



Fatty acid extraction from sewage sludge using a porous polyethylene sorbent obtained from agricultural covers

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ABSTRACT

Fatty acids from a sewage sludge of a wastewater treatment plant were extracted using a porous polyethylene (pPE) material prepared using agricultural plastic films. The pPE fatty acid extraction profile and yield from the sewage sludge was compared to toluene as extraction solvent. The chemical composition of the extracted fatty acids were the same in both cases, but when the extraction yield was normalized by the used mass of pPE or toluene, pPE resulted six times more efficient than toluene.

The pPE bulk density and porosity obtained using different biodiesel:vegetable oil mixtures ranged between 0.24 g cm^{-3} – 0.40 g cm^{-3} and 58–74%, respectively. Critical surface tension of the pPE was $(26.9 \pm 1.8) \text{ dyn cm}^{-1}$ while for the original polyethylene film it was $(19.9 \pm 3.1) \text{ dyn cm}^{-1}$. Biodiesel and oleic acid were used as models of hydrophobic substances for extraction studies. pPE Maximum sorption capacities were: $6.8 \text{ g biodiesel g}^{-1} \text{ pPE}$ and $9.7 \text{ g oleic acid g}^{-1} \text{ pPE}$. Sorption capacity remained practically constant after ten biodiesel sorption/extraction cycles. Pesticide (trifluralin) residues in the pPE were analyzed to assure that xenobiotic presence can be removed during the manufacturing process, finding that less than 0.84% of an initially present pesticide remained in the pPE.

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1. Introduction

Sewage sludge is an important organic stream originated in the treatment of wastewater (Zhang et al., 2018), mainly constituted by water and suspended and dissolved inorganic and organic compounds. Lipids, in particular fatty acids (16:0, 18:0, 18:1, 18:2) and sterols (Quéménéur and Marty, 1994), are prevalent in the organic phase. Although suspended lipids can be removed by flocculation, chemically or physically stabilized lipid/water emulsions demand more complex physicochemical processes for their elimination (Chen et al., 2017). The lipid treatment in the wastewater currents is an important task that may affect aerobic and anaerobic steps down stream. Decrease of their content is necessary because of their contribution to the biological (BOD) and chemical (COD) oxygen demands on the final effluent (Chipasa and Medrzycka, 2006).

An alternative to the lipid extraction from wastewater currents is the biogas production by digestion of the sewage sludge (Budzianowsky, 2016). In particular, the environmental impacts and the economic and energetic requirements for biogas production from sewage sludge have been analyzed for the Argentinean case (Morero et al., 2017).

In an entirely distinct environmental scenario and related to a different waste stream, horticulture and floriculture make significant use of important quantities of plastics with the purpose of microclimate (Tarara, 2000), weeds and insects (McKenzie et al., 2001) regulation. These plastic covers are mainly employed in the construction of greenhouses and as a method of soil mulching. In our previous work, we reported the presence of plastic residues in the horticultural soil of small production units, in amounts equal to 10% of the soil area (Ramos et al., 2015; Supplementary Material, Fig. I-SM). We have shown that these plastics can affect the pesticide environmental fate. It has also been reported, for the case of horticultural tomato productions, that the residual mulch film incorporated into the soil can retard tomato plant growth and diminish fruit yield and quality (Zou et al., 2017).

Agricultural plastic waste reprocessing may be a difficult task (Briassoulis et al., 2012), mainly because of the potential dirt residues in the used film and the consequent additional cleaning steps required. Recycling costs could be higher than the new material. However, some efforts have been directed to the recycling of agricultural covers (Cizravi et al., 1989; LabelAgriWaste, 2006–2009; Briassoulis et al., 2012).

Some concern has been settled about agricultural plastic reuse because of the potential xenobiotic presence in this material. It has been pointed out that greenhouse and mulching covers can be exposed to important amounts of pesticides (Querejeta et al., 2012). In the same sense, recent reports alert about phthalic esters presence in Chinese

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soils (Zhang et al., 2015) and vegetables that were in contact with plastic mulching (Wang et al., 2015).

Taking into account the environmental impact caused by the hydrophobic organic matter present in urban wastewater treatment plants and the environmental and productive drawbacks produced by the plastic residues incorporated in horticultural soils, the general objective of this work is to evaluate the performance of a porous polyethylene (pPE), prepared from a potential waste stream of agricultural plastics, as sorbent of fatty acids present in the stream of a wastewater treatment plant. The specific objectives are: (a) to prepare a porous hydrophobic sorbent material (pPE) from agricultural plastics; (b) to study the pPE capability for the extraction of fatty acids from a sewage sludge; (c) to evaluate the elimination of potential pesticide contamination present in the plastic cover during the preparation procedure of the pPE; (d) to characterize the dependence of some physical pPE properties (density, porosity, critical surface tension) on critical procedure variables (solvent mixtures, plastic aging); and e) to kinetically and thermodynamically characterize the pPE as sorbent of hydrophobic substances (fuel and fatty acids).

2. Experimental

2.1. Materials and equipments

PE films of 100 μm thickness with an unknown percentage of ethylene-vinyl acetate (EVA) were purchased from Termoagro® (Argentina). The following reactants and solvents were employed as purchased: acetone (Sintorgan, ACS, Argentina), 96% ethanol (Wisconsin, technical grade, Argentina), ethyl acetate (Dorwil, p.a. grade, Argentina), glacial acetic acid (HPLC grade, Dorwil, Argentina), hexane (Dorwil, p.a. grade, Argentina), oleic acid (Wisconsin, technical grade, Argentina), toluene (Anedra, ACS, Argentina). Trifluralin (α,α,α trifluoro-2,6-dinitro-*N*, *N*-dipropyl-*p*-toluidine, CASRN [1582-09-8]) was purified from commercial product Trigermin® (CS, 48% w/v, Cheminova, Argentina). Biodiesel was purchased from the Municipal Biodiesel Plant of Malvinas Argentinas district, Buenos Aires province, Argentina. Commercial sunflower oil (Cocinero®, Argentina) was employed as vegetable oil. Sewage sludge samples were provided by AySA, from the Berazategui plant (34°41'55.3"S 58°16'25.5"W), Buenos Aires province (Argentina).

