Waste Management 204 (2025) 114915

Contents lists available at ScienceDirect

Waste Management

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

Research Paper

Eco-friendly recovery of cellulose acetate from combusted cigarette filters and reuse for membrane fabrication

Marco Friuli [a,*], Claudia Grazioli [a], Nauman Sattar [a], Jasim Zia [a], Roberta Del Sole [a], Lucia Mergola [a], Sudipto Pal [a], Antonio Licciulli [a], Christian Demitri [b], Alessandro Sannino [b], Leonardo Lamanna [a]

[a] Department of Engineering for Innovation, University of Salento, Via per Monteroni 73100 Lecce, Italy
[b] Department of Experimental Medicine, University of Salento, Via per Monteroni 73100 Lecce, Italy

ARTICLE INFO

Keywords:
Cigarette litters
Recycled cellulose acetate
Green protocol
Water remediation
Methylene blue

ABSTRACT

Cigarette filters, widely discarded and slow to degrade, represent a significant source of environmental pollution. This study presents a novel eco-friendly protocol for recovering cellulose acetate (CA) from smoked cigarette butts using a solvent-based solubilization–desolubilization method with acetic acid as the green solvent. The novelty of this approach lies in its ability to extract and purify CA under mild conditions while avoiding toxic solvents and multi-step processing, commonly found in previous methods. The recovered cellulose acetate (RCA) was thoroughly characterised using FTIR, TGA, DSC, XRD, and mechanical testing, confirming its chemical and physical equivalence to commercial-grade CA. To validate the functional performance of the recycled material, RCA was repurposed into membranes and tested in a proof-of-concept study for water remediation. These preliminary tests involved the adsorption of methylene blue (MB), with removal efficiencies reaching 55.1 ± 4.8 %, and up to 92.0 ± 13.7 % upon surface modification with TiO_2 under solar lamp irradiation. While not the central focus of this work, the membrane experiments serve to confirm the applicability of RCA in established cellulose acetate use cases. Overall, this work highlights a scalable and sustainable strategy for converting cigarette filter waste into valuable polymeric materials, supporting circular economy principles and offering an alternative to conventional CA recovery processes.

1. Introduction

Despite a decline in global smoking prevalence, about 6 trillion cigarettes are consumed annually. A large number of smokers (75 %) improperly dispose of their butts (corresponding to the cigarette filter) (Wright and Kelly, 2017) making them the most common litter item and significantly contributing to urban and coastal pollution (Mohamed, 2023). Indeed, improperly discarded cigarette butts can release approximately 7000 chemicals (e.g., chromium, cadmium, nicotine, and other carcinogens (Slaughter et al., 2011–05-01,; Mahto et al., 2022 Cesaris et al., 2024) and microplastics during their slow degradation (M, S, xxxx). Consequently, they can contribute to soil and water contamination, reduction in plant growth and they can represent a direct and indirect risk for human and animal health, especially when contamination spreads along the food chain (e.g. they have been found in the stomach of birds and fishes (Novotny at al., 2009; Lamanna et al., 2024; Zhang et al., 2025).

Recycle could be a possible way to reduce cigarette butt's incorrect disposal (Mahto et al., 2022; Afroz et al., 2023). Cigarette filters are made of cellulose acetate (CA), a polymer that has a large range of applications (e.g. composites, fabrics for clothing, sound-absorbing materials, nanocrystal cellulose, supporting materials for construction, and supercapacitor electrodes) (Shah et al., 2023).

Several approaches have been developed for recovering and purifying CA from cigarette filters, each employing different washing and solvent treatment strategies. Mahto et al. (Mahto et al., 2022)proposed a multi-step process that begins with hexane washing, followed by solvent recovery through rotary evaporation and drying at room temperature. The filters are then immersed in acetone and dimethylformamide, centrifuged, precipitated, filtered, and finally dried at 60 °C, ensuring a thorough purification of CA. De Cesaris et al. (Cesaris et al., 20245) focused on polymer purification but highlighted the significant solvent consumption required, using 200 mL per 1.5 g of burned filters. Their

* Corresponding author.
E-mail address: marco.friuli@unisalento.it (M. Friuli).

https://doi.org/10.1016/j.wasman.2025.114915
Received 3 March 2025; Received in revised form 5 May 2025; Accepted 27 May 2025
Available online 4 June 2025

Nomenclature

CA	Cellulose Acetate
RCA	Recovered Cellulose Acetate
CBs	Cigarette Butts
MB	Methylene Blue
TiO_2	Titanium Dioxide
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
WCA	Water Contact Angle
ASTM	American Society for Testing and Materials
Q	Adsorption capacity (mg of dye per g of membrane)
Ci	Initial concentration of dye (mg/L)
Ce	Equilibrium concentration of dye (mg/L)
Cf	Final concentration of dye at time t (mg/L)
Qe	Amount of dye adsorbed at equilibrium (mg/g)
Qt	Amount of dye adsorbed at time t (mg/g)
Qmax	Maximum adsorption capacity (mg/g)
KL	Langmuir constant (L/mg)
K_1	Pseudo-first-order rate constant (min^{-1})
K_2	Pseudo-second-order rate constant (g mg^{-1} min^{-1})
M1-RCA	RCA membrane prepared via Protocol 1
M2-RCA	RCA membrane prepared via Protocol 2
M2-RCA-TiO_2	M2-RCA membrane modified with TiO_2
λ	Wavelength (used in XRD: Cu Kα = 0.154 nm)
R^2	Coefficient of determination (for regression models)

process involves sequential washing, starting with hot water for 15 min, followed by ethanol under gentle stirring, to enhance purification efficiency. Afroz et al. (Afroz et al., 2023) developed a method aimed at repurposing CA for yarn production. This process requires manual removal of filter paper, tobacco, and ash, followed by sequential washing with hydrogen peroxide, sodium hydroxide (NaOH), hot water, and sulfuric acid (H_2SO_4), making it both labor-intensive and chemically demanding. Benavente et al. (Benavente et al., 2018) explored a comparative approach, testing different washing solutions such as sodium chloride (NaCl), sodium acetate (NaAc), and diluted sulfuric acid. The process is completed with ethanol and organic solvent (diethyl ether, hexane) washes, followed by CA solubilization in acetone and precipitation using distilled water.

Extraction processes often rely on toxic solvents such as dimethylformamide, diethyl ether, and hexane to improve their yield. Furthermore, protocols involve multiple labor-intensive and time-consuming steps, including manual separation and washing. These factors contribute to significant environmental impact and high operational costs, ultimately limiting the widespread use of RCA. Additionally, RCA's applicability is often restricted by residual contaminants or degraded material properties, making it unsuitable for certain applications (Friuli et al., 2020). Consequently, the development of easy, environmentally friendly and cost-effective methods for recovering CA from cigarette butts is essential to enhance collection and recycling efforts while promoting a circular economy (Oprea et al., 2023).

To ensure that cellulose acetate recovery is not only environmentally sound but also practically viable, it is crucial to prove that CA obtained through the presented method can be effectively processed to replicate already existing CA-based applications (Rehman et al., 2021). Among these, CA membranes employed as sorbent substrates to remove heavy metals, pharmaceutics and dyes from water (Lamanna et al., 2023; V, A. S., et al., 2024). Although widely studied CA membranes represents a useful benchmark for validating the material's performance. To this aim, preliminary studies on RCA-based membranes for the removal of dyes pollutants were done, in particular for methylene blue (MB) (Nasab et al., 2023).

MB is one of the most widely used synthetic dyes and is commonly employed as a model compound in adsorption studies due to its well-characterized properties. Although MB has some medical applications, its uncontrolled release into water can cause serious ecological harm and health risks, including respiratory, cardiovascular, and neurological toxicity (A, f., e, a., h, d., h, s., mm, f., 11/27/2024). Its known carcinogenic and mutagenic effects further underline the urgency of its removal. To address this challenge, bio-based adsorbents such as biochar, chitosan, and cellulose-derived materials have been applied alone (Zh et al., 07/12/2023) or in combination with other active elements, showing promising results in MB removal.

To date titanium dioxide (TiO_2) is the most extensively used photocatalyst with exceptional photo, thermal, and chemical stability (Atalı et al., 2024). Although TiO_2 in its nanometric powder form shows the best efficiency, recovering it from the treated aqueous solution is very difficult (Sun et al., 2021/10/01). One way to exploit the photocatalytic effect is to integrate TiO_2 with CA membranes to enhance its removal efficacy as well as to minimize the loss of it after the photocatalytic reaction (Pal et al., 2023; Aljawrneh et al., 2022).

