Chemical Engineering Science 157 (2017) 264–271

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Absorption of toluene by vegetable oil–water emulsion in scrubbing tower: Experiments and modeling

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HIGHLIGHTS

- Absorption of toluene per a vegetable oil–water emulsion.
- Vegetable oils used as organic solvent for VOCs absorption.
- Experimental Henry constants values for toluene with sunflower oil.
- Oil cover ratio to appreciate the real interfacial area offer by the droplet emulsion.
- Special modeling approach for mass transfer by an emulsion.
- A transfer model has been established for an emulsion.
- A thermal regeneration (120 °C) of the oil–water emulsion.

ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form
13 May 2016
Accepted 4 June 2016
Available online 6 June 2016

Keywords:
Absorption
VOCs
Emulsion
Spray
Regeneration
Oils of vegetable origin
Henry's constant
Mass transfer

ABSTRACT

The aim of this work is to study continuous counter-current absorption of Volatile Organic Compounds (VOCs) by an oil–water emulsion. This process enables the treatment of hydrophilic and hydrophobic VOC within a gaseous effluent emitted by chemical or food processing industries. Toluene was chosen as the pollutant in this work because of its hydrophobicity and its widespread use in chemical industries. As organic solvents for VOC absorption, vegetable oils were proposed for the treatment process to reduce the impact on the environment. The absorbing oil was selected for its good absorption capacities, its chemical and thermal stability and its low cost. To test their impact on the operational efficiency of the absorption process, numerous parameters were varied, such as liquid and gas flow rates, temperature and nozzle type. Thermal regeneration (120 °C) of the oil was proposed and tested on the experimental device. No impact on efficiency was noted, even after several regenerations. Finally a model was determined to predict the effects of operational conditions on the absorption efficiency of an emulsion.

1. Introduction

Volatile Organic Compounds (VOCs) are molecules composed mainly of carbon, hydrogen and other atoms like oxygen, nitrogen, sulfur or halogens. They have a high vapor pressure, usually greater than 10 Pa (Council directive 1999/13/EC, 1999). This property results in a low boiling point, which causes large numbers of these molecules to evaporate and to be release into the atmosphere. VOCs are present in the gas released in numerous industries, such as food/agriculture, electronics, wastewater treatment, painting/coating manufacture, petrochemical processes, and highway construction, and generate pollution and unpleasant odors. Released into the tropospheric atmosphere, VOCs can react with NOx in presence of solar radiation to form ozone, which is a very strong pollutant molecule. Its influence on human health can be critical, especially in the chemical industry, where long exposure could promote the development of cancers. VOCs can be foul-smelling, oncogenic, teratogenic or mutagenic (Hueper et al., 1962; Somers, 2011; Sram et al., 2007). In addition to irritation of the mucous membranes, skin and eyes, other risks affecting the central nervous system are commonly associated with VOCs. As a consequence of those risks, limit values have been set by the World Health Organization, restricting the concentrations to which people can be exposed and, in late 2013, the

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http://dx.doi.org/10.1016/j.ces.2016.06.008
0009-2509/

