



Absorption of *n*-butyl acetate from tannery air emissions by waste vegetable oil/water emulsions

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ARTICLE INFO

Keywords:

VOC abatement
Oil/water emulsions
Waste oil
Absorption
Desorption

ABSTRACT

Tanning industries emit a huge quantity of Volatile Organic Compounds (VOCs), including hydrophilic and hydrophobic solvents. In this study, vegetable oil/water emulsions with 2 and 5 vol% of corn oil (O) or waste cooking oil (WCO) were prepared. Their potential as absorbents of *n*-butyl acetate (BA), in place of water, was investigated to increase the efficiency of tannery wet scrubbers. BA was selected as a representative component of hydrophobic VOC emissions derived from leather finishing processes. Static and dynamic absorption tests were performed with a BA concentration of 500 ppmv (2.6 g/m³) and a flowrate of 3.0 L/min to evaluate Henry's law constant, absorption efficiency, absorption capacity, and saturation time of the various investigated absorbents. The feasibility of the absorbent regeneration was also studied by hot stripping with nitrogen. The results showed that Henry's constant of BA in oil/surfactant/water or oil/water emulsions (5 vol% oil), regardless of the oil used, were significantly lower than those in water (3.6 versus 15.9 atm), and BA absorption capacity (0.84 g/L) was four times higher than the value in water. The presence of the surfactant (0.2–0.8 vol%) contributed to improving the oil/water emulsions stability without having a significant effect on BA absorption capacity. Almost complete BA desorption from the saturated emulsions was obtained by flowing hot N₂ at 80°C, demonstrating the absorbent regeneration's feasibility followed by recovery and reuse. Therefore, the oil/water emulsions containing 5 vol% of WCO are efficient and sustainable absorbents of BA, with potential use in VOC emission treatment systems.

1. Introduction

Volatile Organic Compounds (VOCs) constitute a huge part of pollutants in air emissions with a great impact on the environment and human health. It was estimated that more than one-third of VOC emissions derive from solvents used in coatings, paints, and inks [1]. This category includes tanneries' air emissions that derive mainly from the leather finishing processes (about 52 g of VOC per square meter of finished leather [2]). If organic degreasing solvents are used during soaking in suede leather manufacture, these may also evaporate into the atmosphere. Many tanneries are implementing water-based coatings to reduce VOC emissions [3]; however, large amounts of VOC emissions continue to come from the tanning industry. These emissions include hydrophilic solvents such as ethanol, 1-methoxy-2-propanol, acetone, isopropanol, ethyl acetate, and hydrophobic compounds such as *n*-butyl acetate and toluene [4]. Over the past decades, several regulations, both European and Italian, have been enacted to control VOCs emissions [5–9] aimed at setting emission limits, and to avoid or reduce emissions

from industrial activities into air, water, and soil. These regulations have stimulated the industry towards the adoption of technical solutions which mainly involve the use of products with lower VOC content (e.g. water-based paints). However, this is not always possible and the VOC emissions have to be inevitably purified with adequate and efficient abatement technologies [10].

The choice of the most suitable abatement system depends on many factors, such as the specific industrial process, type, and concentration of VOCs, feasibility of recovery and/or reuse of VOCs, required removal efficiency, etc. In the last decades, VOC abatement technologies had been focused on VOC recovery and reuse going towards a circular economy approach. Hence, recent studies report VOCs abatement systems based on condensation [11], absorption [12–14], adsorption [15, 16], and membrane separation [17]. However, compared to the other processes, absorption is still considered the cheapest and most suitable technology to treat large gas flows at low VOCs concentrations [17]. To date, tanneries, as well as many other industries, use wet scrubbers, with water as a typical absorbent, as the first step for the treatment of air

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<https://doi.org/10.1016/j.jece.2024.112443>

Received 5 November 2023; Received in revised form 21 January 2024; Accepted 7 March 2024

Available online 8 March 2024

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emissions contaminated by VOCs. These systems show high efficiency in the removal of powders, pigments, and water-soluble solvents such as methanol, butanol, and acetone. On the contrary, the absorption efficiency towards hydrophobic VOCs, such as toluene, benzene, ethyl acetate, butyl acetate, and methyl methacrylate, is very low due to their poor solubility in water. Despite the majority of emitted VOCs are hydrophilic compounds (around 70 wt%), water-insoluble fractions are not negligible and must be considered to comply with emission limits [4]. Thus, the selection of an appropriate absorbent is the key factor to obtain high VOCs abatement efficiency against both hydrophilic and hydrophobic solvents.

Several studies were carried out on the use of organic compounds with more affinity toward hydrophobic VOCs. Heavy organic liquids (polyethylene glycols, phthalates, adipates) [18], silicon oils [19], fresh and waste organic oils [20–22] were successfully investigated as absorbents for toluene and other hydrophobic compounds. The use of pure oils could be a good option for the treatment of gases that contain mainly hydrophobic VOCs; however, oils' high viscosity and costs hinder their application in industrial processes. Tanneries, as well as other industries, produce air emissions containing both hydrophilic and hydrophobic VOCs, thus requiring two absorption steps that use selectively water and organic oils as absorbents to effectively remove both types of VOCs. Therefore, the use of a single absorbent solution suitable for both kinds of VOCs would simplify the process with a significant reduction in capital and operating costs. To this purpose, oil/water emulsions have attracted attention due to their potential capability to absorb both hydrophilic and hydrophobic VOCs coupled with the advantage of having an absorbent with viscosity comparable to that of water.