In this study, a green and cost-effective process was developed to recover CA from cigarette butts and repurpose it for membrane fabrication through solubilization-desolubilization process, using a green solvent (i.e., acetic acid) that is also highly selective for cellulose acetate. Two recovery procedures were explored. A first approach (Protocol 1) included a washing step while a second one (Protocol 2) avoided washing treatment, simplifying the procedure. Each membrane was characterized using FTIR, TGA, DSC, XRD, and mechanical testing and the results were compared with a virgin membrane. The RCA membrane with better characteristics was then investigated for dyes water remediation, using MB as dye model. In detail, batch experiments and kinetic studies were conducted to evaluate MB removal percentage. Finally, to improve efficiency in MB removal process, RCA modified with TiO_2 was also tested by using a solar lamp.This work demonstrates that using acetic acid (a green and not flammable solvent) and a recovery method via precipitation in a non-solvent (desolubization), it is possible to obtain a shorter and effective protocol to recover CA from cigarette litters. Moreover, the work explores the possibility of replicating common CA-based membranes for water remediation using the recovered material, demonstrating its effective potential in practical applications..

2. Materials and methods

2.1. Materials

Cigarette butts (CBs) from various brands and types, different lengths and amounts of unburned tobacco, were collected from designated containers at the Engineering for Innovation Department of the University of Salento. Pure cellulose acetate (CA, Sigma-Aldrich Mw ~ 30,000 g/mol, Milano, Italy) and commercially available virgin cigarette filters (filter tips Rizla slim) were used as control samples to compare the properties of the recovered material. TiO_2 (Aeroxide P25 ~ 21 nm average size, surface area ~ 50m^2g^{-1} Anatase /Rutile weight ratio ~ 80/20) was supplied by Evonik Industries AG (Essen, Germany). Methylene blue (MB), acetic acid (≥99.7 %), hexane (95 %) and absolute ethanol (≥99.5 %) were purchased form Sigma-Aldrich, (Milano, Italy).

2.2. Cellulose acetate extraction and membrane preparation protocols

Recycled cellulose acetate (RCA) fibrils were recovered using two distinct experimental procedures, Protocol 1 and Protocol 2, both based on the precipitation method but presenting some differences, obtaining two different membranes, M1-RCA and M2-RCA respectively (Fig. 1). The precipitation method involves the solubilization of CA into a solvent (acetic acid) and then desolubilization in non-solvent (distilled water) precipitates CA as fibrils that were the raw material for recycled membranes preparation. In Protocol 1, cigarette butts were preliminarily hand-sieved to remove ash and tobacco residues. The material was then stirred in abundant tap water (1L, three times) for one hour to eliminate water-soluble substances. After overnight drying at 50 °C, the filters were stirred in 0.5Lhexane (twice) for one hour to remove non– polar chemical components, then dried at room temperature in a fume hood. The cleaned filters were then stirred to solubilize in acetic acid at a 1:2 solid-to-solvent ratio for two hours. Precipitation was induced by adding water in a 1:5 vol-to-volume (v/v) ratio relative to the volume of acetic acid used, causing the polymer to desolubilize. The fibrils were collected using a sieve and oven-dried at 50 °C to accelerate solvent evaporation. Then, membranes were prepared by dissolving RCA in acetic acid (4.5 % by weight), drop casting the solution into Petri plates, and allowing it to dry overnight in a fume hood at room temperature. Protocol 2 (M2-RCA) followed a more streamlined approach, using only acetic acid as organic solvent. After sieving to remove ash and tobacco residues, the cigarette butts were directly solubilized in acetic acid (5 g per 100 mL) under stirring for two hours. The precipitation process mirrored that of Protocol 1, with water added at a 1:5 ratio, followed by fibril recovery through sieving and drying. For M2-RCA membrane preparation, the RCA fibrils were dissolved in acetic acid (4.5 wt%) and drop casted into Petri plates, followed by drying in the fume hood.

The control membranes were prepared by dissolving virgin chemical grade cellulose acetate (Sigma) and virgin cigarette filters (Rizla) in acetic acid at the same concentrations as the membranes made with RCA (4.5 wt%), followed by solvent evaporation under a fume hood overnight at room temperature.

2.3. Preparation of RCA membrane with TiO_2

M2-RCA membrane, produced by following Protocol 2, was modified with TiO_2. In detail, a 10 %wt (with respect to M2-RCA membrane) of TiO_2 was dispersed in ethanol with a final concentration of TiO_2 equal to 0.2 % (w/v) and sonicated for 5 min to ensure proper dispersion in the solution. Dispersion was drop casted to the dried M2-RCA membrane and the titanium dioxide layer was obtained via solvent evaporation at room temperature overnight to obtain a new modified membrane named M2-RCA-TiO_2.

2.4. Characterization studies

FTIR spectroscopy was used to identify the functional groups present in RCA membranes. Spectra were obtained at room temperature using a Jasco FT/IR-660 plus ATR-FTIR spectrometer (Jasco, Palo Alto, CA, USA). in the range of 800 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. FTIR performance was regularly checked using polystyrene film standards provided by the manufacturer. A micro-ATR tool with a single diamond crystal was used for the spectroscopic investigation directly on the cellulose acetate fibrils. TGA and DSC analysis were performed on RCA membranes respectively with TA Instruments model SDT Q600 and Q2000. TGA was performed in the range 30 °C to 800 °C at a rate of 10 °C/min in an air flow, using alumina pans. DSC experiments were carried out using a heating rate of 10 °C/min from 30 °C up to 250 °C in sealed aluminum pans and analyzed in an air flow. DSC was regularly calibrated using indium and zinc metal standards provided by the manufacturer while TGA routine maintenance and calibration were carried out by the TA Instruments service team, using certified mass standards during on-site visits.

Mechanical properties of the membranes were evaluated by using Zwick/Roell universal testing machine (Ulm, Germany) with a load cell of 100 N and a crosshead speed of 1 mm/min, to produce a stress–strain curve. Dogbone-shaped ASTM D638 Type V specimens were tested (obtained using a dogbone-shaped punch). All the tests were performed in triplicate.

XRD analysis was performed on a Rigaku Ultima X-ray diffractometer (Rigaku, Tokyo, Japan), employing monochromatic Cu Kα radiation ($\lambda = 0.154$ nm) with operating voltage of 40 kV and current of 20 mA. Diffractograms were recorded at 2θ angles ranging from 5 to 30 degrees and a scanning rate of 0.02° min^{-1}. The result for the XRD analysis is presented in Fig. S1 of the Supporting Information.

Water Contact angle (WCA) measurements were conducted on membranes to evaluate the wettability of Pure CA, Virgin Filters, M1-RCA and M2-RCA, and M2-RCA-TiO_2 membrane surfaces. The measurements were performed with a FTA1000 goniometer (First ten Angstrom, Newark, California, USA) equipped with a CCD camera mounted on an optical bench, and a manual Gilmont micrometer syringe used to deposit water droplets on the membrane surface before and after 30 min of solar lamp irradiation. (Sanolux, Radium Lampenwerk, Irradiance 41.4 W m^{-2} at wavelength range of 380–780 nm). Five WCA measurements were recorded for each membrane on different places, and the data were expressed as mean values with standard deviations.

Morphological analysis of the membranes was performed through a scanning electron microscope (SEM EVO® 40; Carl Zeiss AG) to compare the surface morphology of CA M2-RCA, and CA M2-RCA-TiO_2. The surface and cross-sectional SEM images were acquired at an applied voltage of 20 kV.

Adsorption and kinetic studies were conducted using a Jasco V-660 UV–visible spectrophotometer (Jasco, Palo Alto, CA, USA).

2.5. Pollutants adsorption assay on M2-RCA and M2-RCA-TiO_2

Pollutants removal assays were performed to assess the capability of the M2-RCA membranes (with and without TiO_2) to remove MB dye from water.

