewater ratios (MWR). Daily measurements were taken of pH, total solids, COD, and total gas.

Table 1 – Automotive industry wastewater characteristics (Sarioglu, 2015).

Wastewater characteristics	Values
pH	8.8–9.05
COD	63,000–90,000 mg COD/l, usually 70,000 mg COD/l
SS	2700–3400 mg/l
Oil/grease	700 mg/l
BOD_5	6000–7000 mg/L
Conductivity	>3.36 ms/cm
Turbidity	150–900 NTU

2. Materials and methods

2.1. Material

2.1.1. *Wastewater characteristics, granulated anaerobic sludge and molasses*

The wastewater used in this study was collected from Camshaft Factory, Turkey. It contains MWFs used in various manufacturing processes of a factory that manufactures spare engine parts. MWF samples were collected from industry for duration of 3 months and the mean values of the parameters have been tabulated in Table 1 (Sarioglu, 2015). The complete analysis of the wastewater was carried out according to standard methods (APHA, 2005).

The granular sludge from the anaerobic digester section was taken from the Adana Seyhan Wastewater Treatment Plant. pH, Total solids (TS), Volatile solids (VS) Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS) and COD values of the granular sludge were 7.45, 21.5 g/L, 13. 5 g/L, 22 g/L, 12.5 g/L and 17 g/L, respectively.

In this study, molasses was used as co-substrate. Molasses was taken from a commercial sugar factory located in Nigde, Turkey and stored in the refrigerator at 4 °C to minimize substrate decomposition before the experiment. Molasses is one of commercially available organic substrates. It is a cost- effective by product of sugar refining process and contains a high concentration of sugars such as glucose, sucrose and fructose as well as nutrient minerals (Saxena et al., 2009). The COD concentration of molasses used as co-substrate was 1000 g COD/L.

2.1.2. *Experimental procedure*

It is difficult to treat wastewaters with MWFs because they contain oil. In this study, anaerobic treatment was chosen due to high biogas production, which results from the co-substrates' rich organic content. First, in order to remove oil from the wastewater, acid cracking was used by manually adjusting the pH to 2 with sulfuric acid. The reaction time was 1 h. Next, oil was removed by manually adjusting the pH to 8 with NaOH. In chemical treatment experiments using the jar test apparatus (Velp Scientifica, Italy), $FeCl_3{\cdot}6H_2O$ (from Merck, Germany) reagents were used at 2.3 g/L. One hour sedimentation was applied following a coagulation time of 30 min at 40 rpm after flash-mixing for one minute at 200 rpm. Anaerobic batch experiments were carried out in a shaking incubator at 35 °C in working volume 150 mL serum bottles. Each bottle had sludge with a concentration of 5000 mg VSS/L. MWRs of 1:3, 1:1, and 3:1 and SIRs of 0.75 and 1 were prepared. Vanderbilt mineral medium was added to the serum bottles. The inorganic composition of mineral media used in all batch studies is listed in Table 2. pH was kept constant by adding 5000