In this context, aqueous solutions [23,24], and water emulsions containing silicon oil [25–27], paraffin [28], or vegetable oil [12] were investigated as absorbent agents in different kind of systems, such as bio-scrubbers [23], scrubbing towers [12], bubble columns [25,26,28], and spray columns [27]. All the authors showed that emulsions have higher efficiency and absorption capacity than water, improving the global process performance. Moreover, the higher the oil content in the emulsion, the greater the absorption efficiency and capacity due to the increased nonpolar fraction in the solution [28]. Among the organic compounds studied in emulsion with water, vegetable oils are interesting for their chemical and thermal stability, biodegradability, and low cost [12]. However, vegetable oils are commonly used for human consumption, so, the usage options of waste oils instead of virgin ones will not create competition with food purposes. In this context, Ozturk and Yilmaz [20] compared the absorption of waste oils to that of fresh ones reporting similar performance. Thus, showing that waste vegetable oil will be potentially used in the removal of VOCs (like benzene, toluene, carbon tetrachloride and methanol) from air stream to reduce the environmental impact of processes and their costs.

In the last decade, some authors investigated the potential use of waste vegetable cooking oil (WCO) as a bio-solvent for pollutants, for example to remove the tar derived by the rice husk pyrolysis [29], or the mercury from air, water, and soil [30]. However, to the best of our knowledge, only a few studies have reported the use of waste cooking oil for VOCs removal from air [21] and no papers are published on its use in emulsion with water. To date, WCO is mainly employed in various sectors, for example, it is used as raw material in the production of different kinds of organic products such as biofuels, biolubricants, bioplasticizers, and polyurethane foams, or as rejuvenator in asphalt pavement construction, etc. The interested reader can find more information on the WCO applications in a review recently published by Awogbemi et al. [31]. The quantity of WCO produced is huge: in Europe about 0.6 Mtons are currently collected every year with an increase by around 2% per year considering the growing consumption of vegetable oils [32]. Thus, it is estimated that the annual capacity of the collected WCO will reach 4 Mtons/year in the next decade [33]. Significant advantages in both environmental and economic terms are offered by utilizing WCO in industrial applications in place of virgin vegetable oils

[34].

To improve the impact on the environment and the overall economy of VOCs absorption process, the feasibility of regeneration and reuse of the absorbent as well as the recovery of the absorbed VOCs are crucial aspects. A biodegradation step was proposed by Darracq et al. [19] to regenerate the saturated silicon oil. This process was recently studied on an industrial pilot-scale by Lhuissier et al. and reported in the literature [14]. However, biodegradation is useful for regenerating the absorbent but does not allow the recovery of VOCs as it destroys the organic molecules. On the contrary, recovering VOCs from saturated vegetable oils is possible by flowing N_2 and heating in the temperature range of 100 – 250 °C, as reported in the literature [12,20]. Nevertheless, in case of oil/water emulsions, a previous decanting step is introduced to separate the organic phase from the aqueous one [12]. Regenerating the whole emulsion by flowing nitrogen at a relatively high temperature could be an alternative in order to limit the impact of plant modifications on the wet scrubbing units already installed and minimize the costs and the environmental impact. According to our knowledge, no authors have explored this solution.

In this context, the present study aims at investigating the use of vegetable oil/water emulsions to absorb n-butyl acetate with the goal of identifying a single optimized scrubbing system to remove both hydrophilic and hydrophobic VOCs from the tannery air emissions, thus improving the efficiency of the wet scrubbers currently used in tanning industries. n-butyl acetate was selected because is largely used in leather paints and constitutes around 77% of the hydrophobic organic compounds emitted by the local Leather District of Santa Croce (Pisa, Tuscany, Italy), the most important high-quality leather manufacturing area in Italy [4]. Several studies were carried out on the removal of toluene [18–28], but no papers have been published on the absorption of n-butyl acetate.

In order to further reduce the environmental impact and costs of the absorption process, in this work, waste cooking oil was chosen as the vegetable oil in the emulsion. A commercial corn oil was also used for comparison. Emulsions were prepared with different oil/water ratios in the 0–5 vol% range. The addition of a surfactant (up to 0.8 vol%) was also investigated to improve the oil/water emulsion stability. Static and dynamic absorption tests were carried out to evaluate the Henry's law constant, absorption efficiency, saturation absorption capacity, and absorption time of the various selected absorbents (water, virgin oil, waste cooking oil, emulsions). Given that disposing of VOC-saturated absorbents is a significant problem in industry and a significant limiting factor for industrial application of the absorption technique, the feasibility of the absorbent regeneration was preliminarily investigated. From a circular economy perspective, recovery the VOCs absorbed is desired in order to reuse them in the tannery, e.g. for nozzle washing operations or paints preparations. Thus, in situ regeneration without chemical degradation of VOCs was carried out by stripping with nitrogen at 80 °C. The latter temperature was chosen to obtain a rapid VOC desorption.

2. Materials and methods

2.1. Materials

Two vegetable oils were used: a corn oil (O) purchased from the market, and a waste cooking oil (WCO), furnished by the Physis srl (Pisa, Italy), an environmental services company. Span®80, a nonionic surfactant (sorbitane monooleate), typically used to prepare oil/water emulsions, was purchased from Merck Life Science (Germany). Deionized water was also employed for emulsion preparation and for comparative purposes. n-butyl acetate (Sigma-Aldrich, ACS reagent $\geq 99.5\%$) was selected as representative hydrophobic VOC because of its extensive use in leather painting.