Firstly, the adsorption performance of M2-RCA was evaluated by batch rebinding experiments incubating 5 mg of the membrane (10x10 mm) in 5 ml of MB solutions spanning a concentration range from 0.6 to 220 mg/L. All solutions were stirred for 24 h. Then, after membrane removal, the solutions were analyzed by UV–Visible spectrophotometer at fixed wavelength (664 nm) and the adsorption capacity Q (mg/g) of the membrane was calculated as follows:

$$Q = (C_i - C_e)V/m \tag{1}$$

where C_i and C_e represent the initial concentration and concentration at Langmuir equilibrium (mg/L), respectively, V is the volume of water solution (L) and m is the mass of the membrane (mg).

Experimental data were fitted with a Langmuir adsorption isotherm to evaluate the maximum adsorption capacity (Q_{max}) of the membrane (Mergola et al., 2016):

$$1/Q_e = (1/Q_{max}C_eK_L) + (1/Q_{max}) \tag{2}$$

where Q_e and K_L represent the amounts of MB adsorbed at equilibrium (mg/g) and the Langmuir constant (L/mg). Q_{max}, that represents the maximum adsorption capacity (mg/g), was calculated plotting $1/Q_e$ versus $1/C_e$.

Photocatalytic activity of M2-RCA-TiO_2 was evaluated using the pollutant adsorption procedure previously mentioned but adding the solar lamp exposure to promote the effect. The reaction solution was monitored by using UV–vis spectrophotometer at regular intervals, recording the absorbance at 664 nm.

Removal efficiency (%) of each membrane was calculated as follow (V, A. S., et al. 2024):

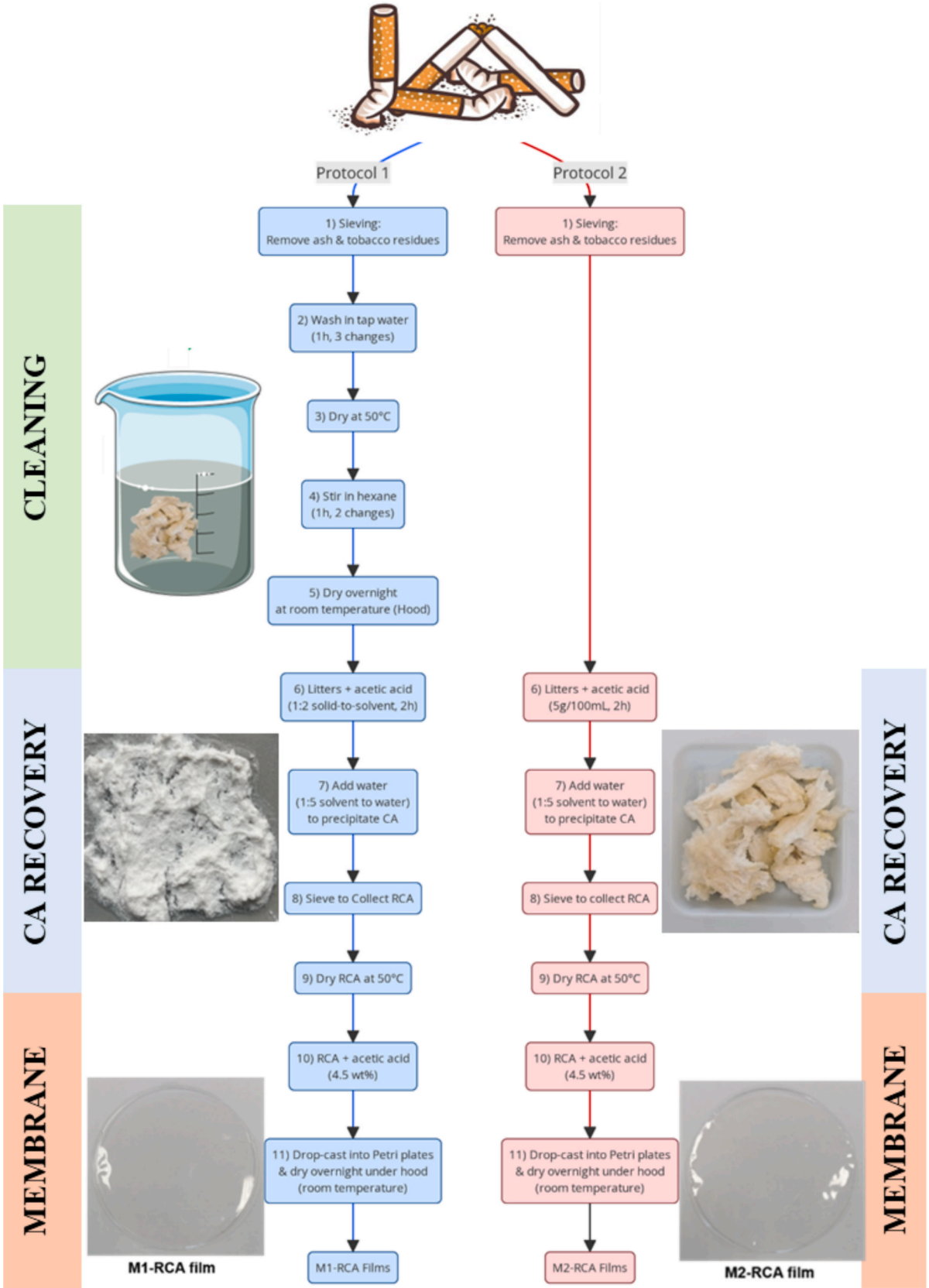

Fig. 1. Schematic diagrams of Protocol 1 and Protocol 2. Protocol 1 includes washing steps with water and hexane; Protocol 2 adopts a simplified, solvent-free cleaning. Both protocols use acetic acid-based solubilization and precipitation, followed by membrane casting.

$$Removalefficiency(\%) = (C_i - C_f)100/C_i \quad (3)$$

where C_i and C_f were the initial and the concentrations at time t(s), calculated from UV–vis measurements.

Linearized forms of a pseudo first order Lagergren model (4) and a pseudo second order kinetic (5) were used to evaluate the kinetic of MB adsorption on the membranes (Mergola et al., 2024):

$$ln(Q_e - Q_t) = lnQ_e - K_1 t/2.303 \quad (4)$$

$$t/Q_t = 1/(K_2 Q_e^2) + t/Q_e \quad (5)$$

where Q_e and Q_t were the amount of MB adsorbed onto the membranes at equilibrium time and at the time t (min) respectively, K_1 (min^{-1}) represents the pseudo first order rate constant and K_2 (g $mg^{-1}min^{-1}$) the pseudo second order rate constant.

3. Results and discussion

FT-IR analysis was carried out on the RCA and control samples to verify whether the recovered material exhibited the same chemical fingerprint as pure CA. Fig. 2, shows the full range spectra of CA, virgin filters, M1-RCA and M2-RCA membranes. The CA membrane shows its main characteristic peaks at 3580 cm^{-1} belongs to stretching vibration of unacetylated hydroxyl groups (OH), a peak at 2920 – 2870 cm^{-1} (stretching of –CH– of methyl and ethyl groups) (Teixeira et al., 2021; Kramar et al., 2023). A sharp band at 1740 cm^{-1} represents stretching vibrations of C=O carbonyl ester, a peak at approximately 1370 cm^{-1} belongs to C–H bending vibration of CH_3 in the acetyl group, A band at 1220 cm^{-1} shows C-O stretching of the acetyl group and a strong peak around 1042 cm^{-1} belongs to C-O-C stretching vibration of ester groups (Narayanan et al., 2023). Furthermore, virgin filters, M1-RCA and M2-RCA membranes show all the characteristic peaks of CA, confirming the potential of both protocols for CA recovery. (Friuli et al., 2020; Bouftou et al., 2024). Slight broadening and minor shifts in peak position were observed in some RCA spectra. These variations can be attributed to hydrogen bonding interactions with residual solvents and plasticizers, as well as the possible presence of trace contaminants in the recovered material. Such contaminants may modulate the stretching vibrations of functional groups, leading to subtle changes in peak intensity and position (Kramar et al., 2023).

