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ECOENG-4896; No. of Pages 9
ARTICLE IN PRESS
Ecological Engineering xxx (2017) xxx–xxx
Contents lists available at ScienceDirect
Ecological Engineering
journal homepage: www.elsevier.com/locate/ecoleng

Fibrous deep-bed filtration for oil/water separation using sunflower pith as filter media

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ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form 7 July 2017
Accepted 10 July 2017
Available online xxx

Keywords:
Oily wastewater
Sorbent
Sunflower
Sorption experiments
Filtration

ABSTRACT

The application of agricultural by-products as filter bed material for the treatment of oily wastewater is preferable due to their biodegradability and availability. The goal of this paper was to examine the sorption and filtration properties of sunflower (Lat. *Helianthus annuus*) fibres in a raw state. SEM imaging and nitrogen adsorption at −196.15 °C were applied to evaluate sorbent morphology. FTIR spectroscopy was used to determine the chemical composition of the pith. Studies on sorption in static conditions (pith fragmentation 1.5–4.0 mm) allowed process kinetics to be specified. The experimental kinetics was fitted to pseudo first-order and pseudo second-order kinetics by a non-linear method. To better predict kinetic parameters, a new modified logistic equation was proposed. Sunflower fibre was found to have high oil sorption capacity (12.67 g/g) and good retention properties.

During filtration experiments, an artificial reservoir brine (0.1, 2.0, and 20.0 g/l of oil) was used as an oil-in-water emulsion; sunflower pith was used as a filter medium. The influence of four process parameters (pH, bed height, initial oil concentration, and flow rate) on removal efficiency was studied. Oil concentrations were determined by gas chromatography. The results demonstrated that the prepared filters operated better at a lower pH, lower flow, a deeper bed material, and higher concentration of inlet oil. The filtration efficiency for the removal of crude oil from oily brines reached more than 99% in the initial stage of the process. The results obtained suggest that natural plant fibres can be an effective bed material to separate oil from oily brine.

1. Introduction

All activities in the petroleum industry generate large quantities of oily wastewater. During exploration and exploitation of oil fields, oily mud and reservoir brine are produced (Caenn et al., 2017). Transporting oil and gas by pipelines is considered relatively safe, but accidental spills may occur (Fernández-Macho, 2016). Onshore pipeline failures can substantially damage surface water, drinking water, and other parts of the ecosystem (Yang et al., 2010). Wastewaters from petroleum refining consist of cooling water, process water, storm water, and sanitary sewage water. Appropriate treatment technology depends on the chemical composition and volume of the discharged wastewater. A typical wastewater treatment plant in a refinery is complex and consists of primary and secondary oil/water separation, followed by biological treatment and tertiary treatment (Ebrahimi et al., 2016; Crespo et al., 2016). Conventional oily wastewater treatment methods include mechanical methods (gravitational separation, flotation, filtration), physicochemical (coalescence, sorption, ultrafiltration), chemical (coagulation, extraction), and biological (Judd et al., 2014; Ahmadun et al., 2009). After processing in an advanced treatment unit, purified water can be discharged into the environment or reused. Oily reservoir brine is produced as a by-product along with oil and gas. The chemical composition of brine is complex and efficient management of formation water is difficult. Brine usually contains dispersed oil droplets, dissolved organic compounds, dissolved inorganic salts, dissolved gases, radionuclides, and chemicals used in hydrocarbon extraction (Al-Haleem et al., 2010). Water reinjection into the formation after primary treatment decreases the cost of surface facilities and increases the oil recovery factor. To avoid a reduction in permeability in the near-wellbore region, it is necessary to remove solid particles and oil droplets. Problems which occur due to the presence of oil include emulsion blockage and deposition of paraffin or asphaltenes (Civan, 2016). Treatment of oily wastewater is challenging due to the complex composition of brine and large volumes of produced water. Fibrous deep-bed filtration has been reported as an efficient treatment technology for oil-water separation. Plant fibre could be used both as sorbents

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http://dx.doi.org/10.1016/j.ecoleng.2017.07.021
0925-8574/

Please cite this article in press as: Knapik, E., Stopa, J., Fibrous deep-bed filtration for oil/water separation using sunflower pith as filter media. Ecol. Eng. (2017), http://dx.doi.org/10.1016/j.ecoleng.2017.07.021

for oil spill removal and as deep bed filter materials. As potential oil biosorbents, various types of biomass have been studied including pineapple leaves (Chin et al., 2016), silkworm cocoon waste (Moriwaki et al., 2009), populus seed fibres (Likon et al., 2013), cattail (Dong et al., 2014), rice husk (Wang et al., 2015), kapok (Wang et al., 2013), cotton grass (Suni et al., 2004), straw biomass (Tijani et al., 2016), and sawdust (Zang et al., 2015). Filtration can be accomplished using other types of filtration media such as activated carbon, modified polymeric resins, sand, anthracite and others. Of natural fibres, kapok is the most commonly used as filter material. Dong et al. (2017) reported a novel filtrating system using a structured kapok filter for which oil removed from wastewater was subsequently recovered by centrifugation. Huang and Lim (2006) found that filtration efficiency using hydrophobic/oleophilic kapok beds reached more than 99.4% for hydraulic oil removal. The authors described the filtration mechanism in detail and distinguished four stages (infiltration, separation, displacement and equilibrium) in the dynamics of oil/water separation. Raw kapok fibres were more effective than solvent-treated ones (Lim and Huang, 2007). As a bed filter, Cambiella et al. (2006) used sawdust mixed with a small amount of calcium sulphate ($CaSO_4{\cdot}2H_2O$) in order to promote coagulation of oil droplets. Oil removal ratios higher than 99% were achieved by maintaining the pressure across the bed at lower than 0.5 bar. Pasila (2004) investigated the possibilities of manufacturing oil adsorbing filter materials from reed canary grass (*Phalaris arundinacea*), flax (*Linum usitatissimum L.*), and hemp fibre (*Cannabis sativa* L.). Ribeiro et al. (2003) used dead biomass derived from a hydrophobic aquatic plant, *Salvinia* sp., as a bed material. Due to its hydrophobicity and the hair-like structure, the aquaphyte biomass achieved better performance than processed peat.

