Journal of Environmental Management 133 (2014) 284–292

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Treatment of biodiesel wastewater by adsorption with commercial chitosan flakes: Parameter optimization and process kinetics

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ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form
4 December 2013
Accepted 9 December 2013
Available online 8 January 2014

Keywords:
Adsorption
Biodiesel wastewater
Kinetics
Chitosan

ABSTRACT

The possibility of using commercial chitosan flakes as an adsorbent for the removal of pollutants from biodiesel wastewater was evaluated. The effect of varying the adsorption time (0.5–5 h), initial wastewater pH (2–8), adsorbent dose (0.5–5.5 g/L) and mixing rate (120–350 rpm) on the efficiency of pollutant removal was explored by univariate analysis. Under the derived optimal conditions, greater than 59.3%, 87.9% and 66.2% of the biological oxygen demand (BOD), chemical oxygen demand (COD) and oil & grease, respectively, was removed by a single adsorption. Nevertheless, the remaining BOD, COD and oil & grease were still higher than the acceptable Thai government limits for discharge into the environment. When the treatment was repeated, a greater than 93.6%, 97.6% and 95.8% removal of the BOD, COD and oil & grease, respectively, was obtained. The reusability of commercial chitosan following NaOH washing (0.05–0.2 M) was not suitable, with less than 40% efficiency after just one recycling and declining rapidly thereafter. The adsorption kinetics of all pollutant types by the commercial chitosan flakes was controlled by a mixed process of diffusion and adsorption of the pollutants during the early treatment period (0–1.5 h) and then solely controlled by adsorption after 2 h.

1. Introduction

Biodiesel is an alternative renewable fuel that has become widely used as a partial replacement for diesel derived from non-renewable fossil fuel due not only to its sustainably renewable nature but also to its high cetane number, lubricity, flash point and biodegradability, plus its low toxicity. Biodiesel is seen as a much safer fuel than that derived from fossil fuel because it has a low emission level of toxic compounds, such as SO_2, hydrocarbons, particulates, polycyclic aromatic hydrocarbons and CO (Knothe, 2005; Smith et al., 2009).

Biodiesel is currently produced from the transesterification reaction between vegetable oils or animal fats and principally methanol (although ethanol is also used to a lesser extent) in the presence of an acidic or alkaline catalyst to form the biodiesel (fatty acid methyl esters (FAME) or fatty acid ethyl esters). The untreated biodiesel contains several impurities, such as free glycerol, soap, metals, methanol (or ethanol), free fatty acids (FFAs), catalyst, water and glycerides, which impact negatively on the performance and durability of the diesel engine (Ngamlerdpokin et al., 2011). Thus, the removal of these components in a purification stage is essential. The traditional purification method utilized is wet washing, which involves using water or a weak acid to remove some of the excess contaminants from the biodiesel. However, the addition of water or a weak acid to the process leads to many disadvantages, including an increased cost and production time, the generation of a highly polluting effluent (wastewater) that needs to be treated prior to environmental discharge (Berrios and Skelton, 2008) and the significant loss of biodiesel into the wastewater phase (Canakci and Gerpen, 2001). For example, more than 6.0×10^6 L/day of biodiesel was produced in Thailand in 2010 (DEDE, 2011), with the formation of at least 1.2×10^6 L/day of biodiesel contaminated wastewater. This wastewater is at a high pH, due to the significant levels of residual alkaline catalyst, and contains a high quantity of hexane-extracted oil and a high solid content. Together, these components inhibit the growth of most microorganisms making this wastewater difficult to biodegrade naturally.

Currently, several processes have been developed to treat biodiesel wastewater, including biological (Kato et al., 2005; Nishiro and Nakashimada, 2007; Siles et al., 2010; Suehara et al., 2005),

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http://dx.doi.org/10.1016/j.jenvman.2013.12.019

chemical and physical processes. Although the biological processes are the most efficient and economic way for reducing the environmental impacts of biodiesel wastewater, they also generate large amounts of low-density sludge that has low and slow decomposition efficiency. Thus, these approaches are time and storage volume consuming. Accordingly, the chemical and physical processes are alternative (but not mutually exclusive) potential procedures for treating the wastewater from biodiesel production plants. The electrocoagulation process, using an aluminum anode and graphite cathode, is potentially suitable as a primary treatment for FAME biodiesel wastewater because it can reduce the oil & grease and total suspended solid (TSS) in biodiesel wastewater by more than 95%, but it can only achieve a 55% reduction in the chemical oxygen demand (COD) due to the poor removal of the residual glycerol and methanol (Chavalparit and Ongwandee, 2009). A two-stage management of biodiesel wastewater comprised of chemical recovery and electro-oxidation was found to be effective in that it removed all of the COD and oil & grease, and reduced the biological oxygen demand (BOD) by more than 95% with pseudo-first-order rate kinetics (Jaruwat et al., 2010). By using chemical coagulation with either $Al_2(SO_4)_3$ or poly-aluminum chloride (PAC) instead of electro-oxidation (Kumjadpai et al., 2011), a similar removal efficiency for BOD, COD and oil & grease was obtained but over a broad wastewater pH range of 4.5–10.0 and 2.5–7.0, respectively. This process provided a 1.6-fold or 38% lower operating cost (1.11 USD/m^3) compared with the electrocoagulation process (1.78 USD/m^3). However, the electrocoagulation process provided a better wastewater quality than the chemical process with either $Al_2(SO_4)_3$ or PAC, with the exception of the reduction of the BOD (Ngamlerdpokin et al., 2011). The use of the dissolved air flotation (DAF) process alone or with acidification of the wastewater could not separate the residual oil & grease from the biodiesel wastewater, and so the use of DAF with acidification (with HCl or H_2SO_4) and coagulation (with Al_2SO_4) was then suggested (Rattanapan et al., 2011).