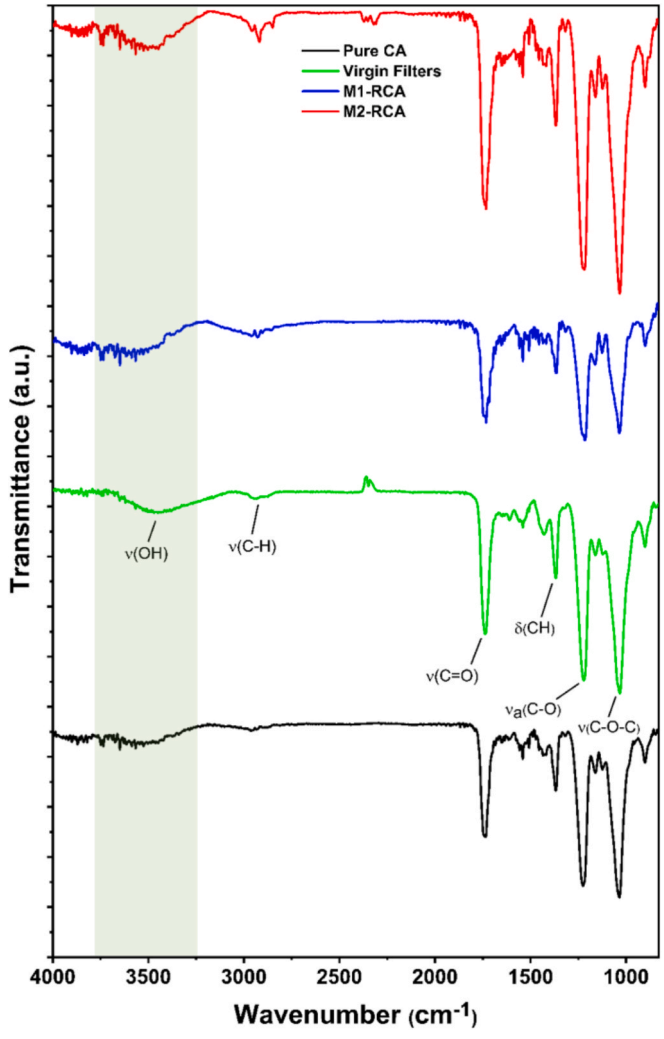

Fig. 2. FTIR spectra for Pure CA, virgin filters, M1-RCA and M2-RCA membranes. The highlighted portion represents peaks that are shifted due to hydrogen bonding interactions.

The following characterization aimed to evaluate the properties of the polymer in comparison with CA from Sigma-Aldrich and Rizla virgin filters (unsmoked). TGA thermograms for pure CA, virgin filters, M1-RCA and M2-RCA membranes are presented in Fig. 3. As shown in Fig. 3a, pure CA exhibited a typical three-step thermal degradation profile. The first step, occurring between 30 °C and 200 °C, is attributed to the evaporation of absorbed moisture. The second stage, from 200 °C to 400 °C, corresponds to the main thermal degradation of the cellulose acetate backbone, involving the breakdown of acetyl groups and the depolymerization of the polymer chains (Bouftou et al., 2024; Kee and Idris, 2010). CA from unused cigarette filters (virgin filters) showed an additional weight loss step at temperatures between 30 to 200 °C, likely due to the decomposition of plasticizing compounds used in adequate amounts in filter manufacturing to ease the polymer processing. CA extracted from waste cigarette filters (M1-RCA and M2-RCA, see Fig. 3a) degraded in three steps, similarly to pure cellulose acetate. A second step of weight loss is still present even though reduced as the plasticizer in the polymer structure was degraded during smoking process. However, the results of the TGA studies confirm that the CA recovered in both protocols have thermal properties comparable to pure CA. These findings suggest that the recovered material retains comparable thermal stability to commercial CA, indicating no early signs of chemical degradation that would compromise long-term performance under typical processing or environmental conditions.

The DSC (Fig. 3b) was employed to evaluate the glass transition and melting temperatures (T_g and T_m respectively) of the pure CA, virgin filters and M1-RCA and M2-RCA membranes. All the samples show sharp endothermic peaks between 60 and 85 °C attributed to the desorption of water from the samples. The difference between the temperatures of the water desorption peaks is due to the difference in the water – polymer interaction. The desorption process depends on the strength of interaction of the water molecules with the hydroxyl groups present in the structure of the polymer through hydrogen bonding (Nu et al., 2019). As further confirmation of the equivalence between the different types of CA, all samples show higher T_g values in the range of 195–205 °C that are close to the T_m as reported in literature. Furthermore, no significant difference is found in the T_m peaks that appears in the range of (226–233 °C) and it is in accordance with the literature. (Friuli et al., 2020; Erdmann et al., 2021).

The results for the mechanical properties are shown in Fig. 3c and d. There is no significant difference in the mechanical properties of all the samples confirming that RCA aligns with pure CA. Elastic modulus ranges from ≈1700-2500 MPa. Some slight differences, as the increase in elastic modulus of M1-RCA and M2-RCA compared to pure CA might be attributed to difference in the molecular weight and crystallinity of the samples due to the heterogeneity of the raw material (cigarette litters are a mix of wastes). Also, elongation at break is similar for all the samples, only virgin filters are showing slightly higher elongation at break (4.95 ± 0.77 %), confirming the presence of plasticizers. The

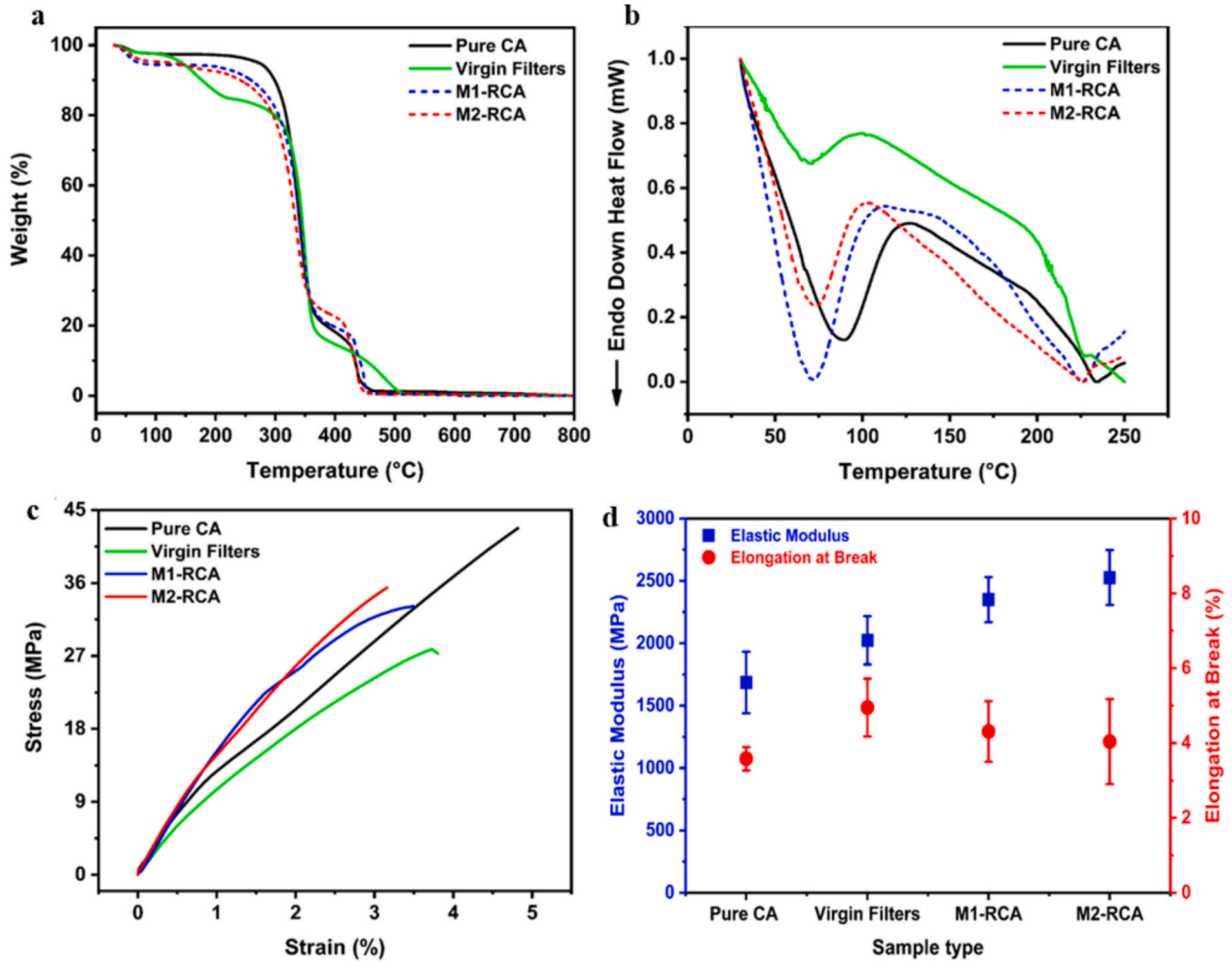

Fig. 3. (a) TGA isotherms and (b) – DSC thermograms of Pure CA, Virgin Filters, M1-RCA and M2-RCA. (c) Representative stress–strain curve and (d) Mechanical properties of Pure CA, Virgin Filters, M1-RCA and M2-RCA membranes.

mechanical variability observed falls within the expected range for recycled polymers, where feedstock heterogeneity and partial loss of additives like plasticizers are known to influence stiffness and ductility.

