Antimicrobial Efficiency and Surface Interactions of Quaternary Ammonium Compound Absorbed on DBD Plasma Treated Fiber-Based Wiping Materials

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KEYWORDS: wipes, nonwoven, textile, disinfectant, plasma, quaternary ammonium salt, antimicrobial

ABSTRACT: The physico-chemical interactions between alkyldimethylbenzylammonium chloride (ADBAC) as disinfectant and 3 commercial wiping materials made from 100% polyester (PET), 55%cellulose/45%PET (blend) and 100% cellulose were investigated after treatment with dielectric barrier discharge (DBD) plasma at atmospheric pressure. Wipe

material type in terms of cellulose content, liquor ratio and immersion time demonstrated a significant influence on the adsorption of ADBAC. The higher the content of cellulose in the material, the higher is the adsorption of ADBAC active ingredient. The antimicrobial tests confirm that the ADBAC adsorbed on pure cellulosic material are inactivated losing their bactericidal activity, while 100% PET and blend wipes showed good antimicrobial efficacy. XPS analysis demonstrates the strong interactions of ADBAC with the plasma-generated oxygen species in the polyester-containing wipes surface. Unexpectedly, plasma-treated blend wipe displays a reverse antimicrobial effect compared to untreated samples, performing better in Gram-negative bacteria. The best result was obtained in the plasma treated 100% polyester wipe showing an improved of about 20% in Gram-positive bacteria and an excellent performance in Gram-negative ones. This method allows the unprecedented use of pure polyester as effective wiping material for surface disinfection eliminating the major drawback of pure polyester, its high hydrophobicity.

1. INTRODUCTION

Healthcare-associated infections (HAIs) due to nosocomial pathogens contaminating high-touch environmental surfaces (e.g. door handles, bedrails, call buttons, toilet seats, intensive care units (ICU), surgical sites) and medical devices (e.g. catheters guidewires, stents, pacemakers) are accountable each year for significant patient's morbidity, mortality and high economic costs.¹⁻³ Nosocomial pathogens can contaminate hospital surfaces at high concentrations, survive for protracted periods of time and persist after simple cleaning processes and cause further transmission.⁴ Moreover, cross contamination has been reported not only in nosocomial environment but also in food processing industry and domestic situations.⁵ Literature based evidence indicates an effective cleaning and disinfection process

is essential in preventing cross transmission and spread of HAIs.⁶⁻⁹ There are many approaches for surface disinfection, for instance, simply by heat, ultraviolet germicidal irradiation, automatic room disinfection (ARD) by hydrogen peroxide vapor system (HPV) or aerosolized hydrogen peroxide system (AHP).¹⁰ However, chemical disinfection is the most widespread in food processing industry and nosocomial environments due to its effective cost performance, simple application and relatively broad antimicrobial spectrum.¹⁰⁻¹³ Disinfectants are composed of a wide range of active ingredients such as alcohol, chlorine and chlorine compounds, hydrogen peroxide, peracetic acid, phenolics, aldehydes, and quaternary ammonium compounds.¹⁴ Among all, quaternary ammonium compounds (QACs) are vastly utilized in surface disinfection because of its thermal stability, low human toxicity and oxidative properties, low cost and adequate germicidal performance.¹⁵ However, in the last years concerns about the fate of QACs in the environment have emerged due to their toxicity to a wide range of aquatic organisms and to the rise of antibiotic resistance.¹⁵ In this context, the proper application and use of the disinfectant in order to minimize QACs unnecessary spread is of paramount importance.¹⁶ The application of a disinfectant on a target surface can be categorized into two methods, without mechanical action (e.g. total immersion and direct spraying) and with mechanical action (e.g. spray & wiping, dipping & wiping, and soaking & wiping).¹⁷ Among these strategies, disinfectants in combination with textile wiping materials are the most applied ones benefiting from their facile application, dependable antimicrobial performance and user-friendly handling.¹⁸⁻¹⁹ Moreover, the visible debris and organic load that could obstacle the disinfectant effectiveness can be easily removed by textile wipes.²⁰⁻²¹ Many studies regarding the efficacy of disinfecting wipes validated the benefits of the application of disinfecting wipes in terms of disinfection performance and working compliance.²⁰⁻²² Cellulose, including cotton and woodpulp, regenerated cellulose materials such as viscose and synthetic polymers like polyester and polypropylene are the

most currently used raw materials for commercial wipe production. However, studies have showed that the selection of an inappropriate textile material could bind with the absorbed active ingredient resulting in reduced or totally inhibited antimicrobial efficacy.²³⁻²⁶ Textile-based materials in contact with an aqueous QACs solution are subjected to 2 main process: i) the absorption of the solution onto the textile material due to its absorbency characteristic, one of the most important physical properties of textile materials, and ii) the adsorption of active ingredients from the solution onto textile material, which can result from the adhesion of the molecule or chemical interaction.²⁷ Adsorption is intended as the accumulation of a substance (active ingredient) at the interface between a solid surface (textile) and the bathing solution (disinfectant). The adsorption effect of QACs, has also been reported in literature with some limitations. Boyce *et al.* studied wipes with different soaking time submerged in the same bucket of QACs solution. However, the decrease of QACs concentration in the bucket due to the wipe adsorption was not taken into consideration.²⁵ Research from Hinchliffe *et al.* shows that the adsorption of QACs on the substrate was progressive by increasing the ratio of fabric to solution.²⁴ Unfortunately, it is not clear the impact of QACs binding to the wipe materials due to the lack of a proper microbiological tests. Bloss *et al.* did not conduct any microbiological test.²⁶ Moreover, little is known about the interaction mechanism between textile materials with disinfectants. The adsorption problems mainly take place between cellulose material and QACs active ingredients.²⁸ Possible factors that influence the adsorption of QACs are the type of wiping material, formulation of the QACs solution, temperature, pH value, immersion time, and target surface.^{24, 29-30} In conclusion, currently, there are no systematic studies that provide solid evidences to scientifically explain i) what is the interaction mechanism between textile substrate and disinfectant active ingredients, including the possible factors that affect it; ii) how this interaction impacts on the antimicrobial activity of the disinfecting wipes.