Chromatographic measurements were done using a Perkin-Elmer gas chromatograph Clarus® 680 equipped with auto-injector and mass spectrometer quadrupole detector Clarus® SQ8T (USA) and a Perkin-Elmer gas chromatograph Autosystem XL® equipped with auto-injector and flame ionization detector (USA). Spectrophotometric determinations were performed with a Perkin-Elmer lambda 25 UV-vis spectrophotometer (USA). For contact angle studies an in-house goniometer using a digital microscope BW-788 and the ImageJ software were employed. For SEM images a Quanta Scanning Electron Microscope (FEG 250, Thermo Fisher Scientific, USA) was used.

2.2. Preparation of the porous polyethylene

A 250 mL beaker, containing 20.0 g PE film cut down into 0.5 cm \times 0.5 cm pieces and 80.0 g biodiesel:vegetable oil (bd:vo) mixture at different mass ratios, was gradually heated using external stirring until complete homogenization (130–220 °C, Fig. II-SM). The melt was poured into an extruder at roughly the same temperature, and 1 mm diameter filaments were recovered. The bd:vo mixture occluded in the filaments was then extracted in a Soxhlet using hexane as solvent (250 mL of hexane/80 g material, 5 h reflux). In all

cases the extracted amount of bd:vo in the hexane phase was determined and compared to the initially used amount. The recovery percentages were $108 \pm 5\%$. In order to eliminate the remaining hexane, the obtained pPEs were dried at room temperature in a hood until constant weight.

2.3. Lipid extraction from sewage sludge

2.3.1. Extraction using pPE

A portion of sewage sludge (circa 50.0 g) was diluted with 50 mL of distilled water in a 125 mL Erlenmeyer flask. The sludge was dispersed by magnetic stirring and 1.00 mL of 98% H_2SO_4 was poured. The mixture was heated at $50^\circ\text{C} \pm 2^\circ\text{C}$ (temperature controlled by an electronic thermometer) and 2.07 g of pPE filaments were added. This system was stirred for 24 h at $50^\circ\text{C} \pm 2^\circ\text{C}$.

Afterwards, the filaments were retrieved with tweezers and rinsed with distilled water in order to eliminate any excess of entrapped solids. Sorbed lipids were extracted in a Soxhlet using ethyl acetate as solvent (100 mL of ethyl acetate, 5 h reflux). Ethyl acetate was then rotary evaporated.

2.3.2. Extraction using toluene

A portion of sewage sludge (circa 50.0 g) was diluted with 25 mL of distilled water in a 125 mL Erlenmeyer flask. The sludge was dispersed by magnetic stirring and 1.00 mL of 98% H_2SO_4 was poured. The mixture was heated at $50^\circ\text{C} \pm 2^\circ\text{C}$ (temperature controlled by an electronic thermometer) and 50 mL of toluene were added. This system was stirred for 24 h at $50^\circ\text{C} \pm 2^\circ\text{C}$.

Afterwards, the system was centrifuged, retrieving the supernatant organic phase. This phase was washed with distilled water (2×10 mL). The original aqueous phase was extracted again with toluene (2×10 mL). All toluene phases were gathered, dried with anhydrous Na_2SO_4 , filtered and rotary evaporated.

2.3.3. Fatty acid derivatization

Extracted lipids (see Sections 2.3.1 and 2.3.2) were dissolved in a mixture of 40 mL of methanol, 20 mL of hexane, and 1.00 mL of H_2SO_4 98%. The mixture was heated for 3 h under constant reflux. Then, the supernatant was centrifuged and extracted with hexane (3×20 mL). The hexane phase was washed with distilled water (2×10 mL) and NaHCO_3 1% (2×10 mL). Finally, this organic phase was dried with anhydrous Na_2SO_4 , filtered and rotary evaporated.

2.3.4. Fatty acids methyl esters (FAMES) analytical methods (GC-MS, GC-FID)

A GC-MS system was used for FAMES and hydrophobic molecules identification. Ionization energy was set at 70 eV, with inlet and ion source temperature at 180 °C and 150 °C, respectively. The capillary column employed was a Perkin-Elmer Elite-5MS (30 m \times 0.25 mm \times 0.25 μm). Injection was performed in a 50:1 split mode, using He at 1 mL min^{-1} . The oven was initially set at 130 °C for 1.50 min, and then gradually heated at 40.0 °C min^{-1} up to 185 °C. Then, it was slowly heated at 5.0 °C min^{-1} up to 240 °C. Finally, the heating was increased to 40.0 °C min^{-1} up to 300 °C, which was maintained for 3.00 min.

For the fatty acid methyl esters quantitation a GC-FID equipment was used. Detector temperature was set at 300 °C. A Perkin-Elmer Elite-5MS (30 m \times 0.25 mm \times 0.25 μm) capillary column was employed. Injection was performed in splitless mode, using N_2 at 30.0 psi. The oven was initially set at 130 °C for 1.50 min, and then gradually heated at 40.0 °C min^{-1} up to 185 °C. Then, it was slowly heated

at $5.0^{\circ}\text{C min}^{-1}$ up to 240°C . Finally, the heating was increased to $40.0^{\circ}\text{C min}^{-1}$ up to 300°C , which was maintained for 5.50 min.