The water contact angle (WCA) measurements, shown in (Table 1, confirm the hydrophilic nature of all samples, with values below 90°. Membranes from virgin filters had a WCA of 71.2 ± 2.5°, higher than pure CA (61.1 ± 2.3°), M1-RCA (65.3 ± 3.1°) and M2-RCA (58.7 ± 1.4°). The increased WCA of virgin filters is due to hydrophobic plasticizers, as also indicated by the TGA analysis, which showed an additional degradation step linked to their presence. The similar WCA values of pure CA, M1-RCA, and M2-RCA further confirm that the washing step effectively removed plasticizer present in virgin filters.

According to the previously performed characterization, there are no significant variations between protocols 1 and 2 for the extraction of CA from used cigarette filters.

However, since Protocol 2 uses environmentally friendly solvents and it is also less time-consuming process as a consequence of fewer extraction steps can be considered as the best performing extraction procedure. For this reason, M2-RCA, obtained using the protocol 2, was additionally coated with TiO_2 following the process described in the Methods section and subjected to further studies.

Table 1
Contact angle average values after UV exposure.

Sample type	CA	Virgin filters	M1-RCA	M2-RCA
WCA	61.1 ± 2.3°	71.2 ± 2.5°	65.3 ± 3.1°	58.7 ± 1.4°

The surface and cross-sectional morphologies of M2-RCA and M2-RCA-TiO_2 membranes are shown in Fig. 4. As shown in Fig. 4a, the M2-RCA membrane has a smooth, flat and homogenous surface without the presence of any pores whereas M2-RCA-TiO_2 (Fig. 4b) membrane surface is rough and TiO_2 particle agglomeration can be observed. Despite these surface differences, the WCA measurements indicate no significant variation between M2-RCA and M2-RCA-TiO_2, suggesting that the TiO_2 coating does not substantially alter the membrane's wettability (Table S1 of Supporting Information).

3.1. *Methylene blue removal assay on M2-RCA and M2-RCA-TiO_2*

M2-RCA was initially tested with different dyes commonly found in water pollution, specifically methylene blue (MB), methyl orange, and rhodamine, each at a concentration of 2 mg /L. Preliminary results showed an affinity of the membrane for MB (Table S2 of Supporting Information). For this reason, all the following experiments were carried out to remove MB from water solutions.

The adsorption behavior of M2-RCA in MB removal from water was evaluated by batch rebinding experiments and the experimental data were processed by a Langmuir model (Fig. 5).

As reported in Fig. 5a, the adsorption capacity of the membrane increases with MB concentration until a plateau is reached, obtaining an experimental maximum adsorption capacity near to 8 mg/g of membrane. Experimental data were processed using the equation (2) to

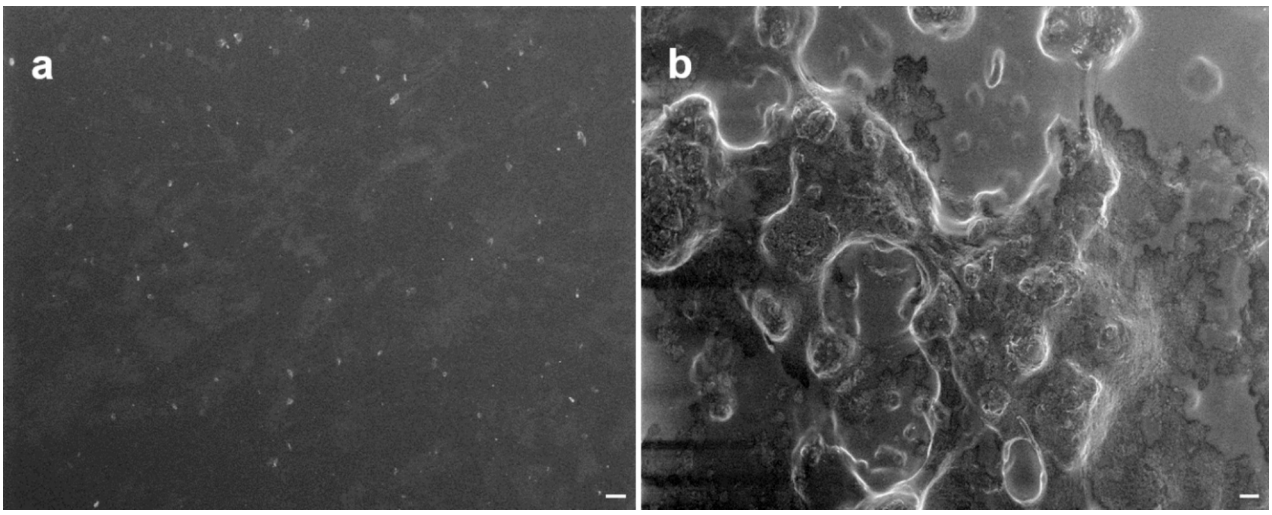

Fig. 4. SEM images of the top surface of (a) M2-RCA and (b) M2-RCA-TiO_2 membranes. The scale bar is 100 μm.

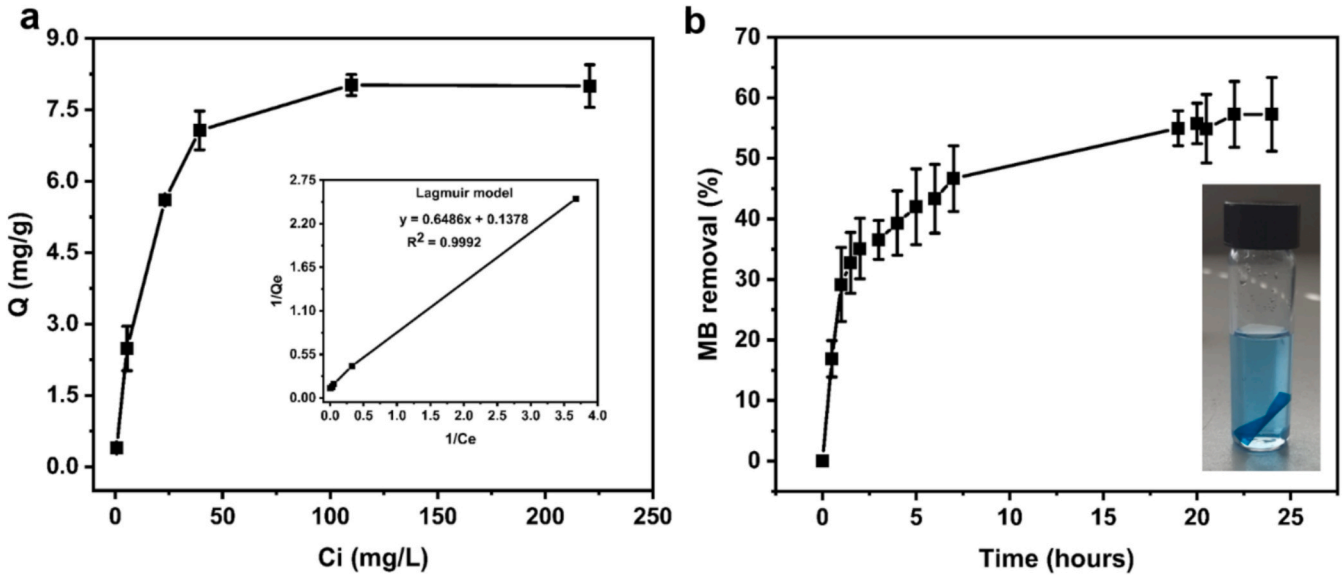

Fig. 5. (a) Adsorption behavior of M2-RCA membrane incubated in MB solutions at different initial concentrations of MB. (b) Kinetic performance of M2-RCA (inset, 2 mg/L MB solution after 24 h of adsorption).

evaluate the nature of interaction between MB and M2-RCA. Langmuir plots obtained (R^2 = 0.9992) showed the presence of homogeneous binding sites on membrane surface with a calculated maximum adsorption capacity Q_{max} equal to 7.26 mg/g of membrane, which is very similar to the experimental data obtained.