In this work, in order to positively improve the interaction among QACs disinfectants and wipe materials, a Double Barrier Dielectric Discharge (DBD) atmospheric plasma treatment was employed. The DBD plasma technology is one of the most effective non-thermal atmospheric plasma sources and has been attracting increasing interest for industrial textile applications because it is a dry (no involvement of water), environment- and user-friendly method to obtain surface modification without changing the bulk properties of the sample materials.³¹ Both surface activation and deposition of functional coatings by means of DBD atmospheric pressure plasma have been investigated in order to confer to textiles various properties, such as affinity for painting and dyeing, stain-resistance, antibacterial, no-shrinking and no-felting character.³² Atmospheric plasma is an alternative and cost-competitive method to low-pressure plasma which uses expensive vacuum equipment and polluting wet chemical treatments, allowing constant and homogenous processing of material surfaces.³³ DBD plasma is able to easily modify the surface of a wide range of natural and synthetic materials such as polyester, polyamide, wool and silk however, for cellulose material, usually only etching effect in terms of surface ablation is expected.³⁴ Therefore, based on the advantages above listed, DBD plasma treatment is deemed and applied as a potential solution to intervene in the interaction of QACs onto wipe materials and thereby improve antimicrobial efficacy.³⁵

A systematic investigation was made to study the interaction between untreated and DBD plasma treated wipes and QACs. Alkyldimethylbenzylammonium chloride (ADBAC) was employed as disinfectant and 3 commercial wiping materials made of polyester (PET), 55% cellulose/45%PET and pure cellulose (cotton) have been chosen for a series of absorption and adsorption tests and antimicrobial analysis. ADBAC is a cationic surface-active agent with a positively charged nitrogen covalently bonded to three alkyl group substituents and a benzyl substituent. It is well known as sanitizers, pharmaceutical antiseptic, medicinal disinfectants,

and germicides as one the most widely used QACs. X-ray photoelectron spectroscopy (XPS) analysis on the interaction between QACs and untreated and DBD plasma treated wiping materials was also carried out.

2. EXPERIMENTAL SECTION

2.1. Materials. Alkyldimethylbenzylammonium chloride (ADBAC) was purchased from the company EMD Millipore Corporation, a subsidiary of Merck KGaA, Germany. The chemical formula is $C_6H_5CH_2N(CH_3)_2RCl$ (where $R=C_8H_{17}$ to $C_{18}H_{37}$). The ADBAC was received in solid status and contained in a plastic bottle. ADBAC was kept in a silica gel desiccants desiccator after its opening since it can easily degrade with humidity. All other chemicals were purchased from Sigma-Aldrich and used without further purification steps.

2.2. Sample characterization. The wipes were pre-washed in a bath equipment, model IBELUS IL-720 (Labelus, Braga, Portugal) coupled with an infrared heating system in 0.05% non-ionic detergent (Diadavin UN from Tanatex chemicals, Ede, The Netherlands) solution with a bath ratio of 1:100 (1 g of wipe per 100 mL of detergent solution). The pre-washing program was performed at 40 rpm with a gradient of $3\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $40\text{ }^{\circ}\text{C}$ and maintained at this temperature for 30 mins. Then, the wipe samples were rinsed three times with distilled water in liquor ratio 1:100 and dried at $40\text{ }^{\circ}\text{C}$ for 24h. Before any test, wipe samples were conditioned at standard atmosphere of $20 \pm 2^{\circ}\text{C}$ and $65 \pm 2\%$ RH for 48 hours. Detailed information, such as fabric thickness and areal density, of the wipe samples selected for the tests can be found in Table 1. A digital thickness gauge M034 A with a pressure of 100 Pascal was employed to measure the thickness of the wipe samples based on the standard ASTM D1777-96 (2015). The wipe samples were prepared with a circular cutter

in surface area of 100 cm² for areal density measurements. The mean of 5 repetitions and their standard deviations (SD) are reported.

Table 1. Information of material, structure, mean of fabric thickness and areal density. Data represents mean values $\pm$ SD (n=5).

Control wipe	Plasma treated wipe	Material (Brand)	Structure	Thickness (mm)	Areal Density (g m ⁻²)
W1R	W1P	100% polyester (Texwipe®)	Hydroentangled nonwoven	0.36 $\pm$ 0.01	40.92 $\pm$ 0.01
W2R	W2P	55%cellulose/45% polyester (Contec®)	Hydroentangled nonwoven	0.54 $\pm$ 0.01	69.58 $\pm$ 0.01
W3R	W3P	100% bleached cotton (UMinho)	1/1 plain weave. Density (yarn cm ⁻¹) 34 warp, 30 weft	0.98 $\pm$ 0.01	118.72 $\pm$ 0.01

2.3. DBD plasma treatment of wipe samples. A semi-industrial prototype (Softal Electronics GmbH/University of Minho, Braga, Portugal) was used for the dielectric barrier discharge (DBD) plasma treatment. The system is equipped with ceramic-coated metal electrodes and silicon-coated counter electrodes together with 50 cm effective width, gap distance fixed at 3 mm, and producing the discharge at high voltage (10 kV) and low frequency (40 kHz). The plasma treatment was conducted on both sides of the wipe samples at room temperature and atmospheric pressure in air without any carrier gas. Optimized parameters resulted from previous study were applied for the operation of the machine: a dosage of 2.5 kW min m⁻² achieved by 1 kW power, 4 m min⁻¹ velocity, 5 passages.³⁶ The plasmatic dosage (kW min m⁻² m) was defined by equation 1:

$$Dosage = \frac{N \cdot P}{v \cdot l} \quad (1)$$

where, N = number of passages, P = power (kW), v = velocity (m min⁻¹), and l = width of treatment (m, 0.5 m in this case).

2.4. Contact angle and surface free energy measurement. An OCA 15 apparatus (Dataphysics Instruments GmbH, Filderstadt, Germany) with OCA20 software was used to characterize the contact angles and surface free energy of sample wipes. Each measurement was repeated five times and the average and standard deviation were calculated. Three liquids with known surface free energy and surface free energy components were used for the calculation of surface free energy, namely: distilled water (γ 72.8, γ^D 29.1, γ^P 43.7) with a dosing volume of 5 μ l and dosing rate of 5 μ l s⁻¹, polyethylene glycol 200 (PEG) (γ 43.5, γ^D 29.9, γ^P 13.6) with a dosing volume of 5 μ l and dosing rate of 12 μ l s⁻¹, and glycerol (γ 63.4, γ^D 37.4, γ^P 26.0) with a dosing volume of 5 μ l and dosing rate of 12 μ l s⁻¹.³⁷ The surface free energy (γ) was defined by polar and dispersive components. Principally, permanent and induced dipoles and hydrogen bonding result in three different intermolecular forces that composed the polar component, whereas the dispersion (non-polar) component of γ results from instantaneous dipole moments. The calculation of polar and dispersive components of the surface free energy (γ^D and γ^P , respectively) is based on the Wu method (harmonic mean) by equation 2:

$$\gamma_{sl} = \gamma_s + \gamma_l - 4 \left[\frac{\gamma_s^D \gamma_l^D}{\gamma_s^D + \gamma_l^D} + \frac{\gamma_s^P \gamma_l^P}{\gamma_s^P + \gamma_l^P} \right] \quad (2)$$

For polar substance (solids or liquids), the total γ , defined by equation 3, is a sum of the always-existing London dispersion forces (γ^D) and intermolecular interactions depending on the chemical nature of the material, compiled as polar forces (γ^P):

$$\gamma = \gamma^D + \gamma^P \quad (3)$$

The work of adhesion (W_{Adh}), representing the energy of interaction between the liquid and the solid phases per unit area, was characterized by equation 4.

$$W_{Adh} = \gamma^l (1 + \cos \theta) \quad (4)$$

where θ is the water contact angle calculated by goniometer and γ^l means the ‘liquid’ surface free energy, calculated by equation 3.