2.1.1. Oil characterization

The oils used were characterized in terms of density, measured at 25 °C by a pycnometer, and dynamic viscosity, determined at 25 °C and 40 rpm using a Brookfield Rotational Viscometer DVII⁺⁺. Fourier Transform Infrared (FT-IR) analysis was performed on the vegetable oils using a Perkin Elmer Spectrum One Spectrometer, in the wavenumber range between 650 and 4000 cm⁻¹ at 4 cm⁻¹ of scanning resolution in attenuate total reflectance (ATR) mode.

2.2. Preparation of emulsions

Water/oil/surfactant emulsions containing 2 or 5 vol% of oil and surfactant (up to 0.8 vol%) were prepared by the following procedure: the desired amount of surfactant, when present, was dissolved in the oil; then the oil phase was added to deionized water, and finally the resulting mixture was placed in a beaker and stirred for 25 min at 4800 rpm by a high shear mixer (Silverson L4R). The beaker was immersed in an ice-bath to compensate for the temperature rise during stirring. The emulsion was considered stable when no visible separation occurred after 2 h from the preparation. Table 1 summarizes the emulsions prepared in this study. The emulsions were labelled as follows: type of oil – vol% of oil – vol% of surfactant; thus, WCO-2-0.2 is the emulsion containing 2 vol% of WCO and 0.2 vol% of surfactant.

2.3. Determination of Henry's law constant

The Henry's law constants of n-butyl acetate (BA) in the oils (O and WCO) and Span80 were determined using the setup reported in Fig. 1. A small quantity of BA, from 50 to 200 µL, was injected by a syringe into a 4 L round bottom flask equipped with a thermometer, containing 5 mL of oil or surfactant at pressure of 1 atm. After about 5 min, BA was completely vaporized. The system was maintained under magnetic stirring for 45 min to ensure that equilibrium conditions were reached. The VOC concentration in the gas phase was measured by a RIKEN KEIKI GX-6000 PID sensor connected to the flask and recorded. During the tests, the temperature was measured and recorded. The time to reach equilibrium was evaluated by monitoring the BA concentration in the gas phase over time.

The Henry's law constant was calculated by Eq. 1:

$$H(\text{atm}) = \frac{P_{\text{VOC}}}{x} \quad (1)$$

where P_{VOC} is the partial pressure of BA in the gas phase (atm) and x is its molar fraction in the liquid phase at the equilibrium. The latter was obtained considering the amount of BA absorbed in the liquid as the difference between the initial and the final BA concentration in the gas phase.

Thermogravimetric analysis (TGA) was also carried out on the oil/surfactant at the end of the test by a thermogravimetric analyser (TA Instrument Q500) to confirm the amount of BA dissolved in the liquid phase at the equilibrium. About 20 mg of oil or surfactant were heated from room temperature to 200 °C, with a heating rate of 10 °C/min

Table 1

List of prepared emulsions.

Label	Water (vol%)	Oil (vol%)	Surfactant (vol%)
O-2	98.0	2.0	0.0
O-2-0.2	97.8	2.0	0.2
O-2-0.5	97.5	2.0	0.5
O-5	95.0	5.0	0.0
O-5-0.5	94.5	5.0	0.5
WCO-2	98.0	2.0	0.0
WCO-2-0.2	97.8	2.0	0.2
WCO-5	95.0	5.0	0.0
WCO-5-0.8	94.2	5.0	0.8

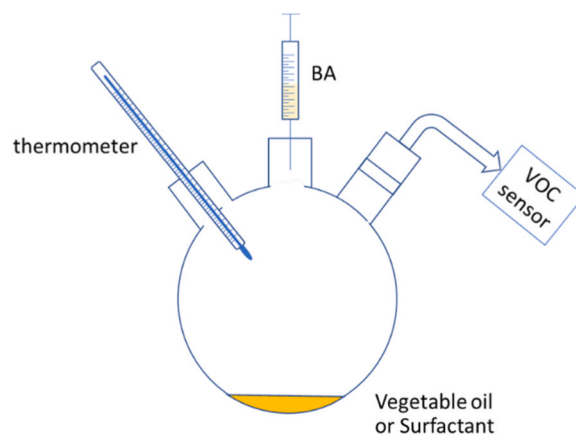


Fig. 1. Setup for Henry's law constant determination.

under nitrogen flow (60 mL/min). The weight of the sample was recorded during the analysis.

The static absorption test could not be used for water and emulsions because the measurement was highly affected by many errors due to the high volatility of water. For this reason, the Henry's constant for water and emulsions were experimentally evaluated by dynamic absorption tests considering P_{VOC} and x at the equilibrium. The experimental H values were compared with the values evaluated using the correlation modified by Darracq et al. [19] (Eq. 2):

$$\frac{1}{H'_{em}} = \frac{\alpha}{H'_{oil}} + \frac{\beta}{H'_{surf}} + \frac{1 - (\alpha + \beta)}{H'_{water}} \quad (2)$$

where H'_{em} is the Henry's law constant of BA in the emulsion expressed in Pa·m³·mol⁻¹, α, β are the volume fractions of the oil and surfactant, respectively, in the emulsion, H'_{oil}, H'_{surf} and H'_{water} are the Henry's law constants of BA in oil, surfactant, and water, respectively. The Henry's law constant of BA in water was obtained from the literature [35].