The kinetic performance of M2-RCA was evaluated by incubating the membrane in MB solution at the concentration of 2 mg /L and monitoring the removal efficiency at regular time intervals over 24 h.

As shown in Fig. 5b, MB adsorption occurred almost within the first 7 h of incubation with a removal percentage of around 46 %, and, after which it stabilized reaching a removal efficiency of 55.1 ± 4.8 %, that correspond to 1.1 mg/g of membrane. Experimental data were plotted with a pseudo-first-order and a pseudo-second-order kinetics to evaluate the adsorption mechanism. In general, a pseudo-first-order model describes the interaction of one MB molecule with a single binding site on the membrane, while a pseudo-second-order model considers the interaction of one MB molecule with two binding sites of the membrane. Based on the correlation coefficient (R^2 = 0.9956), the experimental data closely followed a pseudo-second-order model. Kinetic parameters were reported in Table 2.

Moreover, release studies were conducted incubating the M2-RCA membrane in ultrapure water after one cycle of adsorption and a release of 3.5 % in 24 h was observed. This low desorption rate is particularly interesting, as it suggests strong dye-membrane interactions, making M2-RCA a promising material for stable and efficient MB removal in water treatment application.

The promising results obtained with M2-RCA led to the development of an improved membrane by coating its surface with TiO_2 to enhance its performance. Given the well-known photocatalytic activity of TiO_2 in

Table 2
Kinetic parameters for M2-RCA and M2-RCA-TiO2 membranes related to pseudo-first and pseudo-second-order models.

Membranes	Pseudo-first-order model		Pseudo-second-order model	
	K_1 (1/min)	R^2	K_2 (g mg/min)	R^2
M2-RCA	5.6×10^{-3}	0.9658	1.2×10^{3}	0.9956
M2-RCA-TiO_2	1.8×10^{-3}	0.9971	1.5×10^{6}	0.9100

MB degradation, the modified membrane (M2-RCA-TiO_2) was prepared by coating a predetermined weight of M2-RCA with TiO_2. The resulting membrane was then incubated in an MB solution (2 mg/L) under stirring and exposed to solar lamp irradiation for 24 h, to evaluate kinetic performances. As shown in Fig. 6b, the maximum absorption peak of MB at 664 nm significantly decreases after 24 h of solar lamp exposure, confirming the enhanced removal efficiency due to the photocatalytic effect of TiO_2 on the membrane surface. To ensure completeness, additional control experiments were conducted, verifying that MB did not undergo decomposition when exposed to solar lamp irradiation alone and that the M2-RCA membrane without TiO_{22} did not exhibit improved performance under the same conditions (data not reported). It could be noted that the addition of TiO_2 leads to aremoval efficiency of ~ 92.0 %, that corresponds to 1.84 mg/g of membrane (Fig. 6a and 6c). Kinetic analysis using both pseudo-first-order and pseudo-second-order models (Table 2) indicated that MB removal with the M2-RCA-TiO_2 membrane followed a pseudo-first-order kinetic model (R^2 = 0.9971), a characteristic behavior of organic pollutant photodegradation (Mergola et al., 2024; Tran et al., 2023 Iqbal et al., 2020). These results highlight the significant performance improvement achieved with TiO_2 coating. Additionally, the reduction in MB concentration was visually evident, as the solution transitioned from blue to nearly transparent after solar lamp exposure (inset Fig. 6c). This suggests that hydrogen bonding between MB and the regenerated cellulose acetate membrane promotes direct contact with TiO_2, effectively initiating the photocatalytic degradation process.

4. Conclusion and Perspective

This study introduces an eco-friendly and efficient approach for recovering cellulose acetate (CA) from combusted cigarette filters, employing a streamlined process that reduces solvent consumption and processing steps. Two recovery procedures were explored: Protocol 1, which includes a washing step, and Protocol 2, a simplified method without washing. Both rely on a solubilization–desolubilization process, where CA is first dissolved in a suitable solvent and then precipitated in water. The use of acetic acid as a solvent for CA replacing more traditional and dangerous organic solvents such as acetone plays a pivotal role, demonstrating remarkable selectivity by dissolving CA while leaving other components of the cigarette butt (e.g., adhesives, PLA-based parts) untouched. Moreover, polymer's precipitation in water allows further purification of the polymer, reducing the steps needed to obtain RCA. However, the proposed protocol is validated at lab scale and its scalability will require process optimization in terms of mixing, solvent recovery, and feedstock handling under industrial conditions.

Comparative analysis identified Protocol 2 as the more advantageous option, offering a simpler, cost-effective, and sustainable alternative while yielding CA with properties comparable to those of commercial or virgin filter-derived materials. The protocol also proved robust when applied to mixed-brand, confirming its reproducibility despite variations in filter origin or contamination level.

Comprehensive characterization using FTIR, TGA, DSC, XRD, and mechanical testing confirmed that the CA obtained through Protocol 2

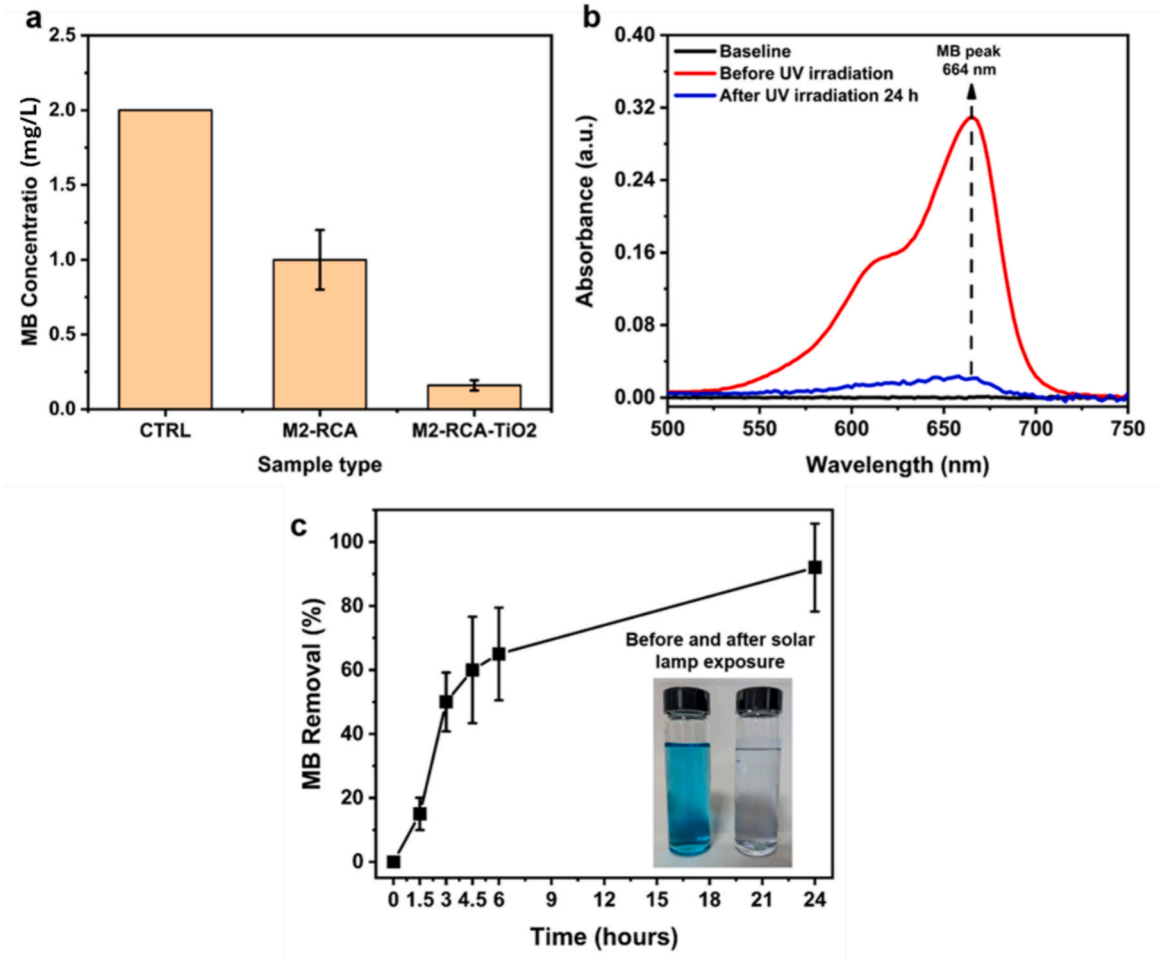

Fig. 6. (a) Comparison of MB removal using an initial concentration of 2 mg/L with M2-RCA (without solar lamp irradiation) and M2-RCA-TiO_2 (after 24 h solar lamp irradiation), (b) UV visible spectra of MB solution before and after 24 h solar lamp irradiation. (c) The adsorption kinetics of MB removal for M2-RCA-TiO_2 membrane. Inset: MB solution before and after 24 h of solar lamp irradiation.