2.5. Absorption and adsorption tests. Wiping materials, immersion time and liquor ratio (fabric mass g: bulk solution mL) variables were studied. Plasma treated and untreated wipe samples were studied at four different immersion time (10, 30, 60, and 90 min) and eleven sets of liquor ratios (fabric mass g: bulk solution mL). The volume of the ADBAC bulk solution was fixed to 10 mL. Thus, the corresponding fabric mass (M_w) to certain liquor ratio is listed in the Table 2.

Table 2. Information of fabric mass to corresponding liquor ratio.

Liquor ratio	1:10	1:15	1:20	1:25	1:30	1:40	1:60	1:80	1:100	1:120	1:200
Fabric mass (g)	1.00	0.67	0.50	0.40	0.33	0.25	0.17	0.13	0.10	0.83	0.05

ADBAC solution (concentration: 0.8 g L^{-1}) was prepared freshly by adding $0.2 \text{ g } (\pm 0.5\%)$ of ADBAC to a 250 mL volumetric flask filled up with distilled water. The concentration of the solutions was calculated by measuring the UV absorbance of the solutions using a previously calculated standard curve. 10 mL of fresh prepared stock solution (C_0) was pipetted in high-density polypropylene conical tubes. This volume of the stock solution was converted in grams (W_0) assuming a density of 1 g L^{-1} for the ADBAC solution. Then, different wipe sample masses (M_w) were immersed to achieve the corresponding liquor ratios. The wipes were immersed for a specific time and then removed with a tweezers. The concentration of the remained solution (C_t) after removing the wipe was then measured. The weights of the tube with the liquid were recorded before the wipe immersion (S_0), during the wipe immersion (S_w) and after removing the wipe (S_t). The calculated ADBAC mass were later converted to volume (mL) assuming a density of 1 g L^{-1} for the ADBAC solution. Graphical representation of the immersion process can be found in Figure S1 in the supporting information. For every liquor ratio and immersion time, 3 independent replicates and 1 water control were performed.

2.6. Calculation of the concentration of ADBAC in the wipe (C_q) and of the weight ratio between the amount of ADBAC on the wipe and the wipe mass (R_w).

The step by step calculation of C_q and R_w is presented in this section and its graphical representation is presented in Figure S2 in the supporting information. The elements (mentioned in section 2.5) involved in the calculation are summarized and listed in Table 3, Table 4, and Table 5.

Table 3. Elements obtained by direct measurement.

Symbol	Definition
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(Unit)	
S₀ (g)	The initial total weight (Tube + ADBAC solution)
S_w (g)	Initial total weight with immersed wipes (Tube + ADBAC solution + Wipe)
S_t (g)	Total weight after removing the wipe (Tube + ADBAC solution - Wipe)
V₀ (mL)	Volume of the initial ADBAC bulk solution (10 mL)
W₀ (g)	Weight of the initial ADBAC bulk solution converted from V₀ assuming a density of 1 g L ⁻¹ for the ADBAC solution (10 g)
Abs₀	Absorbance of the ADBAC stock solution
Abs_t	Absorbance of the ADBAC solution after removing the wipe

Table 4. Elements obtained by primary calculation.

Symbol (Unit)	Definition	Calculation
W_w (g)	Weight of the solution absorbed by the wipe sample	$S_0 - S_t$
V_w (mL)	Volume of the solution absorbed by the wipe sample converted from W_w assuming a density of 1 g L ⁻¹ for the ADBAC solution.	$S_0 - S_t$
M_w (g)	Initial weight of the wipe sample	$S_w - S_0$
C₀ (g L⁻¹)	Initial concentration of the ADBAC stock solution	$0.806 * Abs_0 - 0.007$
C_t (g L⁻¹)	Concentration of the ADBAC solution after removing the wipe	$0.806 * Abs_t - 0.007$

Table 5. Elements obtained by secondary calculation.

Symbol (Unit)	Definition	Calculation
W_t (g)	Weight of the ADBAC solution after removing the wipe	$W_0 - W_w = W_0 - (S_0 - S_t)$
V_t (mL)	Volume of the ADBAC solution after removing the wipe converted from W_t assuming a density of 1 g L ⁻¹	$W_0 - W_w = W_0 - (S_0 - S_t)$

	for the ADBAC solution.	
Q₀ (g)	ADBAC amount in stock solution	$C_0 * V_0 = (0.806 * \text{Abs}_0 - 0.007) * V_0$
Q_t (g)	ADBAC amount remained in solution after removing the wipe	$C_t * V_t = C_t * (S_0 - S_t) = (0.806 * \text{Abs}_0 - 0.007) * (S_0 - S_t)$
Q_w (g)	ADBAC amount absorbed in the wipe sample	$Q_0 - Q_t$

Based on the description above, the concentration of ADBAC active ingredients adsorbed in the wipe samples (**C_q**) and active ingredient weight ratio absorbed by the wipe (**R_w**) are calculated as follow:

$$C_q = Q_w / V_w$$

$$Q_w = (Q_0 - Q_t) ; \quad Q_0 = C_0 * V_0 \quad ; \quad Q_t = C_t * (V_0 - V_w)$$

$$C_q = (C_0 - C_t) * V_0 / V_w + C_t$$

$$C_q = C_0 \times \frac{V_0}{V_w} - C_t \times \left(\frac{V_0}{V_w} - 1 \right) \quad (5)$$

$$R_w = Q_w / M_w$$

$$Q_w = (Q_0 - Q_t) ; \quad Q_0 = C_0 * V_0 \quad ; \quad Q_t = C_t * (V_0 - V_w)$$

$$R_w = [(C_0 - C_t) * V_0 + C_t * V_w] / M_w$$

$$R_w = C_0 \times \frac{V_0}{M_w} - C_t \times \left(\frac{V_0}{M_w} - \frac{V_w}{M_w} \right) \quad (6)$$

2.7. ADBAC concentration assessment by UV-Vis Spectrophotometry. UV-Vis spectrophotometry (Shimadzu, UV-1800) was used to measure the concentration of ADBAC

with a standard quartz cuvette. Initially, the $\lambda_{\max}$ was identified through a full wavelength scans from 200-800 nm. Three peaks at 268.5, 262.5, and 256.5 nm were detected. The wavelength at 262 nm was eventually employed because of its highest response and a corresponding calibration curve of [C] versus Abs (Absorbency) was developed using 5 different concentrations of ADBAC in distilled water (0, 0.2, 0.4, 0.5, 0.8, 1 g L⁻¹) and shown in equation (5):

$$[C_{\text{ADBAC}}] = 0.806 \text{ Abs} - 0.007 \quad (R^2 = 0.9999)$$

(7)

The generated equation (7) was used to calculate the concentration of ADBAC solution in the subsequent tests with the obtained Abs values from the UV-Vis spectrophotometry.