2.4. Trifluralin migration during pPE preparation

A pesticide (trifluralin) mass balance along the pPE preparation process was performed. With this purpose, two PE plastic film sections of 20.0 g each were rinsed with 10.00 mL of trifluralin solution (3022 ppm) in acetone. The PE films were dried for 30 min (room temperature) and cut down into $0.5\text{ cm} \times 0.5\text{ cm}$ pieces. The pretreated PE (20 g) was dissolved in a 250 mL closed Erlenmeyer flask as indicated in Section 2.2. The mixture was extruded as usual and the recovered filaments were stored at 4°C until use.

A portion of the filaments was dissolved in hot toluene. The trifluralin concentration was spectrophotometrically determined by the method of the first derivative (see Supplementary Material, Fig. III-SM). On another different filament portion, the original bd:vo mixture was extracted with hexane in a Soxhlet apparatus and the trifluralin content was spectrophotometrically determined by the method of the first derivative (see Supplementary Material, Fig. IV-SM), both in the bd:vo mixture and in a portion of the extracted filaments by dissolution in hot toluene (see Supplementary Material, Fig. V-SM). Mass balance of trifluralin throughout the entire process was thus established (see Table III-SM, Supplementary Material) as shown in Fig. 2.

2.5. pPE characterization

2.5.1. Density

The following bd:vo ratios were considered for the preparation of pPE: 0:100, 20:80, 50:50, 80:80 and 100:0. The required temperature for homogenizing each mixture was recorded (Fig. II-SM). Each melt

was casted into three similar circular metal molds, and cooled down overnight at room temperature. The bd:vo mixtures were extracted as indicated in Section 2.2. The circular casts were weighted; their volume measured by means of a Vernier caliper, and density was calculated. pPE test pieces were also prepared using PE films kept outdoors during 30, 60, and 1000 days (bd:vo composition 50:50). Density was determined as above. All experiments were done in triplicates (see Table II-SM, Supplementary Material).

2.5.2. Calculated total porosity

Porosity of the pPE test pieces (whether kept outdoors or not) prepared in Section 2.4.1 was determined. Porosity (ϕ) was calculated according to the following equation:

$$\phi = \frac{V_{\text{void}}}{V_{\text{total}}} = \frac{\rho_{\text{PE}} - \rho_{\text{pPE}}}{\rho_{\text{PE}} - \rho_{\text{air}}} \approx 1 - \frac{\rho_{\text{pPE}}}{\rho_{\text{PE}}}$$

where V_{void} is the volume of the void-space contained inside the pPE, V_{total} is the total cast volume, ρ_{PE} is the density of polyethylene (0.96 g/cm^3), ρ_{pPE} is the pPE density, and ρ_{air} is the density of the air enclosed within the pores (considered negligible). All experiments were done in triplicate (see Table II-SM, Supplementary Material).

2.5.3. Critical surface tension

Critical surface tension was estimated using the Zisman method (Zisman, 1964). Contact angle of water:ethanol and water:acetic acid solutions on pPE and PE were obtained using an in-house goniometer. Surface tension of the solutions was obtained from literature (Lide, 2003).

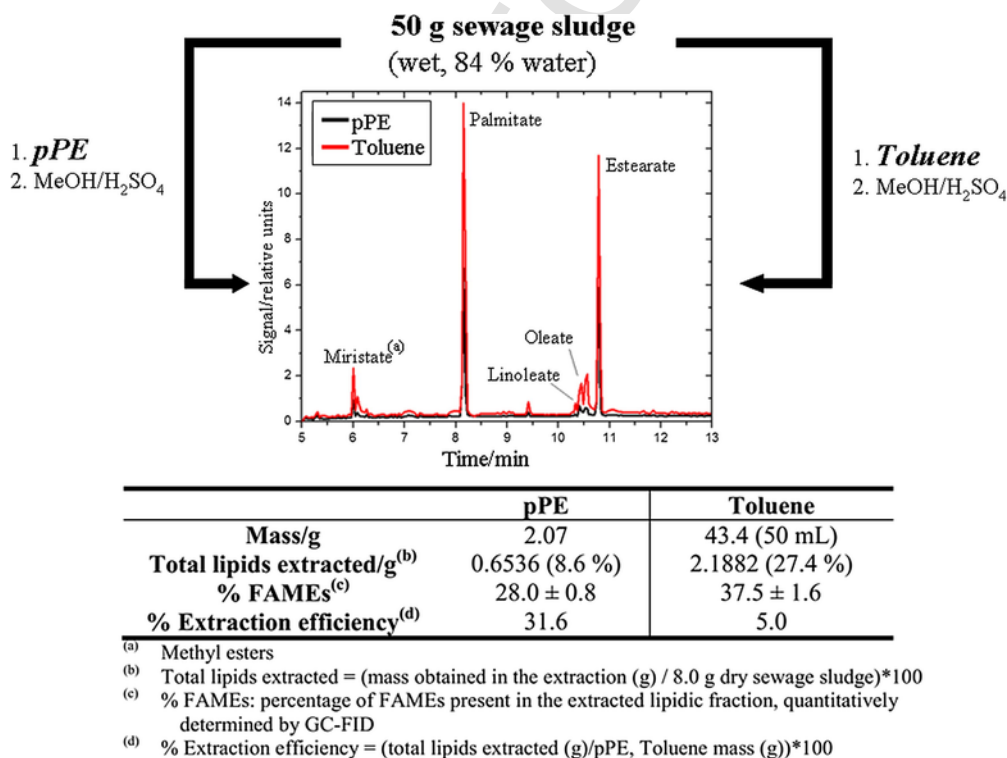


Fig. 1. GC-MS profiles and extraction efficiency of the lipids from the sewage sludge using pPE and toluene.