2.4. Absorption/desorption experiments

Dynamic absorption tests were carried out using O, WCO, water, and oil/water/surfactant emulsions as absorbents. The experiments were performed using the experimental setup reported in Fig. 2. An air stream (3.0 L/min) containing BA at a concentration of 500 ppmv (2.6 g/m³) was fed continuously to a bubbler absorber, filled with 400 mL of absorbent obtaining a liquid head of 17 cm. The air stream was obtained by diluting a primary air stream containing BA with a BA-free secondary air stream, to obtain the desired concentration in the gaseous stream fed to the bubbler. The primary stream was obtained by blowing air, using a diaphragm pump, into a closed flask filled with BA, maintained at 0 °C by using a thermostatic bath. Both the two air streams were preliminarily dried passing through traps filled with a desiccant. A VOC sensor (RIKEN KEIKI GX-6000 PID) was connected to the gas line to measure the BA concentration in the gas stream entering, C_{in} , and leaving, C_{out} , the absorption bubbler.

The absorption tests were stopped when the BA concentration at the outlet equalled the concentration at the inlet, i.e. when equilibrium was reached. After the absorption measurements, the regeneration of the absorbent was conducted by blowing N₂ at 80 °C with a flow rate of 0.6 L/min in the bubbler.

During absorption test, the percent of instant BA absorption efficiency, η , was evaluated by Eq. 3.

$$\eta(\%) = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100 \quad (3)$$

where C_{in} and C_{out} are the BA concentration in the inlet and outlet gas,

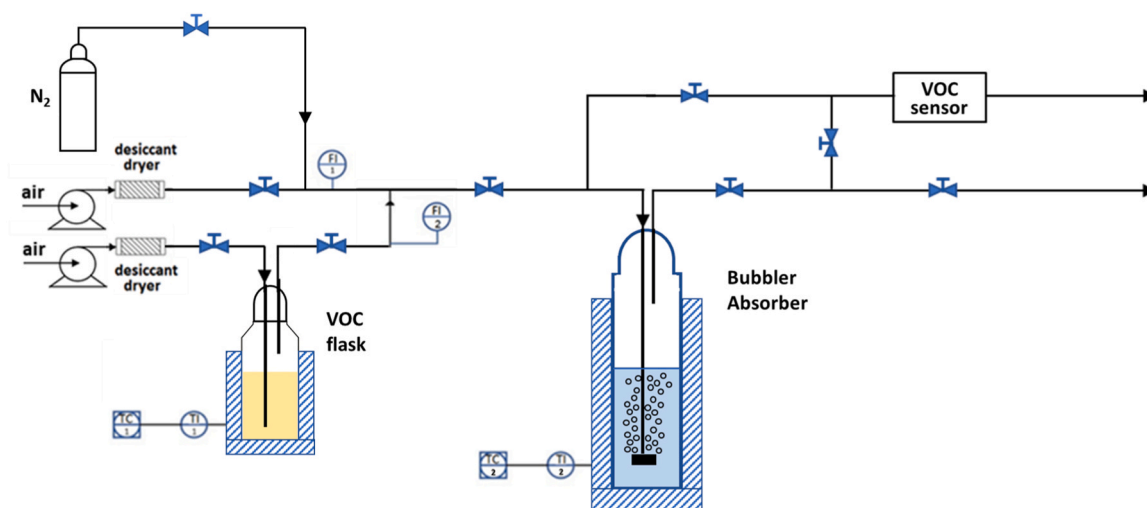


Fig. 2. Layout of the experimental setup used for absorption/desorption tests.

respectively.

The absorption capacity, Q , of the investigated absorbents was determined by the following equation:

$$Q(\text{g/L}) = \frac{F_G \int_0^t (C_{in} - C_{out}) dt}{V_L} \quad (4)$$

where F_G is the gas flowrate ($\text{L}\cdot\text{s}^{-1}$) and V_L is the absorbent's volume (L).

Once the equilibrium has been reached, i.e. the saturation of the absorbent solution, the BA concentration in the gas and in the liquid phase at the equilibrium were used to evaluate the Henry's law constant of BA in water and the emulsions. Two tests were carried out for each absorbent due to the high repeatability of the experiments. The values thus obtained were compared with those reported in the literature (for water) and those calculated for emulsions using the Eq. 2.

3. Results and discussion

3.1. Oil characterization

Table 2 reports the densities and viscosities measured for the vegetable oils used in this study. It is interesting to note that O and WCO showed similar values. WCO had a slightly higher viscosity compared to O, probably related to its composition that is a mix of different vegetable oils, such as peanuts, olives, sunflower with higher viscosity than corn oil [36].

Similar chemical characteristics were confirmed by FT-IR spectra, reported in Fig. 3. As can be observed, the spectra of O and WCO showed the typical peaks of triglycerides: the stretching of the unsaturated CH at 3010 cm^{-1} , CH_3 and CH_2 at 2920 and 2855 cm^{-1} , $\text{C}=\text{O}$ at 1744 cm^{-1} , double bond $\text{C}=\text{C}$ at 1653 cm^{-1} , the bending of CH_2 and CH_3 at 1464 and 1378 cm^{-1} , symmetric and asymmetric stretching of $\text{C}-\text{O}$ at 1237 and 1160 cm^{-1} , and asymmetric bending of CH_2 at 723 cm^{-1} . Analogous results are reported in the literature for FT-IR analysis of edible vegetable oils [37–39]. It is worth noting that the WCO spectrum is almost superimposed to the O one, without changes attributable to the degradation of the waste oil. Only a small difference can be observed for the peaks at 3010 , 1744 , and 723 cm^{-1} related to the numbers of double