Most of the described fibres are not widely available on a large scale; therefore, new biofilter materials are still being developed. This study evaluated the ability of sunflower pith to remove hydrocarbons from oily brine in a deep bed filtration system. Sunflower is an important agricultural crop cultivated for its valued healthy oil. Sunflower by-products (stalk, leaf and flower-head) may be managed in different ways. In most cases, these waste materials are either left in the fields or burnt as biomass. Low-methoxyl pectins from sunflower heads are used as gelling agents in the food industry (Sosulski et al., 1978). Aksogan et al. (2016) reported that sunflower stalk ash can improve many durability properties of concrete. The hygro-mechanical properties of sunflower stems were characterized by Sun et al. (2013). Due to its good heat insulation properties, the stem was intended for use in bio-sourced composite materials suitable for building insulation. Composites containing crushed sunflower stem particles can also be used for sound absorption (Mati-Baouche et al., 2016). Jimenez and Lopez (1993) have investigated the uses of sunflower stalk in the manufacture of paper pulp. There are few reports on environmental applications of sunflower fibres. Sunflower stalks modified chemically by grafting quaternary ammonium groups was an efficient sorbent for removal of anionic dyes (Shi et al., 1999). Alkali-treated dried sunflower seed hull also exhibited good sorption properties for the decolourization of wastewater effluent from the textile industry (Oguntimein, 2015). The competitive sorption of Cd, Cu, Ni, Zn, Fe, and Mn from aqueous solutions by residues of sunflower was evaluated by Feizi and Jalali (2015). Jain et al. (2013) reported effective cadmium removal from wastewater in a fixed bed column using sunflower waste carbon calcium–alginate beads. A literature survey has indicated that sunflower pith has not been used for removal of hydrocarbons (both crude oil and petroleum products) through deep bed filtration. Therefore, the authors have attempted to use sunflower pith as filter media in a fixed-bed glass column at laboratory scale to treat oily wastewater.

Table 1
Oil types and their properties.

Oil types	Density (g/cm^3)	Viscosity (mm^2/s)
gasoline	0.749	0.75
crude oil	0.819	5.5
diesel oil	0.861	4.3
motor oil SAE 15W/40	0.879	14.1 at 100 °C

2. Materials and methods

2.1. Preparation and characterization of sorbent

The sunflower species used for this study was grown in the Małopolska region of Poland in 2014. The fibres were dried outdoors for about 3 months, assuring a maximum humidity of 5% wt. The external fibrous part of the stalk was mechanically separated from the spongy pith. These pith specimens were cylindrical in shape, with a diameter ranging from 1.0 mm to 2.5 cm. The material was washed with water at 40 °C to remove soluble pigments and dust and dried overnight at 80 °C. The pith was ground mechanically, sieved and stored in an airtight plastic container for further use. As filter media, a fraction of 2.0–8.0 mm was used; smaller particles were not suitable for filtration due to extensive fouling.

2.2. Physico-chemical characterization of sunflower pith

Solid morphology of sunflower pith was determined by scanning electron microscopy (FEI Quanta FEG 250). SEM analysis was carried out at room temperature with accelerating voltage of 10 kV. Specific surface area was measured using an ASAP 2420 apparatus (Micromeritics, USA) through nitrogen adsorption at −196.15 °C. Pith was degassed overnight at 100 °C under vacuum. The chemical composition of fibres was analysed by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometry (Nicolet iS 50, IR- Thermo Scientific Spectrometer). The spectra of the samples were traced in the range of 4000–400 cm^{-1} and the band intensities were expressed in transmittance (%).

2.3. Crude oil and oil products

For the sorption and filtration experiments, different oils were used, including crude oil from the Grobla oilfield, Poland, gasoline, diesel oil, and motor oil SAE 15W/40. The oil products were purchased at a local petrol station. Density and kinematic viscosity of liquids were measured at 20 °C by the pycnometer and capillary method employing an Ubbelohde type viscometer. The properties of the tested liquids are presented in Table 1.

2.4. Sorption properties

All sorption tests were performed in static conditions. 1 g of sorbent with the selected particle size was placed in a 250-ml beaker with 50 g of crude oil or petroleum products. After the required period, the content of the beaker was filtered for 10 min on steel sieves. Once the excess of the liquid was completely filtered, the remaining material was weighed in sieves. Sorption capacity is expressed as the mass of sorbed liquid per mass of sorbent. The sorption capacity was defined as:

$$S_c = (m_t - m_s)/m_s \quad (1)$$

where: S_c is the sorption capacity (g of sorbate/g of sorbent), m_t is the weight of the oiled sorbent (g), m_s is the weight of pure sorbent (g). Every test was performed twice and the mean/average result is presented. The reason for the observed discrepancies in results was the heterogeneity of the sorbent structure.

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