Among the several chemical and physical methods utilized, the adsorption process is one of the effective methods. The most common adsorbents used are peat (Calderón et al., 2008; Ringqvist et al., 2002; Xiong and Mahmood, 2010), bentonite clay (Koswojo et al., 2010; Shi et al., 2011; Tahir and Naseem, 2007; Zhu and Ma, 2008), activated carbon (El-Naas et al., 2010; Huang and Su, 2010; Soleimani and Kaghazchi, 2008) and agricultural waste (Moussavi and Khosravi, 2010; Šćiban et al., 2007). Nevertheless, these systems still require physicochemical and microbiological pretreatment to enhance the adsorption (Ahmad et al., 2005). Another promising candidate adsorbent for wastewater treatment is chitosan, a partially deacetylated form of the natural biopolymer chitin (poly(β-(1-4)-2 D-acetamido-2-deoxy-β-D-glucosamine)) that is found in the exoskeleton of crustaceans and fungal cell walls and is a waste product from the marine seafood (especially shrimp) industry (Fereidoon and Jozef, 1991). The potential of chitosan lies in part in that it has various excellent properties, including biodegradability, hydrophilicity, biocompatibility, good adsorption properties, flocculating ability, polyelectrolisity, and its capacity of regeneration in a number of applications (Feng et al., 2000; Majeti, 2000). It can be used either in the original deacetylated form (with varying degrees of deacetylation) or in a chemically modified form depending on the properties of the wastewater (Chiou and Li, 2002). Both unmodified and chemically modified chitosan have been used to adsorb heavy metals (Kumar et al., 2009; Paulino et al., 2008), reactive dyes (Chen, 2008; Kyzas and Lazaridis, 2009; Momenzadeh et al., 2011), organic compounds (Wan Ngah et al., 2008; Wang et al., 2009) and oil residues from wastewater (Ahmad et al., 2005; Piyamongkala et al., 2008; Sokker et al., 2011). However, no work in the available literature has reported on the use of either unmodified or modified chitosan to adsorb pollutants from biodiesel wastewater. In this work, a series of adsorption experiments were performed to evaluate the feasibility of using unmodified commercial chitosan flakes as an adsorbent for removing pollutants from biodiesel wastewater. The effects of varying four key operating parameters (adsorption time, initial wastewater pH, dosage of adsorbent and the mixing rate) were investigated. The reusability of the commercial chitosan flakes following washing in alkali, and the adsorption kinetics were also examined.

2. Materials and methods

The treatment of wastewater from a conventional biodiesel production plant of our country, that uses waste used-vegetable oil as the feedstock to form biodiesel with an alkali catalyst, was carried out on a laboratory scale at ambient temperature. The original wastewater with the properties demonstrated in Table 1 was first pre-treated by the addition of H_2SO_4 (98.08% QReC Grade AR) to reduce the pH to ~2.0, as previously reported (Ngamlerdpokin et al., 2011). The mixture was then shaken for 2 h before being left for 30 min to allow the complete phase separation between the upper FAME-rich phase and the lower acidic aqueous phase. Both phases were then separated by slow decantation. The remaining discharged wastewater (aqueous phase) after the extraction of upper FAME-rich phase was then treated by the adsorption process with the commercial chitosan flakes (Taming Enterprises, Thailand).

Prior to the adsorption stage, the moisture content in the commercial chitosan flakes was eliminated by drying at 105 °C for 30 min. Meanwhile, the pH of the extracted aqueous wastewater phase was adjusted to be within the preferred range (pH 2–8) by the addition of NaOH (1 M, Earth Cheme Lab., Thailand). Subsequently, approximately 100 mL of wastewater was conventionally treated by the addition of commercial chitosan flakes (range 0.5–5.5 g/L) as the adsorbent in a conical flask with a constant stirring rate (range of 120–350 rpm) for a selected adsorption time (0.5–5 h). Finally, the treated wastewater was separated from the adsorbent by vacuum filtration through filter paper No.1 (Whatman 70 mm # 1001070). The concentration of pollutants in the treated wastewater was measured in terms of the BOD, COD, oil & grease, total dissolved solids (TDS) and TSS according to standard methods (APHA, 1998). In addition, to characterize the types of compounds in the wastewater, gas chromatography–mass spectroscopy (GC–MS) analysis was performed (6890N, Agilent of GC/Pegosees III, Lego of MS).

To test the reusability of spend chitosan, 0.35 g of used-chitosan flakes were dipped in 100 mL NaOH at three different concentrations (0.05, 0.10 and 0.2 M) and then shaken at a constant rate of 130 rpm for 3 h. Afterward, the flakes were separated from the basic solution by filtration and rinsed several times with distilled water to remove the excess base. The ready-to-use regenerated chitosan was obtained after drying in an oven at 70 °C for 24 h. Finally, it was subjected to treat wastewater from biodiesel production plant at optimum adsorption condition.

3. Results and discussion

3.1. Properties of the original biodiesel wastewater and pretreated-wastewater

The original wastewater obtained from the waste used-oil biodiesel production plant had an opaque white color and a high pH (range of 9.25–10.26). It contained very high BOD, COD, oil & grease, TDS and TSS in comparison to the government standard (Table 1). From the GC–MS analysis, the main components in the