2.8. Laser scanning microscope (LSM). The untreated and plasma treated wipe samples were analyzed with an LSM from Keyence microscope (Osaka, Japan), model VK-X160 equipped with a red semiconductor laser supplied at the wavelength of 658 nm. The parameters of arithmetical mean height (Sa), maximum height (Sz), arithmetic mean peak curvature (Spc), and developed interfacial area ratio (Sdr) were measured to evaluate the surface roughness. Scanning was stitched 80 times composing an area of 10mm².

2.9. X-Ray photoelectron spectroscopy (XPS). The XPS analyses were carried out on the PHI-TFA XPS spectrometer produced by Physical Electronics Inc. (Chanhassen, EUA) to determine the surface functional groups. The base pressure during the XPS analyses was in the range of 10⁻⁹ mbar. Sample surfaces were excited by X-ray radiation over a 0.4 mm spot area (about 3-5 nm in analysis depth) with a monochromatic Al source at photon energy of 1486.6 eV. The survey wide-energy scan spectra were taken over an energy range of 0-1400

eV with pass energy of analyzer of 187 eV in order to identify and quantify present elements on the surface. The high-energy resolution spectra were acquired with energy analyzer operating at pass energy of 29 eV and resolution of about 0.6 eV. During data processing the spectra were aligned by setting the C1s peak at 284.8 eV, characteristic for C-C/C-H bonds. The accuracy of binding energies was about ± 0.3 eV. Two places on every sample were analyzed and average composition was calculated. XPS spectra were analyzed for elemental composition by a Multipak software, version 8.0 from Physical Electronics Inc. (Chanhassen, EUA). Deconvolution into sub-peaks was performed by least-squares peak analysis software, XPSPEAK version 4.1, using the Gaussian/Lorentzian sum function and Shirley-type background subtraction. The peaks were constrained to have equal FWHM to the main peak. No tailing function was considered in the peak fitting procedure. The components of the various spectra were mainly modelled as symmetrical Gaussian peaks unless a certain degree of Lorentzian shape was necessary for the best fit.

2.10. Antimicrobial Tests. The impact of interaction between wipes and active ingredients on its antimicrobial activity was evaluated by ASTM E 2149-13a Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents under Dynamic Contact Conditions. To achieve an evident distinction in the antimicrobial performance among the three wipe samples, the standard was modified enhancing bacteria inoculum concentration up to $1.5\text{-}3.0 \times 10^9$ CFU mL⁻¹ and reducing the wipe sample size (0.05g) and volume of bacteria inoculum (5mL). Gram-positive *Staphylococcus aureus*, ATCC 6538 and Gram-negative *Escherichia coli*, ATCC 25923 bacteria were used as working bacteria. Freeze-dried ampule was divided into several vials and stored at -80 °C as the stock culture. A subculture (G1) was produced from the frozen stock culture on tryptone soya agar (TSA) plates and incubated at 37 °C for 24 h. The working culture was freshly prepared prior to performing the test from G1 in the sterile Tryptic Soy Broth (TSB) for 18 h

at 35 ± 2 °C. Testing samples were prepared by pipetting 40 μL of 6300 $\mu\text{g mL}^{-1}$ ADBAC stock solution onto wipe samples. 40 μL was chosen because all wipes (0.05 g) were able to absorb all the liquid without any remaining excess. In the bactericidal testing study of ADBAC, Ioannou, et al. adopted 35, 45, and 55 $\mu\text{g mL}^{-1}$ as the final concentrations of ADBAC in the reaction vessel.³⁸ In this study, 50 $\mu\text{g mL}^{-1}$ was designated for the final concentration in the bacteria suspension. The testing samples were prepared in three repetitions, 1 min before inserted in the bacteria suspension (5 mL). Every testing sample was complemented with a water control (40 μL sterilized distilled water instead of ADBAC). A platform with orbital shaking at 120 rpm and 37 °C was used to keep the testing samples and the 5 mL bacterial suspension contained in a 15 mL sterilized conical tubes for 1 hour. Liquid from each sample was collected for plating after the agitation. Plates were incubated at 35 ± 2 °C for 18-20 hours for CFU counting. The other test procedure and calculation without specification follow Standard ASTM E 2149-13a. Log reduction was calculated by subtracting the CFU Log data of distilled water from the CFU Log data of ADBAC.

2.11. Statistical analysis

The experiments were performed in 3 replicates otherwise specified and the mean value and standard deviation (SD) of each results were obtained. A Two-way ANOVA analysis was applied to analyze the significance of the absorption/adsorption and antimicrobial testes. The level of significance (α) was set as 0.05.

3. RESULTS AND DISCUSSION

3.1. Absorption and adsorption. Both the absorption and adsorption of ADBAC onto the wiping materials were studied considering several parameters such as wiping material, immersion time, and liquor ratio. Wipe samples with different mass weights were immersed

in the ADBAC solution for a certain time. Three variables were considered as the most important indicators for the disinfection efficacy: i) The absorption ability of the wipes, due to the liquid availability to the target surface; ii) The concentration reduction of ADBAC in the bulk solution (C_R), due to the interaction between disinfectant and wipe while contact; (iii) The concentration of ADBAC eventually absorbed in the wipe (C_q), which reflects the final concentration of disinfectant that can be applied on the target surface, assuming that all the active ingredient absorbed by the wipe will be released on the target surface; iv) The weight ratio (R_w) that reflect the amount of active ingredient remaining on the wipe calculated as the amount of ADBAC absorbed in the wipe divided by the weight of the wipe. R_w allows estimating how long the disinfection ability could be sustained during a wiping process.

3.1.1. Absorption ability of ADBAC on wiping materials. The absorption can have a significant impact on the disinfectant ability due to the amount of disinfectant solution that can be delivered to the target surface. The final effect will be more pronounced if most of the liquid absorbed is available on the wipe surface instead of the bulk. Fitting of the absorption tests shows that the liquid absorbed by the wipe (V_w) is in a linear relationship with the fabric mass (M_w) independently of the used liquor ratio (1:200 up to 1:10) because the amount of liquid to be absorbed by the wipes is always in excess (Figure 1). The slope of the linear fitting represents the water absorbency ability of the material. The higher the slope is, the better is the water absorbency property of the material. On one hand, control nonwoven wipes W1R and W2R displayed very similar values suggesting that pure polyester (W1R) and polyester/cellulose blend (W2R) has comparable volumetric absorption in this structural configuration (Figure 1a). On the other hand, the woven fabric of pure cellulose (W3R) shows the lowest value mainly due to the higher degree of geometrical complexity. Differently to the homogeneous and structurally isotropic nonwoven textiles, the water

absorption of a woven fabric is mostly driven by the fabric thickness, solid volume fraction, and air permeability.³⁹ After DBD plasma treatment W1P shows a slight increase in water absorbency clearly due to the plasma treatment that significantly enhances the polar component of polyester material. On the contrary, W3P displays a small decrease because of the surface cleaning effect of plasma treatment on the top layer of the cotton fabric.⁴⁰ W2P shows the most significant decrease suggesting that the cellulose micro-fibrillated moiety and the nonwoven geometry have a considerable impact on the liquid absorbency even if the polyester structure hydrophilicity was improved by the plasma treatment.⁴¹

Figure 1. Correlation between fabric mass (X) and liquid absorption: a) for control wipe samples and b) for plasma treated wipe samples ($R^2=0.99$). $W1R=6.39X+0.21$; $W2R=6.41X+0.16$; $W3R=2.58X+0.08$; $W1P=6.71X+0.11$; $W2P=5.85X+0.17$; $W3P=2.35X+0.06$.