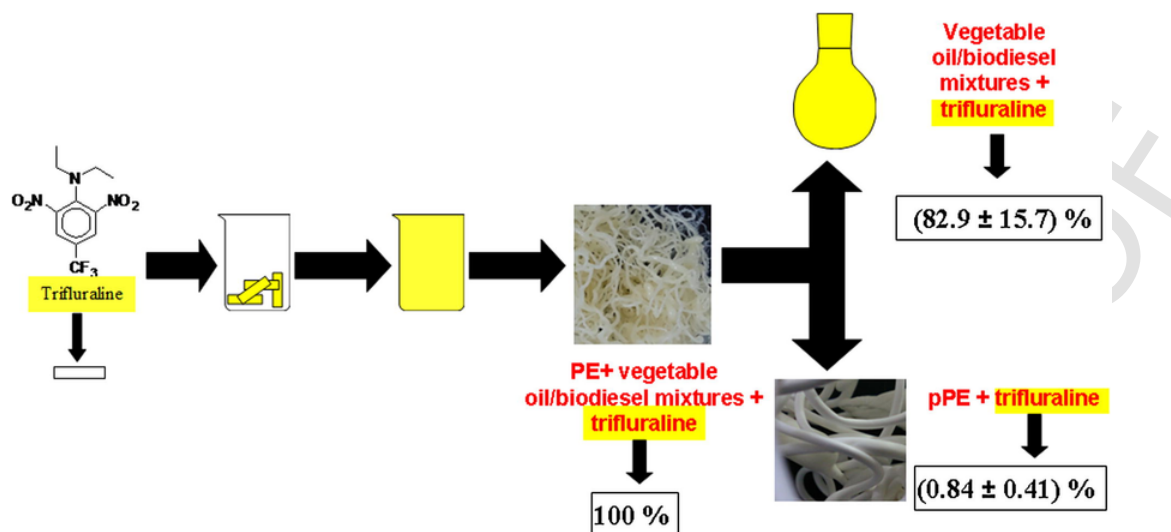


Fig. 2. Trifluralin mass balance in the migration experiments from PE covers to pPE.

2.6. Kinetic experiments

2.6.1. Biodiesel sorption kinetics

Eighteen closed flasks of 30 mL were filled with 0.16 g of biodiesel and 30 mL of distilled water and an emulsion was achieved through sonication. Then, 0.2 g of pPE filaments were added to each flask and the set was stirred in an orbital shaker for 0, 15, 30, 60, 90, and 120 min. At each time three flasks were removed, and the biodiesel was extracted from the pPE using hexane (3×20 mL). The extracts (organic solution) were dried with anhydrous Na_2SO_4 and concentrated using a rotaevaporator. All the experiments were repeated by triplicate using 2.0 g of biodiesel.

2.6.2. Oleic acid sorption kinetics

Eighteen closed flasks of 30 mL were filled with 0.16 g of oleic acid and 30 mL of distilled water and an emulsion was achieved through sonication. The pH was adjusted (3 and 5) with HCl or NaOH solutions for each experiment. Then, 0.2 g of pPE filaments were added and the system was stirred in an orbital shaker for 0, 10, 20, 30, 60, and 90 min. At each time the pPE was removed from three flasks, the remaining oleic acid emulsion was acidified, extracted with ethyl acetate (3×20 mL), dried with anhydrous Na_2SO_4 and rotary evaporated. The obtained oleic acid was weighted. All measurements were done by triplicate.

2.7. pPE-Oleic acid isotherm

A set of 30 mL closed flasks were filled with oleic acid and water in different proportions (from 0.16 g to 5 g of oleic acid in 30 mL of water) and emulsion was achieved through sonication. The pH was adjusted to 5 with HCl or NaOH solutions for each experiment. Then, 0.2 g of pPE filaments were added to each flask and the set was stirred in an orbital shaker for 72 h. The pPE was removed and the remaining oleic acid was acidified, extracted with ethyl acetate (3×20 mL), dried with anhydrous Na_2SO_4 and rotary evaporated. The oleic acid mass was weighted. The sorbed oleic acid was extracted from the pPE with hexane in a Soxhlet extractor. The extract was dried with anhydrous Na_2SO_4 and the solvent was rotary evaporated. The mean mass balance of oleic acid for all the experiments was $86 \pm 9\%$.

2.8. Practical sorption amount (PSA) measurements

A 50 mL flask was filled with 30 mL of biodiesel and 0.2 g of pPE filaments. The system was stirred for 20 h, then the filaments were retrieved and the sorbed biodiesel was extracted with hexane in a Soxhlet apparatus. The remaining biodiesel in the flask was weighed, as well as the extracted filaments. This process was repeated ten times. PSA (Lin et al., 2010) is calculated according to the following equation:

$$PSA = \frac{m_s}{m_{pPE}}$$

where m_s is the mass of sorbed biodiesel in g, and m_{pPE} is the mass of pPE in g. All experiments were done in triplicate.

3. Results and discussion

3.1. pPE preparation

One of the objectives of this work was to study the potential recycling of agricultural plastic films employing a dissolution process. This strategy was selected taking into account that xenobiotics (pesticides, phthalic esters), potentially present in agricultural plastics, could be separated from the plastic matrix by this process. PE was dissolved in variable proportions of biodiesel and vegetable oil. This mixture was chosen considering the easy availability and high flash points of its components, compared to common low molecular weight organic solvents. Small pieces of an agricultural plastic cover (for normalizing the experiments, new 100 μm clear PE + EVA films were employed) were dissolved in a mixture of biodiesel (bd) and vegetable oil (vo) in variable proportions. When less than 10% (m/m) of PE was used in the bd:vo mixture, an unstructured plastic phase in the form of powder was obtained (Table I-SM, Supplementary Material). For PE percentages between 10% and 30%, well defined plastic solids occluding the bd:vo phase were obtained except for the mixture 10% PE - bd:vo 0:100 (Table I-SM, Supplementary

Material). For the rest of the experiments a fixed PE percentage of 20% was employed.