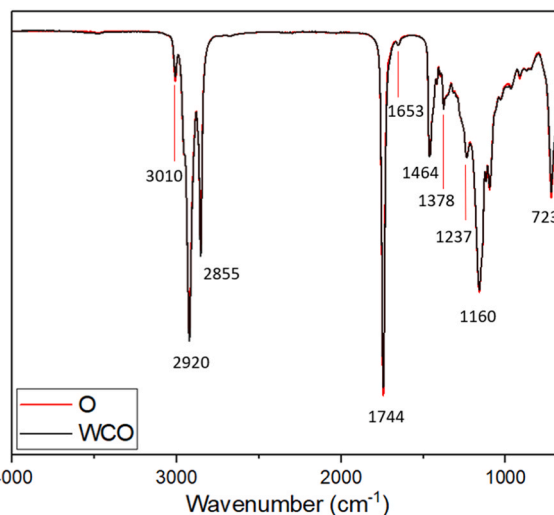


Fig. 3. FT-IR spectra of O and WCO.

bonds, carboxyl groups and skeleton's CH. However, these differences can be ascribed to the composition of the waste oil that is a mixture of different vegetable oils with various unsaturation degrees [39] thus confirming the density and viscosity discrepancy between the two oils reported in the previous table.

From these results, a physical and chemical similarity between the waste oil and the virgin oil, with the absence of significant changes due to degradation phenomena, was observed.

3.2. Henry's law constant

Fig. 4 reports the Henry's law constant, H , of BA in the investigated absorbents. For O, WCO, and Span80, H was obtained from the static absorption tests, and it was found to be 0.0057 , 0.0061 , and 0.0125 atm , respectively, i.e., much lower than for water (about 15 atm). This indicates, as expected, a greater solubility of BA in the organic compounds than in water. The measured values are also smaller than the ones reported by Hariz et al. [12] for toluene in sunflower oil (average value of 0.017 atm) at $21\text{--}24^\circ\text{C}$. Therefore, compared to toluene, BA showed a greater solubility in the investigated vegetable oils. This could be explained considering that BA has a chemical structure similar to oils, being an aliphatic compound containing ester functionality.

It is worth highlighting that the measured value for water (15.9 atm)

Table 2

Densities and viscosities of O and WCO at 25°C .

Property	O	WCO
Density (kg/m^3)	919	916
Viscosity ($\text{Pa}\cdot\text{s}/\text{cP}$)	0.052/52	0.078/78

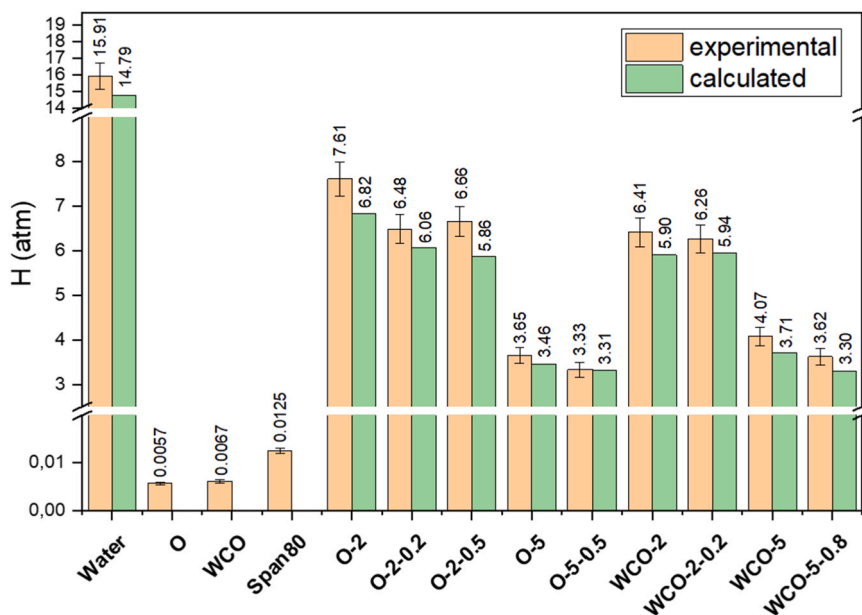


Fig. 4. Henry's law constant for n-butyl acetate in the investigated sorbents measured at 19–22 °C and calculated by Eq. 2.

is in line to what reported in literature [35], confirming the accuracy of the measuring method. As shown in Fig. 4, the experimental values for the emulsions are similar to those calculated by the Eq. 2, proving the higher the volume fraction of the oil, α , the lower the emulsion Henry's constant. This result was expected considering the higher solubility of BA in oil than in water.

3.3. Absorption tests

The absorption curves of the investigated absorbents are reported in Fig. 5. As shown, water reached the saturation more rapidly than the other absorbents: after 60 min the outlet BA concentration was equal to 95% of the inlet concentration. In the case of emulsion with 2 and 5 vol % of oil, a C_{out}/C_{in} ratio of 0.95 was reached after 155 and 235 min, respectively. More than 20 h were required by oils to reach the 95% of saturation conditions. Thus, oil/water emulsions containing 2–5 vol% oil showed better absorption performance than water: the higher the oil content, the greater the performance. These results confirm the smaller value of Henry's constant in the emulsions compared to water.