3.1.2. Concentration reduction of ADBAC in the bulk solution (C_R). The concentration reduction in bulk solution (C_R) is calculated in equation 8:

$$C_R = 100 \times \frac{C_0 - C_t}{C_0} \quad (8)$$

The higher is the concentration reduction (C_R) values, the stronger is the adsorption of active ingredients in the solution. C_R is clearly dependent on the set of liquor ratio and immersion time. Detailed information of C_R on control and plasma treated wipe samples regarding all the liquor ratios and immersion times can be found in Table S1 in the supporting information. On one hand, liquor ratio, as shown in Anova analysis (Table S2 in the supporting information), it has a significant impact on the concentration reduction of ADBAC for all wipe samples in both untreated and plasma treated samples. Moreover, in W2 and W3 wipes the C_R decrease with the reducing of liquor ratio following a S-type adsorption

isotherm (in W1 the C_R is too small to see a trend). On the other hand, regarding immersion time, it is evident from the data that the adsorption of ADBAC took place in the first 10 mins after the wipe contact in both untreated and plasma treated samples (Figure 2, 3 and 4). Excluding W1, which does not show significant adsorption of ADBAC, both W2 and W3 wipes presented an increase of C_R in function of the immersion time (see Anova analysis in Table S2 in supporting information). For both untreated and plasma treated samples from 10 mins to 30 mins, the C_R values showed a small increase in W2 and a significant increase in W3 wipe (Figure 3 and 4) especially for the highest liquor ratios (e.g. 1/10 and 1/15) diminishing to a plateau at lower liquor ratios (e.g. 1/100, 1/120, and 1/200). Then, the adsorption slowed down showing no significant difference between immersion time at 60 mins and 90 mins.

Also the materials have a significant effect on the C_R variability. W1 displayed a very low C_R value while after plasma treatment a slight increase of C_R was noticed meaning that a higher amount of ADBAC is present in the wipes. WR3 showed the highest C_R value, almost double than WR2, under the same condition (immersion time and liquor ratio) due to the different cellulose content (Figure 3 and 4). This is in accordance with the literature showing significant binding of quaternary ammonium compounds by cellulosic material.⁴²⁻⁴³ Additionally, it was found that the binding degree is proportional to the content of cellulose in the fabric.²³ After plasma treatment, W3P displayed a significant reduction of the C_R compared with the W3R, while W2P showed an opposite behavior (Figure 3 and 4).

Figure 2. Concentration Reduction (C_R) $\pm$ SD of untreated and plasma treated W1 samples changing with immersion time and liquor ratio.

Figure 3. Concentration Reduction (C_R) $\pm$ SD of untreated and plasma treated W2 samples changing with immersion time and liquor ratio.

Figure 4. Concentration Reduction (C_R) $\pm$ SD of untreated and plasma treated W3 samples changing with immersion time and liquor ratio.

3.1.3. Concentration of ADBAC absorbed in the wipe (C_q). The concentration of ADBAC active ingredients adsorbed in the wipe samples (C_q) is calculated based on Equation 5 in material and method. Liquor ratio is expressed in the formula as M_w / V_0 in this study. The ratio (V_w / M_w) between the volume of the ADBAC solution absorbed by the wipe (V_w) and the mass of the wipe (M_w) representing the material's water absorbency ability, is a fixed value to the same type of material (as discussed in the absorption section). Consequently, the ratio between V_0 to V_w can also be interpreted as a value only depended on the value of V_0 / M_w (in reciprocal function of the liquor ratio M_w / V_0) for each type of material. Thus, the factors: C_0 the initial concentration of ADBAC solution, V_0 / V_w depending on the material water absorbency or liquor ratio when it comes to the same type of material and C_t the remaining concentration of ADBAC solution after removing the wipe, have a positive impact on the final value of C_q . Thus, it can be concluded that, the smaller the liquor ratio is, the higher the concentration of ADBAC in the immersed wipe is.

The C_q results of both untreated and plasma treated wipe samples vary with liquor ratio (Figure S3, S4 and S5 in supporting information). In all W1 wipes no significant adsorption of ADBAC was observed. In this case, the textile substrate is acting as a vehicle that only transfer the ADBAC solution from the stock to the surface applied, thus in equation 5 can be assumed that $C_0 = C_t$. In untreated and plasma treated W2 and W3, the C_q is generally increasing with the decrease of the liquor ratio. The plasma treated wipe samples showed slightly lower values of C_q than untreated ones as previously observed for C_R .

3.1.4. Weight ratio between the amount of ADBAC on the wipe and the wipe mass (R_w). The weight ratio between the amount of ADBAC on the wipe and the wipe mass (R_w) can be calculated using equation 6 in materials and methods. This ratio was calculated because different wipes may show the same C_q value but, if the wiping material presents a

higher water absorbency property (V_w) it will consequently display a larger weight ratio (R_w) of active ingredients in the wiping material allowing the wipe application on a larger surface area or for longer wiping time. In W1, R_w displayed quasi-constant values independently of the used liquor ratio due to the very low adsorption of ADBAC (Figure S6 in supporting information) that is dependent on C_0 and the material type of the wipe. However, the R_w of W2 and W3 increased with the diminishing of the liquor ratio (Figure S7 and S8 in supporting information). As expected, W3 shows in general lower R_w than W2 due to its poorer water absorbency properties. Comparing control and plasma, it is noticed that R_w is very similar in higher liquor ratio (e.g. 1/10, 1/15 and 1/20) in both W2 and W3 wipes, but plasma treated samples in lower liquor ratios display a diminishing R_w . This phenomenon can be explained by the plasma effect on cellulose that reduce the water absorbency of the wipes. However, this is only noticed in the lower liquor ratios because of the higher quantity of ADBAC that is available in the lower liquor ratios. In higher liquor ratio in which the wipe adsorbs almost all the available volume, and subsequently almost all the ADBAC mass in solution, the phenomenon will be less pronounced.

3.2. Contact angle and surface free energy measurement. The results of stationary contact angle, surface free energy and work of adhesion of both untreated wipe samples (R) and plasma treated wipe samples (P) are displayed in Table 6. W1R (PET) shows hydrophobic behavior with a contact angle of 139° . All of the other wipes including the plasma treated ones showed hydrophilic property with a contact angle of 0° . The improved hydrophilicity after the plasma treatment is due to the newly formed polar functional groups on the polyester surface, and the increased surface roughness providing higher surface area for adsorption.⁴⁴ This hypothesis is validated by the enhanced polar component value of the plasma treated wipe (W1P) that increased from 0.68 to 68.14 mJ m⁻². On the contrary, W2 and W3 surface energies and works of adhesion decreased after plasma treatment due to the

surface plasma etching effect reaching similar values to W1P.³¹ Due to these similar values it is difficult to distinguish the effect of cotton and polyester components in W2P. In W3P, the plasma treatment acts on the microfibrillated morphology of the cellulose on the top surface layer of the wipes, reducing the surface area for water absorption by eroding the amorphous regions of the cellulose and maintaining the crystalline domains.⁴⁵

Table 6. Stationary contact angle, surface free energy and work of adhesion of (raw and plasma treated) wipe samples. Data represent mean values $\pm$ SD (n=5).