The effect of varying the bd:vo proportion was studied. It was observed that mixtures richer in vegetable oil required higher dissolution temperatures (step 1, Fig. II-SM). The PE/bd:vo mixture was transferred in hot to an extruder to obtain ca. 0.5–1 mm diameter filaments (step 2, Fig. II-SM). These filaments occluded the bd:vo mixture which was extracted using a Soxhlet apparatus with hexane as solvent (step 3, Fig. II-SM). The porous polyethylene (pPE, Fig. II-SM) obtained in this way was dried at room temperature to evaporate the hexane.

3.2. Lipid extraction of a sewage sludge using pPE

The pPE lipid extraction capacity was studied using sewage sludge from a waste water treatment plant. With this purpose, two parallel experiments were done: the same amount of sewage sludge, (see Sections 2.3.1 and 2.3.2) at 50°C and pH circa 1–2 was exposed in different erlenmeyers to pPE (2.07 g) and toluene (43.4 g, 50 mL) for 24 h. This set of experimental parameters did not represent optimized extraction conditions but a combination of possible scalable operative variables. In the case of toluene, phase separation was difficult because there was no clear interphase, so a centrifugation step was necessary.

The lipid fractions obtained (considered as total lipids extracted, Fig. 1) from pPE and toluene were derivatized using methanol in acidic media (see Section 2.3.3) and their content was analyzed by GC–MS (see Fig. 1). It is interesting to observe that in both cases the chromatographic profile was similar (Fig. 1), being the main components fatty acids methyl esters (palmitate methyl ester, estearate methyl ester, oleate methyl ester). Other lipidic components, like steroids derivatives probably coming from sterols elimination together with minor amounts of dioctyl phthalate (see GC–MS qualitative characterization of the extracted lipids, Supplementary Material) were also identified in the GC–MS analysis. The fatty acid methyl esters were quantitated in the lipidic fraction extracted (Fig. 1) finding (28.0±0.8)% in the pPE case and (37.5±1.6)% in the toluene extraction.

When the extracted lipid masses from pPE and toluene were normalized using the mass of pPE and toluene, respectively, the relative extraction efficiency of pPE (31.6%, Fig. 1) was better than that of toluene (5.0%, Fig. 1).

3.3. Trifluralin elimination along the pPE preparation

Pesticides presence in the agricultural plastic waste is a main concern regarding the use of this material. To evaluate if the plastic dissolution process in bd:vo mixtures could remove pesticide contamination, a pPE preparation procedure was done spiking the initial PE pieces with the pesticide trifluralin (Fig. 2). Trifluralin is a pre-emergence herbicide commonly used in horticulture with a characteristic absorption band in the visible region. This property allows to spectrophotometrically quantify trifluralin in the presence of bd:vo without sample pretreatment procedures (see Supplementary Material, Trifluralin quantitative determination), a required step for other analytical techniques like GC.

The pPE preparation process was done as indicated in the Experimental Section (Section 2.2). The mean trifluralin content (all the procedure was repeated ten times, see Table III-SM, Supplementary Material) in the bd:vo phase was (82.9±15.7) % while the amount found in the pPE filaments was (0.84±0.41)% (Table III-SM) show-

ing an efficient migration of the trifluralin from the plastic cover to the bd:vo mixture (Fig. 2).

3.4. pPE density and porosity

Fig. 3 shows pPE bulk density and total porosity of test pieces of known volume, obtained using 20% PE (new films) and different proportions of bd:vo, extracted as previously described. It is interesting to observe that using higher proportions of vegetable oil, the bulk pPE density diminished, increasing the total porosity circa 75%. Although a lower PE dissolution temperature, like the obtained using 100% biodiesel, is energetically convenient (Fig. II-SM), bd:vo mixtures with vegetable oil ratios higher than 50% yielded lower pPE densities and higher pPE porosities, both desirable pPE properties.

It is known that solar aging can induce chemical and mechanical changes in plastics (Andrady et al., 2011). To study the effect of solar aging of the agricultural plastic on pPE density and porosity, these properties were measured on pPE obtained from PE (20% PE dissolved in bd:vo 50:50) previously exposed to sun (Fig. 3). An increase in the bulk density and a decrease in the total porosity can be observed for longer exposure times. To confirm that this pPE preparation method can be applied to an agricultural plastic waste stream, pPE filaments were obtained using real solarized plastics recovered from an orchard. pPE filament images and their oleic acid sorption capacity are shown in the Supplementary Material (Fig. VIII-SM).

In an attempt to characterize the pPE porous distribution and the total surface area, nitrogen adsorption isotherm of pPE obtained using a bd:vo 50:50 was done (see Fig. VI-SM, Supplementary Material). Unfortunately no hysteresis in the adsorption volume versus relative pressure was observed, indicating possible predominance of macroporous structures. With the same purpose SEM images of bulk and filament pPE surfaces were obtained (Fig. 4). When bulk pPE pieces were prepared using 20% PE (new), bd:vo ratios of 50:50, a regular 1–10 µm porous distribution is observed (Fig. 4A and B). When the same experiments were done using solarized PE a much irregular porous distribution (Fig. 4C and D) was found, possibly as a consequence of the polymer deterioration. Fig. 4E and F show pPE filament structure obtained from new agricultural films. The vertical lines observed in Fig. 4E were generated in the extrusion process. A more complex porous structure of the surface can be seen in Fig. 4E (20 µm amplification), probably as a consequence of the differences in the manufacturing processes between the bulk and filament geometries.

3.5. pPE critical surface tension

Zisman's method was used to estimate critical surface tension of both pPE and PE (Fig. VII-SM, Supplementary Material), showing the linear distribution of contact angles in both materials, and the extrapolated critical surface tension with their respective 95% confidence intervals. Such values seem to be different, with no overlapping confidence intervals.