International Agency for Research on Cancer assessed the carcinogenicity of outdoor air pollution (Loomis et al., 2013). Consequently, rules concerning industrial gas emissions are gradually becoming stricter. Processes could be optimized and the use of solvents reduced in order to decrease the VOC concentration in the air but, unfortunately these actions are not sufficient or cannot be applied in all chemical processes. Thus specific treatments have to be used to reduce emissions, with the aim of eliminating or recovering VOCs. Eliminative treatments, such as thermal processes and biochemical methods, have been developed recently but many of them are still in the research or development phases with new and innovating technologies (Khan and Ghoshal, 2000). Recovery could be achieved by several methods: condensation, absorption, adsorption and membrane separation. The most commonly used is adsorption, classically with activated carbon (Subrenat and Le Cloirec, 2006). It is usually a batch process, using heating or stripping with steam for the regeneration, and is limited by the adsorbent capacities (Hester and Harrison, 1995). Absorption is based on the transfer of the soluble gas molecule to a solvent liquid (water or low volatility hydrocarbon molecules). An absorption tower can be used for high VOC concentrations (500–5000 ppm). A condensation technique can also treat waste gases with high VOC concentrations but it is more suitable for organic pollutants with high boiling points. Absorption is used to remove VOCs from the gaseous effluent by creating a contact between the liquid solvent and the contaminated gas. Soluble VOCs can transfer to the liquid and the air stream is scrubbed. This operation takes place in a tower designed to provide the contact area necessary to perform the mass transfer. Trays and packed columns or atomizers can provide such contact (Roustan, 2003). Scrubbing promotes gas–liquid contact by using packing material, which can either be randomly dumped or stacked in the tower. It varies widely in shape, size, cost, contact surface area, pressure and material of construction and each packing design has its own advantages (Kherbeche et al., 2013). The packing increases the contact surface area between the phases and reduces the height needed for the tower (Bhatia et al., 2004) but the pressure drop and energy needed are much greater than in empty spray towers (Brasquet and Le Cloirec, 1997). Packed towers are also more expensive and more sensitive to clogging, especially for flue gas treatment, and they cannot be adapted for viscous solvents such as oil. As the VOCs can be hydrophilic or hydrophobic, water is widely used as an absorbent of hydrophilic VOCs (Biard and Couvert, 2013) and oil is used for hydrophobic VOCs. However, two columns are necessary and the high viscosity of oil makes the energy expenditure prohibitive for this application (Darracq et al., 2010). The use of a water/oil emulsion is an alternative that reduces the number of towers of a process (Tatin et al., 2015) and thus reduces the initial investment in equipment and the cost of energy supplies while increasing the contact surface area available for gas–liquid exchange and the amount of VOCs that can be treated in a counter-current packed system (Dumont et al., 2011). So, when the goal of the treatment is to absorb both hydrophilic and hydrophobic VOCs by using an emulsion, the spray column is the most appropriate apparatus to handle the viscosity issue. Other works have been published on the absorption method using a siloxane/water emulsion (Dumont et al., 2012), or silicone oil/water emulsion (Tatin et al., 2015). Most of these studies operated in a semi-batch system using recirculation of the emulsion without any regeneration of the VOC-saturated oil. To date, no work has dealt with the regeneration of the solvent, which is nevertheless a major step of the global process if steady state operation is desired. Obviously, regeneration has the advantages of (i) reducing the solvent consumption and (ii) enabling the VOC to be recovered when this constitutes added value for the process. The originality of the present study basically lies in the selection of the absorbent oils. The vegetable oils chosen were environmentally friendly, without any oil-VOC release and had good temperature resistance. Thus thermal regeneration of the oil was possible to ensure continuous treatment of the polluted gas with lower oil consumption. The first objective of this paper is to characterize the absorption process in the aim of evaluating the influence of temperature, nozzle size, gas and liquid flow rates, and regeneration on the process efficiency. The second objective is to establish a model to describe the continuous absorption processes at steady state in function of flow rates and temperature.

2. Material and methods

2.1. Vegetable oil characteristics

The use of vegetable oils as organic solvents for VOC absorption has been proposed to reduce the impact on the environment. Vegetable oils have shown good affinity for the capture of VOCs such as toluene. Two kinds of sunflower oils were selected: a commercial (30.2% Oleic Acid) and high oleic sunflower oil (HOSO, with 86.3% Oleic Acid) obtained from sunflower seeds purchased by Arterris (*France*). Before choosing an oil for the absorption process, it is recommended to study its physical properties in order to predict its behavior under the experimental conditions. The physicochemical characteristics of the sunflower oils measured and studied in this work are reported in Table 1.

Oil oxidation reactions leading to oil degradation with loss of properties, could occur during the VOCs absorption experiments. The oxidative stability of oil depends on the fatty acid composition of its constituent triacylglycerol. The inherent stability is a theoretical value defined as the weighed sum of relative oxidation rates multiplied, respectively, by the percentage content of each constituent fatty acid, in such a way that the lower the inherent stability value, the more stable an oil is. The inherent stability of HOSO was 1.9 versus 6.8 for commercial sunflower oil (Erickson, 2006). Highly unsaturated such as oil rich in linoleic acid are especially susceptible to the autoxidation reactions and the Iodine value is a measure of the average number of double bond of an oil. For comparison, the oxidation rate of linoleic acid is 10 times the oxidation rate of oleic acid. HOSO was chosen in this work in because it presented a lower iodine value, correlated to the content in monounsaturated and polyunsaturated fatty acids (Table 1), than commercial sunflower oil. Indeed lower is the iodine value, better is the inherent stability of the oil and higher was the ability of the oil to keep its properties (Erickson, 2006; Dufaure et al.,

Table 1
Physicochemical characteristics of the sunflower oils studied.

Candidate oils	Density (kg/m^3)	Viscosity (Pa s)	Surface tension (mN/m)	Iodine Value (cg I_2/g)	Saturated fatty acids (%)	Monounsaturated fatty acid (oleic acid)	Polyunsaturated fatty acids (linoleic acid)
HOSO	910.91 ± 0.1	0.077 ± 0.001	34.32 ± 1	85 ± 0.1	6.5	89.5% (86.3%)	3.9% (3.8%)
Commercial sunflower oil	918.25 ± 0.1	0.057 ± 0.001	34.89 ± 1	125 ± 0.1	10.8	30.5% (30.2%)	58.7% (58.7%)