(M2-RCA) retained its structural integrity, thermal stability, and mechanical strength, making it suitable for further applications. M2-RCA was then investigated for water remediation, demonstrating effective adsorption of methylene blue (MB). When further modified with TiO_2 nanoparticles and exposed to solar lamp, the membranes exhibited a significant improvement in photocatalytic degradation, increasing MB removal efficiency from ~ 55 % to ~ 92 %.

These findings highlight the potential of repurposing waste cigarette filters into valuable materials for water treatment, supporting circular economy principles while mitigating environmental pollution.

Currently, recycled cellulose acetate can be employed in a limited number of applications due to potential contaminants and the difficulty of fine-tuning its properties both issues arising from the heterogeneity of the waste stream. However, this situation may change with the growing adoption of heated (non-combusted) tobacco products. Since no combustion occurs, the resulting polymer is of higher quality and less contaminated, thus opening the door to a wider range of potential applications and more cost-effective recovery processes. The extraction of cleaner cellulose acetate could open the door to potential applications of this material in the biomedical field. However, this material would need to undergo further analytical tests (e.g. HPLC and mass spectrometry) to identify and possibly reduce the presence of contaminants, as well as to verify its biocompatibility.

Moreover, these products often include a ferromagnetic component (used to heat the tobacco via electromagnetic induction). In theory, this allows selective waste separation (for example, using magnets), which would yield a polymer with more uniform characteristics and better control over the final properties of RCA.

CRediT authorship contribution statement

Marco Friuli: Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Formal analysis, Data curation, Conceptualization. **Claudia Grazioli:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Nauman Sattar:** Writing – original draft, Formal analysis, Data curation. **Jasim Zia:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation. **Roberta Del Sole:** Writing – review & editing, Supervision, Resources, Data curation. **Lucia Mergola:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Sudipto Pal:** Writing – review & editing, Resources. **Antonio Licciulli:** Supervision, Resources. **Christian Demitri:** Supervision, Resources, Funding acquisition. **Alessandro Sannino:** Supervision, Resources, Funding acquisition. **Leonardo Lamanna:** Writing – review & editing, Writing – original draft, Supervision, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Marco Friuli reports article publishing charges and equipment, drugs, or supplies were provided by University of Salento Department of Engineering Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Alessandro Sannino A.S. and Leonardo Lamanna L.L. acknowledge the support of the PNRR –MUR for the funding allocated to Research Initiatives for Innovative Technologies and Pathways in Healthcare and Assistance (Decree No. 931, June 6, 2022), under the ANTHEM project (AdvaNced Technologies for HumancentEred Medicine), CUP B53C22006710001.

This research was funded by Ministry of Education, University and Research of Italy, PON “Research and Innovation” 2014–2020, Action IV.6 “Research contracts on green topics”. The authors thank the University of Salento–Department of Engineering for Innovation for funding this work (Fondi per la Ricerca di Base) grant number 21101001. A.S. and L.L. acknowledge the support of the PNRR – MUR for the funding allocated to Research Initiatives for Innovative Technologies and Pathways in Healthcare and Assistance (Decree No. 931, June 6, 2022), under the ANTHEM project (AdvaNced Technologies for HumancentEred Medicine), CUP B53C22006710001.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2025.114915.

Data availability

Data will be made available on request.

References

A, F.; E, A.; H, D.; H, S.; MM, F. A comprehensive study on methylene blue removal via polymer and protein nanoparticle adsorbents - PubMed. Scientific reports **11/27/2024**, 14 (1). DOI: 10.1038/s41598-024-80384-4.

Afroz, F., Mahmud, R.U., Islam, R., Farhana Afroz, R.U., 2023–05-29. M., Raijul Islam. Green Approach to Recover the Cellulose Acetate Fiber from Used Cigarette Butts, and Characterize the Filter Fiber. AATCC J. Res. 10 (5). https://doi.org/10.1177/24723444231175209.

Aljawrneh, B.; Alsaad, A.; Albiss, B.; Alrousan, S.; Alshanableh, A.; Mutlaq, S.; Aljawrneh, B.; Alsaad, A.; Albiss, B.; Alrousan, S.; et al. Cellulose acetate membranes treated with titanium dioxide and cerium dioxide nanoparticles and their nanocomposites for enhanced photocatalytic degradation activity of methylene blue. Journal of Materials Science: Materials in Electronics 2022 33:14 **2022-03-31**, 33 (14). DOI: 10.1007/s10854-022-08115-x.

Atalı, Ş.G., Akbal, F., Gürbüz, M., Turan, B.C., 2024/05/01. Granular titanium dioxide and silicon-doped titanium dioxide as reusable photocatalysts for dye removal. Int. J. Appl. Ceram. Technol. 21 (3). https://doi.org/10.1111/ijac.14603.

Benavente, M. J.; Caballero, M. J. A.; Silvero, G.; López-Coca, I.; Escobar, V. G.; Benavente, M. J.; Caballero, M. J. A.; Silvero, G.; López-Coca, I.; Escobar, V. G. Cellulose Acetate Recovery from Cigarette Butts. Proceedings 2018, Vol. 2, Page 1447 **2019-02-25**, 2 (20). DOI: 10.3390/proceedings2201447.

Bouftou, A., Aghmih, K., Lakhdar, F., Abidi, N., Gmouh, S., Majid, S., 2024/09/01. Enhancing cellulose acetate film with green plasticizers for improved performance, biodegradability, and migration study into a food simulant. Meas.: Food 15. https://doi.org/10.1016/j.meafoo.2024.100180.

Cesaris, M.G.D., Felli, N., Antonelli, L., Francolini, I., D'Orazio, G., Bosco, C.D., Gentili, A., 2024/06/15. Recovery of cellulose acetate bioplastic from cigarette butts: realization of a sustainable sorbent for water remediation. Sci. Total Environ. 929. https://doi.org/10.1016/j.scitotenv.2024.172677.

Erdmann, R.; Kabasci, S.; Heim, H.-P.; Erdmann, R.; Kabasci, S.; Heim, H.-P. Thermal Properties of Plasticized Cellulose Acetate and Its β-Relaxation Phenomenon. Polymers 2021, Vol. 13, Page 1356 **2021-04-21**, 13 (9). DOI: 10.3390/polym13091356.

Friuli, M.; Nitti, P.; Cafuero, L.; Prete, A.; Zafar, M. S.; Madaghiele, M.; Demitri, C. Cellulose Acetate and Cardanol Based Seed Coating for Intraspecific Weeding Coupled with Natural Herbicide Spraying. **2020**, 28 (11), 2893-2904.

Iqbal, A.; Ibrahim, N. H.; Rahman, N. R. A.; Saharudin, K. A.; Adam, F.; Sreekantan, S.; Yusop, R. M.; Jaafar, N. F.; Wilson, L. D.; Iqbal, A.; et al. ZnO Surface Doping to Enhance the Photocatalytic Activity of Lithium Titanate/TiO2 for Methylene Blue Photodegradation under Visible Light Irradiation. Surfaces 2020, Vol. 3, Pages 301-318 **2020-07-07**, 3 (3). DOI: 10.3390/surfaces3030022.

Kee, C.M., Idris, A., 2010/10/13. Permeability performance of different molecular weight cellulose acetate hemodialysis membrane. Sep. Purif. Technol. 75 (2). https://doi.org/10.1016/j.seppur.2010.08.013.