Though the reported critical surface tension values for PE (Zisman, 1964) were higher than the obtained for the PE cover (Fig. VI-SM), pPE has a slightly higher critical surface tension than PE, corresponding to more wettable surfaces, i.e., less hydrophobic surfaces.

3.6. pPE uptake of biodiesel and oleic acid

Considering the pPE porosity and hydrophobicity, the sorption of highly lipophilic substances from water is a potentially interesting

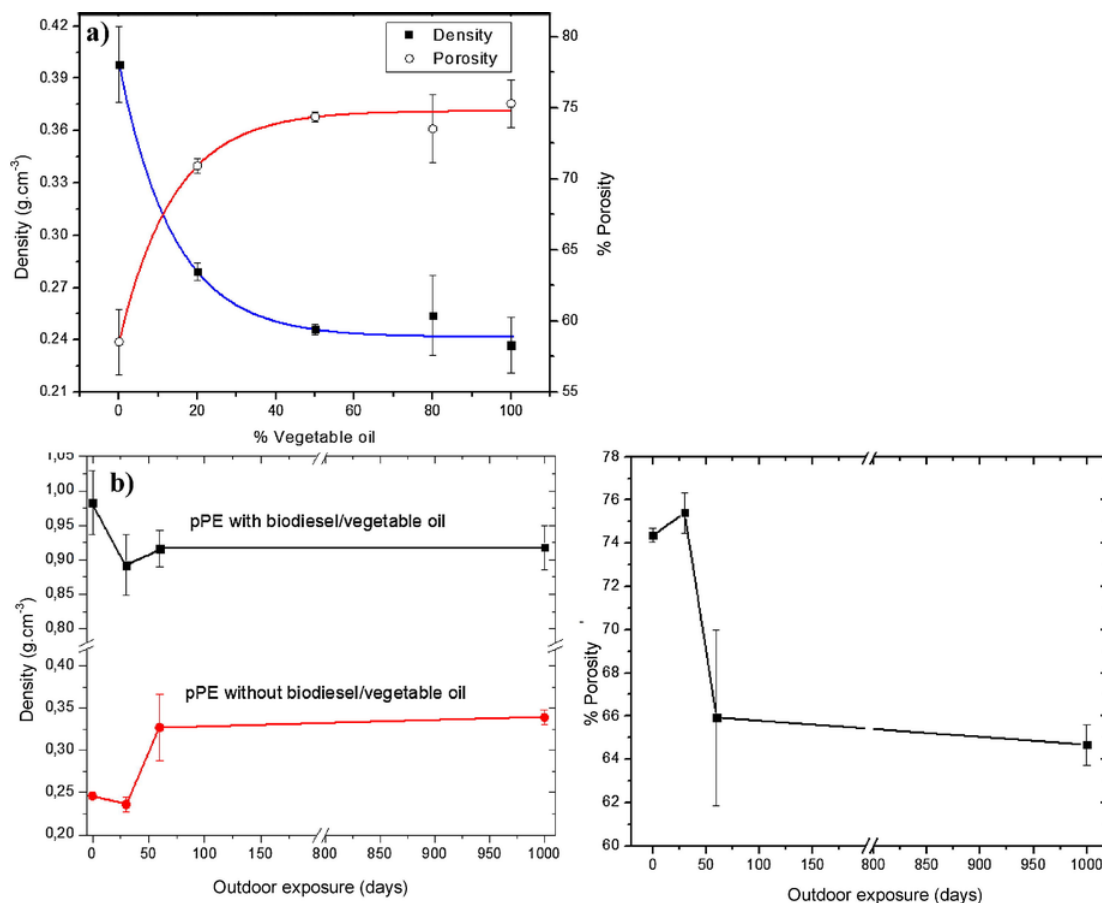


Fig. 3. pPE density and porosity as function of the vegetable oil/biodiesel ratio (a) and as function of the plastic aging (b).

application. Then, biodiesel (as a model of a light, viscous, oily substance) sorption kinetic was studied using 0.2 g of pPE filaments in contact with 0.16 g and 2.00 g of biodiesel. In the first case $79 \pm 11\%$ of the initial biodiesel was removed in 120 min, while in the second, $66 \pm 5\%$ was sorbed from water in the same time (Fig. 5). It is interesting to remark that in this last case the ratio between the mass of the sorbed biodiesel per gram of pPE was $(6.5 \pm 0.6) \text{ g biodiesel g}^{-1} \text{ pPE}$. A sorbent prepared from waste PE has been reported, where 3 g of PE powder and 4 g of plastic sheet were necessary to obtain 80% sorption efficiency when 1 g of petroleum was used, which is equivalent to $0.33\text{--}0.25 \text{ g petroleum g}^{-1} \text{ PE}$ (Aboul-Gheit et al., 2006). If much higher oil uptake capacity is desired, synthetic materials obtained from blends between high density PE (HDPE) and ultra high molecular weight PE (UHMWPE) in a 7.5:2.5 ratio are necessary (Saleem et al., 2015), requiring specific plastic recycling streams.

As we mentioned before, oil and fatty acids, mainly originated in domestic activities, are important components in the affluent currents to wastewater treatment plants. We have previously shown the pPE capacity for fatty acid sorption in a complex matrix like sewage sludge (Section 3.2). In order to characterize the fatty acid sorption on pPE we decided to use oleic acid as an example of water emulsified hydrophobic material. An exploratory sorption kinetic study using an oleic acid emulsion ($0.53 \text{ g oleic acid} \cdot 100 \text{ mL}^{-1}$ emulsion) was done to study the effect of pH on the pPE sorption capacity (Fig. 5B). Although a slower kinetic was observed at pH=5 than at pH=3, in both cases practically all the oleic acid was sorbed in 90 min. Using a different fatty acid, like myristic acid, sorption kinetic on pPE was

studied at different pHs observing a similar effect: the sorption kinetics were faster at lower pHs (3 and 5) than at pH=7 (see Fig. IX-SM, Supplementary Material). In both cases the faster kinetic at lower pH can be rationalized considering that the pKas of the fatty acids are ca. 5, which means that at pH=3 practically all the molecules are in their carboxylic acid forms and not in their ionic states (carboxylates).