Sample	$\theta_{\text{Distilled water}}$	$\theta_{\text{Polyethylene glycol}}$	θ_{glycerol}	Surface energy (mJ/m ²)	Dispersive (mJ/m ²)	Polar (mJ/m ²)	Work of adhesion (mJ/m ²)
W1R	139.1 $\pm$ 3.6	27.9 $\pm$ 10.0	140.1 $\pm$ 8.0	11.58	10.90	0.68	19.05
W2R	0	22.7 $\pm$ 9.9	118.3 $\pm$ 7.1	113.22	0.27	112.95	226.44
W3R	0	58.4 $\pm$ 7.1	47.7 $\pm$ 8.1	123.49	5.53	117.96	246.98
W1P	0	0	42.4 $\pm$ 7.9	81.84	13.70	68.14	163.68
W2P	0	0	27.9 $\pm$ 4.7	80.14	16.50	63.64	160.28
W3P	0	0	40.4 $\pm$ 5.8	81.56	14.09	67.48	163.12

3.3. Laser scanning microscopy (LSM). The 3D surface roughness of the wipes before and after plasma treatment was evaluated by laser scanning microscopy (LSM). Figure 5 displays the color-coded height representations of the surface topography of the wipes (red and blue represent the highest and lowest peaks and valleys, respectively). It is evident that W1 and W2 present differences between the back and front side due to the one-side hydroentangling fabrication method in which a high-pressure water jet produced large spaced nonwovens structures with high and low density regions. W1 structure is more uniform because exclusively composed of thin polyester fibers while W2 clearly shows the entangled

structures of the cellulose component in the backside. W3 did not show any difference in both side (data not shown) and the LSM image clearly shows the woven structure of the wipe with few fibers protruding from the surface. After plasma treatment, the surfaces seem more uniformed, which could be a result of the plasma erosive effect (3D image can be observed in Figure S9 in supporting information). Table 7 shows the corresponding roughness parameters for the wipes 1, 2 and 3 before and after plasma treatment in both sides for the nonwovens wipes (W1 and W2) and just in one side for the woven wipe (W3) since its side structure does not present differences. For the nonwoven wipes (W1 and W2) the arithmetical mean height (Sa) and the maximum height (Sz) values are higher in the front sides. These parameters are significantly affected by any surface variability including holes and protruding fibers and provide a measure of the average roughness. After plasma treatment, Sa and Sz values increase in the nonwoven wipes except for the W1 in the front side. It seems that plasma was able to increase roughness due to the erosion of the nonwoven surface structure creating sharper and deeper valleys. This is also confirmed by the hybrid parameters arithmetic mean peak curvature (Spc) and developed interfacial area ratio (Sdr) that increase after plasma treatment. A larger value of Spc indicates pointed peaks on the contact surface while Sdr, expressed as the percentage of the additional surface area contributed by the texture as compared to an ideal plane ($Sdr=0$ in a flat surface), implies an increase of the surface complexity. The results of the cotton woven wipe after plasma treatment (WP3) showed opposite behavior decreasing in all the parameters suggesting a smoother surface. This is in accordance with the observed reduced water absorbency of WP3 and reinforces the hypothesis that its primary cause is the removal of the micro-fibrillated cellulose on the fabric surface due to plasma etching.

Sample	Laser Scanning Microscopic Image of heights
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	Front	Back
W1R
W1P
W2R
W2P
	Untreated	Plasma treated
W3

Figure 5. Laser Scanning Microscopic Images of the untreated and plasma-treated wipes in both sides (only for nonwovens). The coloration represents different heights from a theoretical plane in the middle of the sample.

Table 7. Laser scanning microscope results of the untreated and plasma treated wipes with analyzed surface area of 10 mm².

Sample	Sa - Arithmetical mean height (μm)	Sz - Maximum height (μm)	Spc - Arithmetic mean peak curvature (mm^{-1})	Sdr - Developed interfacial area ratio (%)
W1R front	78.2	580.5	2255.9	7.9
W1R back	34.1	358.9	1548.7	1.7
W1P front	45.5	510.6	2614.9	10.7
W1P back	37.8	427.9	1563.8	1.7
W2R front	41.7	457.6	1267.2	5.1
W2R back	23.7	206.6	1051.1	2.0
W2P front	47.0	540.3	3161.5	20.1
W2P back	24.5	330.9	1085.1	2.3
W3R	31.5	568.5	1842.2	6.7
W3P	25.9	415.0	1560.7	4.9

3.4. XPS analysis. The wipe samples selected for XPS analysis are the ones with liquor ratio 1/20 and 90 minutes of immersion time in ADBAC in order to reach the equilibrium in the ADBAC adsorption. The relative chemical composition of untreated and DBD plasma treated wipe samples immersed in water or in ADBAC are reported in Table 8. For W1 sample, made of 100% polyester, a significant increase (24% from 26.35 to 32.55) of oxygen content was noted after plasma treatment. The addition of oxygen species after DBD plasma treatment in polyester is a well-known effect.⁴⁶ DBD discharge in air is able to generate oxygen-containing functional groups, increasing the surface energy and enhancing the

surface wettability of polyester, due to the inclusion of the atomic oxygen from the atmosphere formed from the electron-impact dissociation of O₂ molecules.⁴⁷ The observed residual nitrogen component in the untreated control wipes is due to the adsorbed N from the atmosphere since none of the used wipes polymers contain nitrogen in its structure. After plasma treatment, the increase in N component in these wipes is due to the incorporation of atmospheric nitrogen to the fabric surface during the plasma reactions as previously observed.⁴⁸ Due to the introduction of ADBAC (W1Q), both untreated and plasma treated W1 showed, as expected, an increase in N/C atomic ratio since every ADBAC molecule contains a nitrogen atom. However, plasma treated W1Q shows a higher N/C atomic ratio comparing with the untreated W1Q (about 50%). This suggests that a significant part of the adsorbed ADBAC remains on the surface of the polyester and after plasma treatment, its surface concentration increases even more, reacting with the newly formed oxygen species. For W3, plasma treatment seems to provide only etching effect, because no significant difference in oxygen content between untreated and plasma treated was observed. However, after the immersion of ADBAC, a slight difference of the nitrogen content between untreated and plasma treated W3 (28% reduction from 0.90 to 0.65) was observed. This is in accordance with the LSM results showing a cotton surface roughness reduction (Table 7). It was previously observed that the etching of the cotton surface microfibrils is able to promote the reorientation of the polar surface functional groups reducing the active ingredient adsorption.⁴⁹ For W2 sample, a slight increase (around 8% from 30.65 to 33.25) of oxygen and a 9% growth in the nitrogen content can be observed. This is due to the blended composition of polyester and cellulose. Since the cellulose fibers are only etched and adsorb the ADBAC in its inner structure, in W2 the increase in oxygen and nitrogen content can be mainly attributed to the plasma treated polyester component and the ADBAC in its surface, respectively.