Fig. 6 reports the instant BA absorption efficiency as a function of

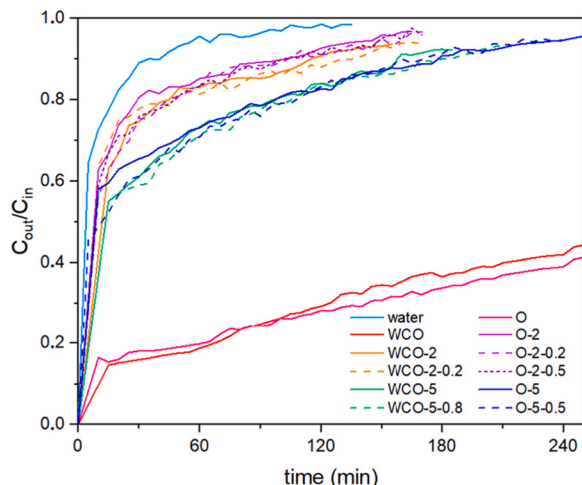


Fig. 5. Curve of BA absorption in water, oils, and emulsions.

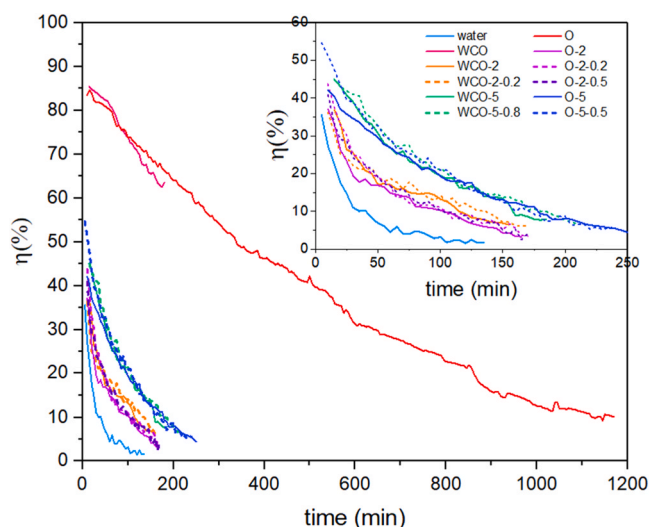


Fig. 6. Absorption efficiency as a function of time for water, O, WCO, and emulsions.

time derived from the absorption curves. As can be noted, the instant efficiency of all absorbents decreased over time due to the gradual saturation of absorbent solution that leads to the progressive reduction of the driving force in BA mass transfer. The driving force is related to the difference between the BA concentration in the gas phase and in the liquid phase. As the absorption continued, the inlet concentration in the gas flow remained constant, on the contrary, the BA concentration in the absorbent progressively increased. The presence of surfactant up to 0.8 vol% had no effect in terms of improving the absorption efficiency. As shown, pure water had lowest absorption efficiency and shortest saturation time for BA. So, water is not a suitable absorbent for BA but the presence of 5 vol% of oil significantly improved the absorption performance. Therefore, WCO-5 emulsion results a very attractive absorbent, in place of water, for controlling air emissions containing BA as in the tanning industries.

Fig. 7 reports a comparison of the absorption capacity, Q , calculated at the equilibrium according to Eq. 4. Under the testing conditions (BA concentration of 2600 mg/m³), O and WCO showed BA absorption

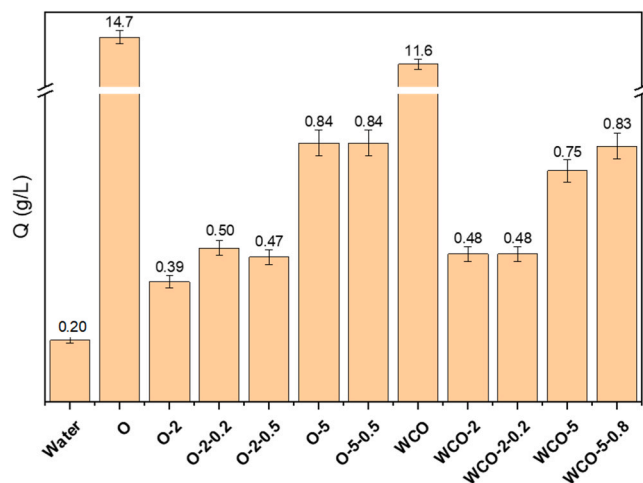


Fig. 7. Absorption capacity of BA in water and emulsions.

capacity of 14.7 and 11.6 g/L, corresponding to 16.0 and 12.6 mg/g, respectively. These values are higher than those reported by Zhu et al. [22] for toluene. The authors obtained saturation concentrations between 1.56 and 7.15 mg/g with vegetable oil used for the treatment of air containing toluene at concentrations between 1000 and 10,000 mg/m³. These high Q values are in accordance with the low Henry's constants measured for O and WCO demonstrating a greater absorption capacity of the vegetable oils toward BA than toluene. This is an important finding for the use of the vegetable oils as absorbents in tanning industries given that, as already mentioned, a major part of hydrophobic solvents is represented by BA [4]. It is worth highlighting that WCO showed comparable absorption performance compared to the fresh oil. The use of a waste oil in place of a virgin oil offers advantages in both economic and environmental terms reducing the operating costs of BA abatement system and it does not create competition with food supply chain. As shown, the presence of 2 and 5 vol% of oil (O or WCO) increased the absorption capacity of pure water from 0.2 to around 0.48 and 0.82 g/L, respectively. It is worth noting that, neglecting the absorption contribution of the water, the concentrations of the absorbed VOC are about 2–2.5% and 4.5–5% of the absorption capacity of the pure oil, respectively, similar to the volume fraction of the oil in the emulsions. This indicates that the majority quantity of n-butyl acetate was absorbed by the oil fraction. The type of oil used had no effect on the absorption capacity of the emulsion. It is interesting to observe that the presence of the surfactant (up to 0.8 vol%) led to a slight improvement in the early stages of the absorption test, but it does not affect the overall absorption capacity of the emulsion. The use of Span80 is recommended when the stabilization of the emulsion is needed during the process to avoid phase separation; however, the lack of a surfactant is desirable to facilitate the separation, regeneration, and recycle of both emulsion components. In fact, the emulsions prepared without surfactant, at the end of the absorption test, tend to demulsify after less than an hour as shown in Fig. 8 for WCO-5.