The oleic acid/pPE sorption isotherm at pH=5 is shown in Fig. 5C. A maximum sorption value of $(9.7 \pm 0.5) \text{ g}$ of oleic acid per gram of pPE was obtained, adjusting to Langmuir model. For a detailed discussion of the best fitting isotherm model see Supplementary Material.

3.7. Practical sorption amount and pPE mass in multiple reuses

For studying pPE sorption capacity considering multiple reuses, the Practical Sorption Amount (PSA) of the pPE for biodiesel sorption was obtained, repeating ten cycles of use (Fig. 6, red¹ line). The pPE mass after each biodiesel extraction was weighted to take into account any sorbent loss occurred during the reuse cycles (Fig. 6, blue line). PSA remained practically constant after ten reuses, and a negligible pPE mass reduction (c.a. 5%) was observed. These results emphasize the mechanical stability of the pPE, which is an essential material property for potential applications in waste water treatment plants.

¹ For interpretation of color in Fig. 6, the reader is referred to the web version of this article.

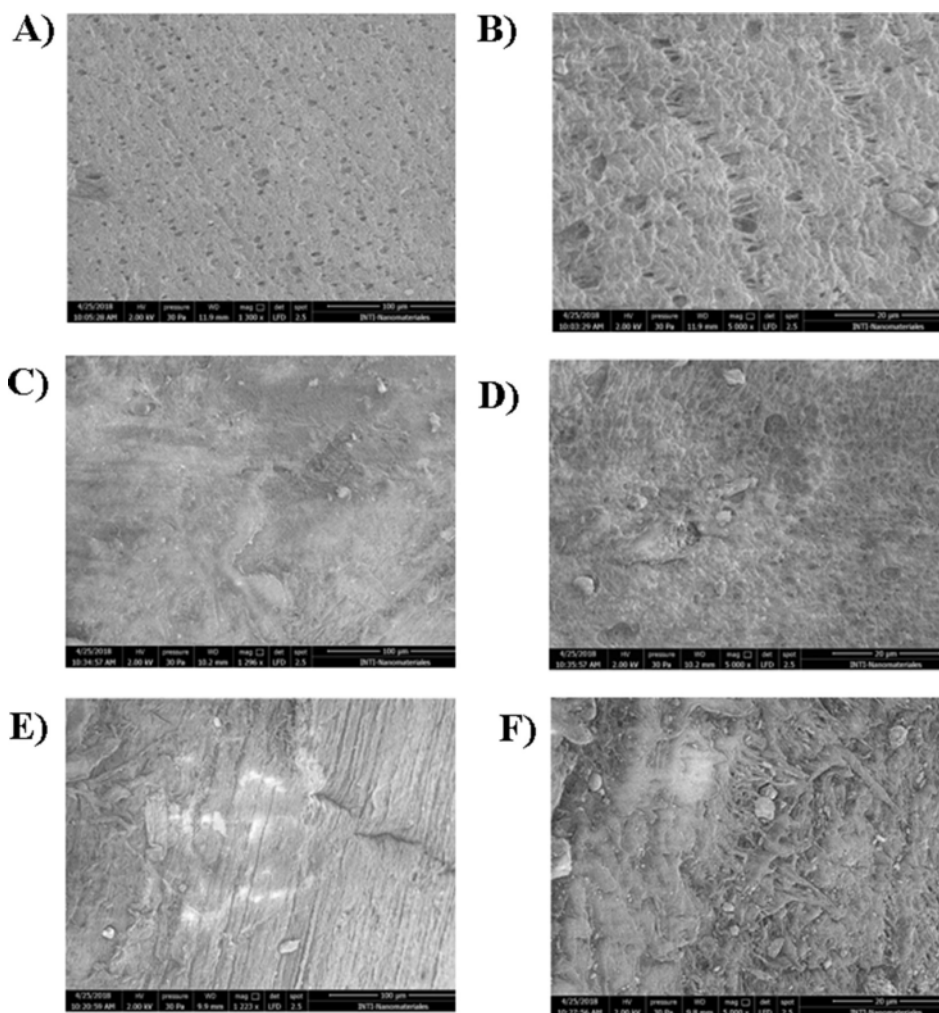


Fig. 4. SEM images of 20% PE (BD: VO 50:50), bulk: (A) not solarized, 100 μm . (B) not solarized, 20 μm . (C) solarized, 100 μm . (D) solarized, 20 μm . 20% PE (new film, BD:VO 50:50), filaments: (E) 100 μm . (F) 20 μm .

4. Conclusions

Lipids were extracted from a sewage sludge using a porous polyethylene obtained from agricultural covers with density and porosity tuned in the fabrication process to porosity range: $(58.3 \pm 3.3)\%$ to $(70.8 \pm 1.9)\%$ and density range: $(0.237 \pm 0.016) \text{g cm}^{-3}$ to $(0.398 \pm 0.022) \text{g cm}^{-3}$. When pPE extracted lipids were compared to those obtained using toluene as extraction solvent, both GC-MS profiles resulted similar, being pPE extraction efficiency per gram higher than in the toluene case.

It was proved that during the pPE preparation process, trifluralin, a potentially present pesticide in the plastic covers, migrate to the solvent phase (biodiesel:vegetable oil) with high efficiency remaining in the pPE less than 0.84% of the original pesticide. Considering that most of the fungicides and insecticides used in horticulture have not very different molecular weights and polarities than trifluralin, the xenobiotic extraction capacity of the pPE manufacturing process could be extrapolated to other cases.

pPE biodiesel uptake kinetic was obtained, finding a sorption of $6.8 \text{g biodiesel g}^{-1}$ pPE in 90 min. The oleic acid/pPE sorption

isotherm was studied, obtaining a maximum value of $(9.7 \pm 0.5) \text{g}$ of oleic acid per gram of pPE at $\text{pH}=5$ and fitting to Langmuir model

Biodiesel sorption by pPE was tested along ten recycles observing that the sorption capacity remained practically constant.