Table 8. Chemical composition and atomic ratio of untreated and DBD plasma treated water/ADBAC immersion wipe samples result from XPS analysis.

Sample	Untreated					Plasma Treated				
	Chemical composition (%)			Atomic ratio		Chemical composition (%)			Atomic ratio	
	C	O	N	O/C	N/C	C	O	N	O/C	N/C
W1	73.10	26.35	0.60	0.36	0.01	65.85	32.55	0.75	0.49	0.01
W2	68.90	30.65	0.40	0.45	0.01	65.75	33.25	1.05	0.51	0.02
W3	61.70	37.80	0.50	0.61	0.01	60.65	38.8	0.55	0.64	0.01
W1Q	82.70	14.65	1.65	0.18	0.02	79.95	18.00	2.00	0.23	0.03
W2Q	61.30	38.15	0.55	0.62	0.01	61.85	37.55	0.60	0.61	0.01
W3Q	63.50	35.55	0.90	0.56	0.01	62.80	36.60	0.65	0.58	0.01

The deconvolution result of the high-resolution XPS spectra of C1s, O1s, and N1s was summarized in Table 9. All the deconvolution graphs can be found in Figure S10, S11 and S12 in supporting information. For W1, of 100% polyester, the C1s envelopes of both untreated and plasma treated samples were deconvoluted in 3 peaks attributed to C-C or C=C or C-H (284.8 eV), C-O or C-O-C (286.5 eV), and O-C=O (288.8 eV).⁵⁰ After plasma treatment, there is a slight change of the bonding distribution (increasing of the carbon-oxygen intensity) due to the inclusion of oxygen species from the atmosphere (Figure S10 in supporting information). This was also confirmed from the result of O1s where the envelope can be deconvoluted in two peaks at 532 eV and 533.3 eV attributed to the carbonyl oxygen and the oxygen atoms single bonded to carbon atoms of the PET structure, respectively.⁵¹⁻⁵² After plasma treatment, an increase in the carbonyl oxygen can be noted. After the introduction of the ADBAC, there is a negative shift of C-C binding energy (from 284.8 eV to 284.4 eV) as well as an increase in the peak relative percentage (W1R from 68.3% to 79.2%, and W1P from 58.8% to 76.6%), resulting from the increased amount of

phenyl aromatic group and long alkyl group chain of ADBAC on the wipe surface.⁵³⁻⁵⁴ In the W1RQ sample, the new peak at 285.7 eV is attributed to the C-N bond of ADBAC confirming its presence on the surface of the W1.⁵⁵ The peak attributed to the O-C=O group was significantly reduced (from 12% to 6%) due to the introduction of the long alkyl chain of ADBAC and shifted to lower binding energies at 288.5 eV suggesting an interaction of ADBAC molecule with the oxygen species on the polyester surface. The plasma-treated surface of W1PQ shows similar binding energy and intensity for the C-C and O-C=O components to the untreated sample W1RQ. However, the significant shift of the C-N bond to higher binding energy (286.2 eV) suggest a strong interaction of the ADBAC molecule with the oxygen single bonded to carbon. The new peak at 530.8 eV, appearing in the O1s deconvolution result of both W1RQ and W1PQ, may be attributed to the ADBAC oxidation and interaction with the polyester.⁵⁶⁻⁵⁷ After plasma treatment, these peaks increase from 24.8% to 29.9% due to the ADBAC surface interaction with the newly formed polyester oxygen species. The confirmation of the surface deposition of ADBAC onto the W1 surface comes to the deconvolution of the N1s high-resolution spectra (Figure S10 in supporting information). Among all the analyzed wipes, only W1PQ (plasma treated pure polyester with ADBAC) shows peaks with intensities well above the detection limits. Moreover, only this sample can be deconvoluted in two well distinct peaks at 405.8 eV and 401.8 eV. The peak at 401.8 eV can be assigned to the N-C bonding of the ADBAC structure while the peak at 405.8 eV is associated to the nitro group confirm the strong interaction of the ADBAC with the oxygen species on the polyester surface.⁵⁸⁻⁵⁹ All other wipes containing ADBAC showed only a very faint peak, in the edge of the detection limit, associated to the ADBAC structure at 401.8 eV indicating that only the plasma treated W1 retains a significant amount of ADBAC onto the very surface of the wipe interacting with the newly generated oxygen species of polyester.

For W2, that is a mix of polyester and cellulose, the C1s spectra of both untreated and plasma treated wipe samples were deconvoluted at the same peak positions of W1 (Figure S11 in supporting information). Also in this case, after plasma treatment, an increase of the carbons bonded to oxygen species was observed. However, the peak at 286.2 eV attributed to the oxygen atoms single bonded to carbon atoms show a significantly higher relative percentage compared to W1 due to the presence of cellulose. Deconvolution of the O1s core level of W2R consists of two peaks. The first at 532.8 eV is attributed to the single-bonded oxygen of the ester functional group ($\text{O}=\text{C}-\text{O}$) of polyester and $\text{C}-\text{OH}$ from cellulose.⁶⁰⁻⁶¹ The second, at 531.5 eV to the $\text{O}-\text{C}-\text{O}/\text{C}-\text{O}$ functional group of cellulose and to the double-bonded oxygen of polyester ($\text{O}=\text{C}-\text{O}$).⁶² After plasma treatment, W2P displays a shift of the peaks to higher binding energies due to the increase of the oxidation state on the wipe surface. The introduction of ADBAC in W2 radically change the peak intensities showing the typical C-C (284.8 eV), C-O (286.5 eV) and O-C-O (287.8 eV) components and relative percentages of cellulose.⁶³ It seems that the adsorption of ADBAC addition promotes the swelling of the cellulose component of the wipe W2 resulting in the predominant species on the wipe surface during the XPS analysis. This is also confirmed by the absence of significant nitrogen component on the wipe surface. However, the O1s deconvolution shows a dominant peak at 532.8 eV in both W2RQ and W2PQ attributable to the single-bonded oxygen of cellulose. The component at 530.8 eV of the ADBAC interaction with the oxygen species on polyester fibers results in only about 5% of the O1s envelope deconvolution confirming that most of the disinfectant is adsorbed by the cellulose component and is not available on the wipe surface.

The woven W3 wipe composed exclusively of cotton shows the typical C1s spectra of cellulose. C1s envelope was deconvoluted for all the samples into the same three peaks at 284.8 eV, 286.5 eV, and 287.8 eV corresponding to the C-C, C-O and O-C-O components of

cellulose.⁶⁴ The deconvolution of the O1s high-resolution spectra of the W3 wipes displays the two typical peaks of cellulose at 531.8 eV and 533.3 eV except for W3PQ that show a shift to lower binding energies at 531.5 eV and 532.8 eV.⁶⁵ This shift could be attributed to the swelled and lower oxidized plasma treated cotton surface after ADBAC adsorption.⁶⁶

Table 9. Results of the deconvolution analysis of the C1s, N1s, and O1s peaks for the untreated and DBD plasma treated wipes before and after ADBAC adsorption. Reported binding energies have an associated error of ± 0.3 eV.