An additional analysis was carried out on some saturated emulsions without surfactant to estimate the distribution of the BA between the two phases. At the end of the absorption test, the emulsion was kept in stagnant condition to demulsify and segregate forming two distinct phases, the supernatant oil phase was then separated from the water and analysed by TGA to quantify the BA concentration. As an example, Fig. 9 shows the thermogram of the BA-saturated oily fraction deriving from the WCO-2 emulsion and the one of the pure WCO. The TG curve of the saturated oil shows a small weight loss (around 2%) from 50 to 110 °C, not present in the TG curve of WCO, attributable mainly to the desorption of BA, followed by a large degradative event in the temperature range of 200–500 °C related to the thermal degradation of the

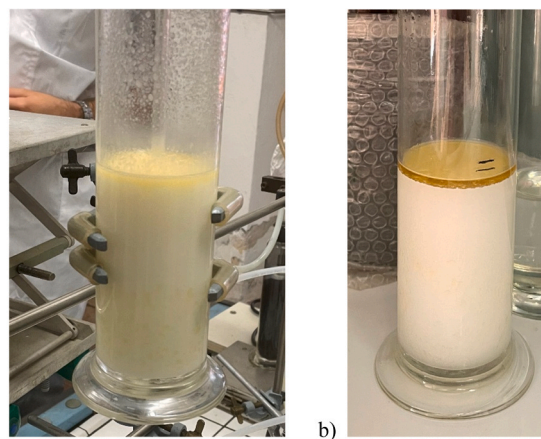


Fig. 8. Photos of WCO-5 emulsion immediately after absorption in bubble column (a) and after an hour left in stagnant condition (b).

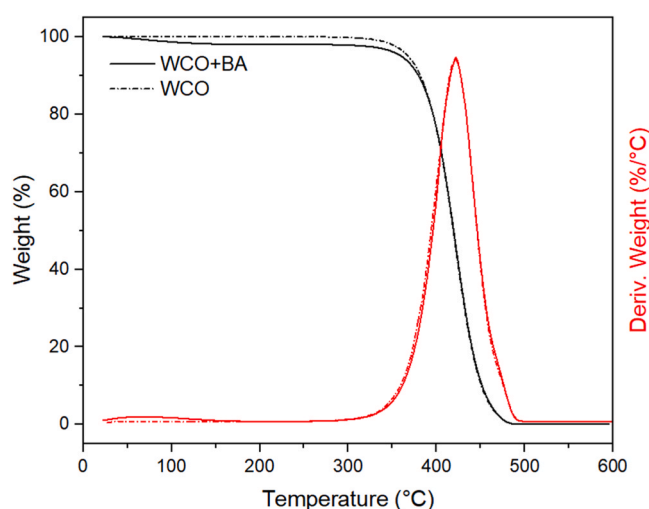


Fig. 9. TG (black) and DTG (red) curves of the oily fraction of WCO-2 after absorption and WCO.

triglyceride. Considering the quantity of BA desorbed and the weight of the sample analysed, the estimated concentration of BA in the oil was 18 g/L. This confirms that BA is mainly present in the oily phase being preferentially absorbed by non-polar compounds.

3.4. Absorbent regeneration

TGA analysis of the BA-saturated WCO, above reported in Fig. 9, suggested that BA could be removed from the oily phase by heating. As shown, the BA desorption occurred in the temperature range from 50 to 110 °C, with a peak rate at about 80 °C. Based on this result, preliminary tests were carried out to evaluate the feasibility of the in situ regeneration of the emulsions by flowing nitrogen at 80 °C. As example, the results of absorption in WCO-5 under an air flowrate of 3.0 L/min containing 500 ppmv BA followed by desorption under a nitrogen flowrate of 0.6 L/min at 80 °C are reported in Fig. 10. Comparing the absorption BA capacity (Q) with the desorbed amount, an almost complete emulsion regeneration was obtained. As expected, the nitrogen flow downstream of the desorption phase had an average BA concentration three times higher than that of the air flow fed in the absorption phase. The desorption tests demonstrated the feasibility of a complete regeneration of emulsions using nitrogen flow heated at 80 °C.