The pPE performance as hydrophobic sorbent under laboratory conditions, establish the bases for potential applications for lipid removal in waste water treatment plants, which is a relevant environmental issue.

5. Uncited reference

Dirección de Oferta Exportable (xxxx).

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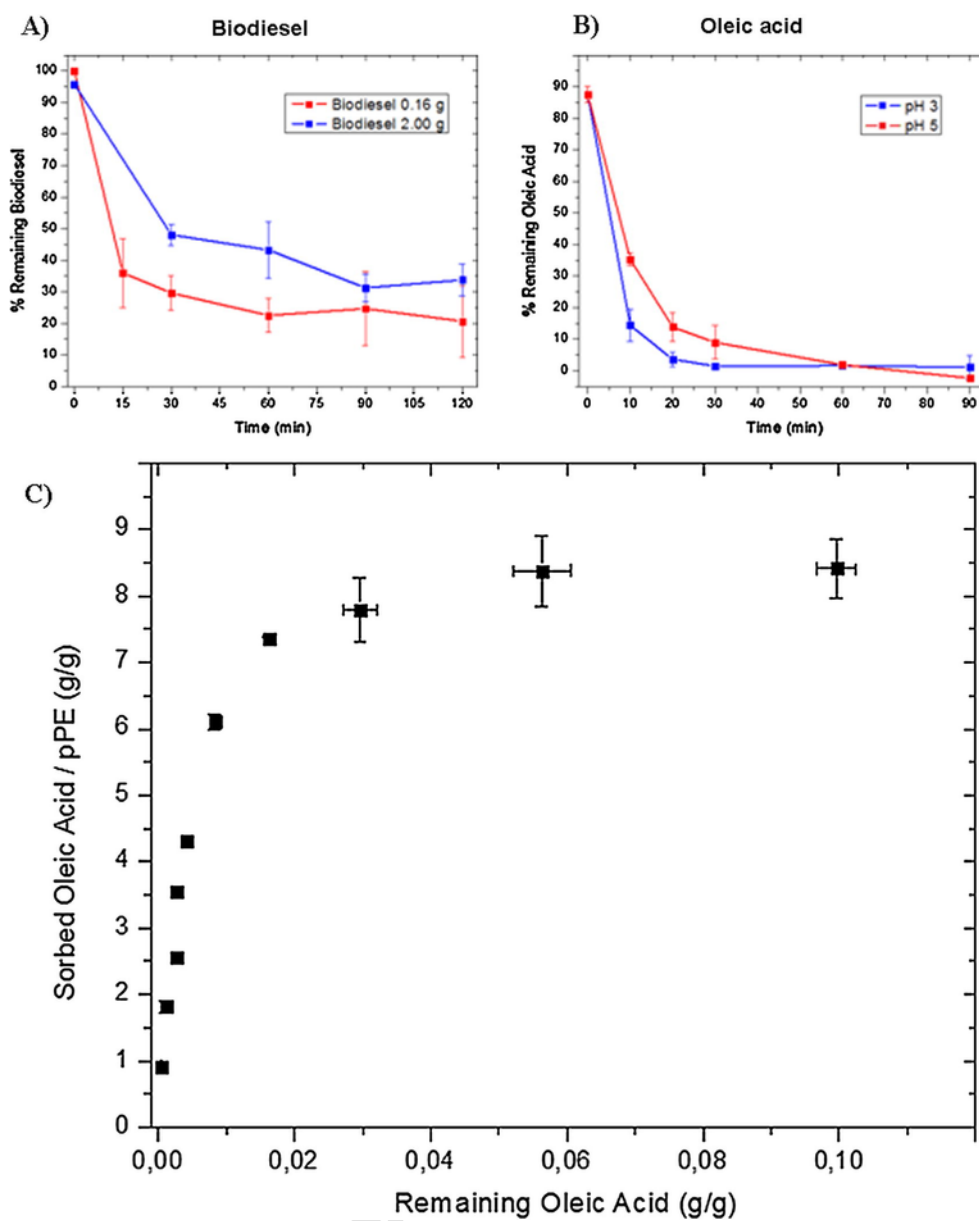


Fig. 5. (a) pPE sorption kinetic of biodiesel. (b) pPE sorption kinetic of oleic acid. (c) pPE isotherm of oleic acid (pH=5).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.wasman.2018.06.026>.

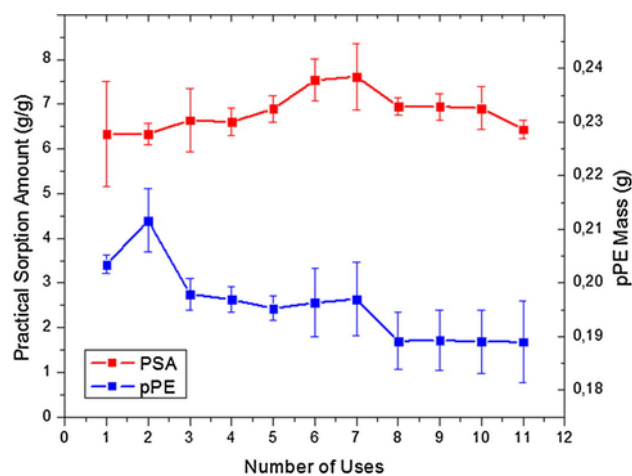


Fig. 6. pPE mass and PSA for ten biodiesel sorption reuses (each point in triplicate).

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