Kramar, A.; Rodríguez Ortega, I.; González-Gaitano, G.; González-Benito, J.; Kramar, A.; Rodríguez Ortega, I.; González-Gaitano, G.; González-Benito, J. Solution casting of cellulose acetate films: influence of surface substrate and humidity on wettability, morphology and optical properties. Cellulose 2023 30:4 **2023-01-09**, 30 (4). DOI: 10.1007/s10570-022-05026-2.

Lamanna, L., Giacoia, G., Friuli, M., Leone, G., Carlucci, N., Russo, F., Sannino, A., Demitri, C., 2023. Oil-Water Emulsion Flocculation through Chitosan Desolubilization Driven by pH Variation. ACS Omega 8 (23), 20708–20713. https://doi.org/10.1021/acsomega.3c01257 From NLM.

Lamanna, L., Corigliano, G., Narayanan, A., Villani, S., Friuli, M., Chietera, F.P., Stanca, B.D.C., Giannotti, L., Siculella, L., Colella, R., et al., 2024/10/15,. Beyond Plastic: Oleogel as gel-state biodegradable thermoplastics. Chem. Eng. J. 498. https://doi.org/10.1016/j.cej.2024.154988.

M, S.; Y, L.; B, S.; C, Z.; J, G.; G, Z. Smoked cigarette butts: Unignorable source for environmental microplastic fibers - PubMed. The Science of the total environment **10/15/2021**, 791. DOI: 10.1016/j.scitotenv.2021.148384.

Mahto, A., Halakarni, M.A., Maraddi, A., D'Souza, G., Samage, A.A., Thummar, U.G., Mondal, D., Nataraj, S.K., 2022/08/01. Upcycling cellulose acetate from discarded cigarette butts: Conversion of contaminated microfibers into loose-nanofiltration membranes for selective separation. Desalination 535. https://doi.org/10.1016/j.desal.2022.115807.

Mergola, L.; Scorrano, S.; Bloise, E.; Di Bello, M. P.; Catalano, M.; Vasapollo, G.; Del Sole, R.; Mergola, L.; Scorrano, S.; Bloise, E.; et al. Novel polymeric sorbents based on imprinted Hg(II)-diphenylcarbazone complexes for mercury removal from drinking water. Polymer Journal 2016 48:1 **2015-09-16**, 48 (1). DOI: 10.1038/pj.2015.79.

Mergola, L.; Carbone, L.; Bloise, E.; Lazzoi, M. R.; Sole, R. D.; Mergola, L.; Carbone, L.; Bloise, E.; Lazzoi, M. R.; Del Sole, R. Sustainable and Reusable Modified Membrane Based on Green Gold Nanoparticles for Efficient Methylene Blue Water Decontamination by a Photocatalytic Process. Nanomaterials 2024, Vol. 14, Page 1611 **2024-10-08**, 14 (19). DOI: 10.3390/nano14191611.

Mohamed, A.R., 2023/06/02. Impacts of Used Cigarette Butts on Soil Properties and Local Plants Growth. Sirte Univ. Sci. J. 13 (1). https://doi.org/10.37375/susj.v13i1.1379.

Narayanan, A., Friuli, M., Sannino, A., Demitri, C., Lamanna, L., 2023/12/01. Green synthesis of stretchable ethyl cellulose film plasticized with transesterified sunflower oil. Carbohydr. Polym. Technol. Appl. 6. https://doi.org/10.1016/j.carpta.2023.100378.

Nasab, E. A.; Nasseh, N.; Damavandi, S.; Amarzadeh, M.; Ghahrchi, M.; Hoseinkhani, A.; Alver, A.; khan, N. A.; Farhadi, A.; Danaee, I.; et al. Efficient purification of aqueous solutions contaminated with sulfadiazine by coupling electro-Fenton/ultrasound process: optimization, DFT calculation, and innovative study of human health risk assessment. Environmental Science and Pollution Research 2023 30:35 **2023-06-26**, 30 (35). DOI: 10.1007/s11356-023-28235-z.

Novotny, T. E.; Lum, K.; Smith, E.; Wang, V.; Barnes, R. Cigarettes Butts and the Case for an Environmental Policy on Hazardous Cigarette Waste. International Journal of Environmental Research and Public Health **2009 May 20**, 6 (5). DOI: 10.3390/ijerph6051691.

Nu, D. T. T.; Hung, N. P.; Hoang, C. V.; Bruggen, B. V. d.; Thi To Nu, D.; Phi Hung, N.; Van Hoang, C.; Van der Bruggen, B. Preparation of an Asymmetric Membrane from Sugarcane Bagasse Using DMSO as Green Solvent. Applied Sciences 2019, Vol. 9, Page 3347 **2019-08-14**, 9 (16). DOI: 10.3390/app9163347.

Oprea, M.; Voicu, S. I.; Oprea, M.; Voicu, S. I. Cellulose Acetate-Based Materials for Water Treatment in the Context of Circular Economy. Water 2023, Vol. 15, Page 1860 **2023-05-14**, 15 (10). DOI: 10.3390/w15101860.

Pal, S.; Padmanabhan, S. K.; Kaitheri, A.; Epifani, M.; Licciulli, A. Efficient Solar Light Photocatalyst Made of Ag3PO4 Coated TiO2-SiO2 Microspheres. Nanomaterials **2023 Feb 1**, 13 (3). DOI: 10.3390/nano13030588.

Rehman, A., Jahan, Z., Sher, F., Noor, T., Niazi, M.B.K., Akram, M.A., Sher, E.K., 2022/11/01. Cellulose acetate based sustainable nanostructured membranes for environmental remediation. Chemosphere 307. https://doi.org/10.1016/j.chemosphere.2022.135736.

Shah, G., Bhatt, U., Soni, V., 2023/06/01. A comprehensive review on triple R eco-management strategies to reduce, reuse and recycle of hazardous cigarette butts. Heliyon 9 (6). https://doi.org/10.1016/j.heliyon.2023.e16642.

Slaughter, E., Gersberg, R.M., Watanabe, K., Rudolph, J., Stransky, C., Novotny, T.E., 2011–05-01. Toxicity of cigarette butts, and their chemical components, to marine and freshwater fish. Tob. Control 20 (Suppl 1). https://doi.org/10.1136/tc.2010.040170.

Sun, L., Jiang, Z., Yuan, B., Zhi, S., Zhang, Y., Li, J., Wu, A., 2021/10/01,. Ultralight and superhydrophobic perfluorooctyltrimethoxysilane modified biomass carbonaceous aerogel for oil-spill remediation. Chem. Eng. Res. Des. 174. https://doi.org/10.1016/j.cherd.2021.08.002.

Teixeira, S.C., Silva, R.R.A., Oliveira, T.V., d., Stringheta, P. C., Pinto, M. R. M. R., Soares, N. d. F. F, 2021/08/01,. Glycerol and triethyl citrate plasticizer effects on molecular, thermal, mechanical, and barrier properties of cellulose acetate films. Food Biosci. 42. https://doi.org/10.1016/j.fbio.2021.101202.

Tran, H.D., Tran, H.D., Nguyen, D.Q., Nguyen, D.Q., Do, P.T., Do, P.T., Tran, U.N.P., Tran, U.N.P., 2023/06/05. Kinetics of photocatalytic degradation of organic compounds: a mini-review and new approach. RSC Adv. 13 (25). https://doi.org/10.1039/D3RA01970E.

V, A. S., Subash, A., Gholap, V., Kandasubramanian, B, 2024/08/01. Electrospinning of cellulose acetate for methylene blue dye removal. Hybrid Adv. 6. https://doi.org/10.1016/j.hybadv.2024.100205.

Wright, S.L., Kelly, F.J., 2017. Plastic and Human Health: A Micro Issue? Environ. Sci. Tech. 51 (12). https://doi.org/10.1021/acs.est.7b00423.

Zh, M., Lr, A.-A., Ff, A.-Q., If, D., H, k., s, c., 07/12/2023. A comprehensive review on adsorption of methylene blue dye using leaf waste as a bio-sorbent: isotherm adsorption, kinetics, and thermodynamics studies - PubMed. Environ. Monit. Assess. 195 (8). https://doi.org/10.1007/s10661-023-11432-1.

Zhang, L., Du, P., Zheng, Q., Zhao, M., Zhang, R., Wang, Z., Xu, Z., Li, X., Thai, P.K., 2025/02/01. Exposure to smoking and greenspace are associated with allergy medicine use – A study of wastewater in 28 cities of China. Environ. Int. 196. https://doi.org/10.1016/j.envint.2025.109291.