Subsequent recovery of the VOCs could be performed by removing BA from the nitrogen stream by condensation at low temperatures. The

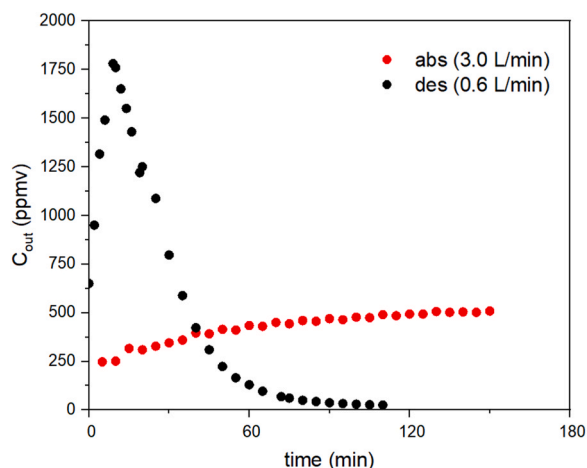


Fig. 10. Results of absorption (air flow rate of 3.0 L/min, 22 °C, 500 ppmv BA) (red) and desorption (nitrogen flow rate of 0.6 L/min, 80 °C) (black) in WCO-5.

condensate will contain a mix of VOCs and water that could be reused in the tannery, for example, for machinery clean operations. In this work, the desorption tests were carried out at 0.6 L/min, which was one-fifth of the flow rate used during the absorption. This flowrate value was the lowest one permitted by the used setup, in particular, it was related to the sensitivity of the VOC sensor used. However, in the real plant lower flow rates would make it possible to obtain currents more concentrated in VOC thus increasing the quantity of BA that can be recovered by condensation. It is worth noting that low flow rates at high VOC concentrations are recommended to reduce the energy cost per mass of condensed VOC. In fact, the condensation method for VOC recovery is simple to operate but consumes large amounts of energy and has high operating costs. For this reason, it is used for low flow rates of waste gases at high VOCs concentration.

In view of the treatment of smaller volumes of sorbents, a first separation between the organic and the aqueous fractions would be an alternative option. In this context, novel 3D air-superhydrophobic/superhydrophilic diatomite porous ceramics could be employed to separate oil/water emulsions even in the presence of a surfactant [40, 41]. In this way, the stripping operation could be limited to the oily phase in which BA is concentrated with the advantage of managing much smaller volumes of absorbent and the possibility to recover BA condensate with virtually no water. However, this option will require significant changes in the already existing equipment with consequent increase of investment and operating costs. On the contrary, the proposed in situ regeneration of the entire emulsions will have a low impact on the costs and plant layout, also avoiding issues related to the management of VOC-saturated absorbers.

4. Conclusions

In this study, the use of vegetable oil/water emulsions as absorbents in place of water, was investigated to improve the efficiency of the currently used wet scrubbers as VOCs abatement systems adopted by the tanning industries. The n-butyl acetate was selected as representative hydrophobic VOC because is the typical hydrophobic solvent used in the leather finishing products. Two vegetable oils were investigated: a commercial corn oil (O) and a waste cooking oil (WCO). The use of Span80 as a surfactant was also evaluated to improve the emulsions stability. Emulsions with 2 and 5 vol% of oil, with and without the surfactant (up to 0.8 vol%), were prepared and tested at room temperature in a bubbler using an air flowrate of 3.0 L/min at BA concentration of 500 ppmv. Compared to water, all the emulsions showed lower Henry's constants and, consequently, higher absorption efficiency and capacity thus demonstrating that oil/water emulsions could be

absorbents more suitable than water for the VOCs abatement of tannery air emissions. The presence of 5 vol% of oil (O or WCO) increased the absorption capacity of water from 0.20 to 0.82 g/L. Moreover, the type of oil used, virgin or waste cooking oil, as well as the presence of the surfactant did not affect the absorption performance of emulsion. Thus, the use of a waste oil instead of virgin oil is recommended as it allows to reduce operating costs and does not create competition with food uses. In addition, due to the huge amount of waste cooking oil produced every year, find another industrial application for this material will enhance the circular economy. Preliminary desorption tests by hot stripping with N₂ confirmed the feasibility of a in situ complete regeneration of emulsions followed by BA recovery. However, given the preferential distribution of BA in the oily fraction, an initial separation of the two phases, oily and aqueous, could be performed to treat much lower volumes and to recover pure BA condensate.

In conclusion, vegetable oil/water emulsions were found to be suitable sorbents for the treatment of the tannery air emissions. Moreover, they could be easily applied in place of water in the already existing VOC abatement systems thus not requiring significant costs and/or changes in the equipment.

CRediT authorship contribution statement

Elisabetta Brunazzi: Methodology, Supervision, Writing – original draft, Writing – review & editing. **Miriam Cappello:** Data curation, Investigation, Writing – original draft, Writing – review & editing, Formal analysis, Validation, Conceptualization. **Maurizia Seggiani:** Funding acquisition, Supervision, Writing – review & editing, Conceptualization, Methodology, Resources, Validation, Writing – original draft. **Damiano Rossi:** Formal analysis, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

The authors would like to thank the Tuscany Region that has provided the financial support of the project VOC TAN (Volatile Organic Compound abatement system in TANnery environment) through the fund POR FESR 2014 – 2020 (Bando 2) [Grant number: 3553.04032020]; the European Union for the financial support of the project ReVoc4LIFE (Pilot plant for Recovery of VOCs by reversible adsorption on sintered granulate from sewage sludge treatment) under the LIFE 2020 research programme [Grant number LIFE20 ENV/IT/000688]; the Ministry of University and Research (MUR) as part of the PON 2014–2020 “Research and Innovation” resources – Green Action - DM MUR 1062/2021 - Title of the Research: From waste to resource: “zero waste” industry. Moreover, thanks go to SPIN-PET srl (Pisa, Italy) for the support in choosing the surfactant and emulsions formulations. Finally, the authors would like to thank Simona Morano for conducting the absorption and desorption tests.

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