Relative area corresponding to different chemical bonds (%)																
Sample	C1s								O1s						N1s	
	284.4 eV	284.8 eV	285.7 eV	286.2 eV	286.5 eV	287.8 eV	288.5 eV	288.8 eV	530.8 eV	531.5 eV	531.8 eV	532.0 eV	532.8 eV	533.3 eV	405.8 eV	401.8 eV
W1R	-	68.3	-	-	19.4	-	-	12.3	-	-	-	49.1	-	50.9	-	-
W1P	-	58.8	-	-	22.3	-	-	18.9	-	-	-	50.5	-	49.5	-	-
W1RQ	79.2	-	15.1	-	-	-	5.8	-	24.8	-	-	43.1	-	32.1	-	100*
W1PQ	76.6	-	-	17.5	-	-	5.9	-	29.9	-	-	43.7	-	26.4	35.4	64.6
W2R	-	56.7	-	-	28.1	-	-	15.2	-	36.0	-	-	64.0	-	-	-
W2P	-	50.7	-	-	29.7	-	-	19.6	-	-	41.1	-	-	58.9	-	-
W2RQ	-	17.2	-	-	67.6	15.2	-	-	4.4	-	-	-	95.6	-	-	100*
W2PQ	-	29.7	-	-	57.2	13.1	-	-	5.9	-	-	-	94.1	-	-	100*
W3R	-	27.7	-	-	60.2	12.1	-	-	-	-	28.8	-	-	71.2	-	-
W3P	-	24.9	-	-	64.9	10.2	-	-	-	-	33.1	-	-	66.9	-	-
W3RQ	-	28.5	-	-	59.4	12.1	-	-	-	-	16.1	-	-	83.9	-	100*
W3PQ	-	35.1	-	-	54.2	10.7	-	-	-	37.7	-	-	62.3	-	-	100*

*Residual values based on peaks on the threshold of the detection limit.

Antimicrobial efficacy test with ASTM E2149-13a. In this study, a modified standard ASTM E2149-13a was used. This test method allows direct and complete contact between microorganism and active ingredients, which eliminates interferences from other parameters (i.e. mechanical action and surface contact). The chosen method gives a straightforward observation of how the disinfectant/substrate interactions impact on the antimicrobial efficacy. The log reduction and standard deviation from the shaking flask test are presented in Figure 6 including both untreated and plasma-treated wipe samples and control of pure ADBAC. ANOVA results (Table S3 in supporting information) show that the population means of the different testing wipe types are much more significant of the population means of the two bacteria types. W1 showed an excellent log reduction for both Gram-negative and Gram-positive bacteria. Compared to the pure ADBAC control sample W1 displays similar results for *S. aureus* bacteria but lower values for *E. coli*. As proved by XPS analysis, ADBAC in W1 is fully available on the wipe surface, thereby yielding a very good antimicrobial efficacy. After plasma treatment W1 shows similar results for *E. coli* but an improved bacterial reduction against *S. aureus*. Since the ADBAC efficacy in Gram-positive or Gram-negative bacteria is function of the N-alkyl chain length, it is reasonably suppose that the plasma generated species interacting with the ADBAC molecule improved the N-alkyl chain orientation in order to have more chains of 12-14 alkyls (optimal for Gram-positive bacteria) then of 14-16 alkyls (optimal for Gram-negative bacteria).⁶⁷ However, it will be necessary to isolate each component of the ADBAC commercial preparation in function of the N-alkyl chain length and test them separately to confirm this hypothesis. This will be the subject of the following work. Since ADBAC is sold as an unknown mixture of $C_6H_5CH_2N(CH_3)_2RCl$, where R can vary from C_8H_{17} to $C_{18}H_{37}$, it will be necessary to isolate each different quaternary ammonium compound in the ADBAC mixture by chromatography. Then,

each compound interacting with the plasma generated species will be analyzed by XPS and for its antimicrobial performance.

W2 surprisingly exhibited a relatively high log reduction, almost as good as W1 (at least for Gram-positive bacteria), even though strong adsorption of ADBAC was previously observed. The possible reason could be that the function of bacteria reduction to the ADBAC concentration applied is not in a linear relationship, means a small concentration reduction of ADBAC may not cause a dramatic log reduction loss.⁶⁸ The plasma-treated W2 showed a decreased log reduction against *S. aureus* and an increased one in *E. coli*. Also, in this case, the explanation could be the different interaction kinetic and adsorption of the ADBAC species. It seems that plasma treatment improves the availability of the longer N-alkyl chain ADBAC species (14-16 alkyls), with more affinity for Gram-negative bacteria, on the wipe surface. This can be caused by plasma-induced changes in the critical micelle concentration in which the ADBAC monomers undergo self-assembly to form spherical aggregates showing different adsorption mechanisms (adsorption by electrostatic or hydrophobic interactions) in the function of the wipe material and N-alkyl chains length.⁶⁹ W3 cannot be considered as having an antimicrobial effect (Log reduction <3) but only a bacteriostatic one. Both Gram-positive *S. aureus* and Gram-negative *E. coli* bacteria showed a significant reduction in antimicrobial efficiency compared to W1 and W2 wipes due to the strong adsorption of ADBAC on cellulose as previously observed. After plasma treatment, a slight improvement in W3's antimicrobial efficacy for Gram-negative *E. coli* can be noted, confirming the ADBAC adsorption reduction with plasma-treated W3 and also validating the hypothesis of selective adsorption of the ADBAC species on cellulose after plasma treatment.

It seems that the antimicrobial test result did not show a significant increase from the plasma-treated wipe samples even though a higher ADBAC concentration was observed from the XPS

analysis. However, in a previous ageing study of the plasma effect on antimicrobial efficacy, it was found that plasma treatment can prolong the release of increased ADBAC on the surface of W1 (polyester) doubling the shelf time.⁷⁰ This result, in addition to the fact that only in the pure polyester wipe (W1) it was possible to observe a significant amount of ADBAC on the wipe surface, demonstrate the efficacy of plasma treatment in tightly maintain the disinfectant where is really needed for a long time. Besides, plasma treatment is a dry and ecofriendly surface modification method that significantly reduces the consumption of water and the use of chemical stabilizers.

Figure 6. Bacteria log reduction with the untreated (R) and plasma-treated (P) wipe samples in the shaking flask test.

4. CONCLUSION

W1 (100% polyester) showed the best disinfectant performances and roughly no adsorption of ADBAC. In the plasma-treated wipe, XPS analysis confirms that ADBAC is located on the wipe surface interacting with the plasma-generated oxygen species, despite the increased adsorption compared to control wipe. W2 (55% cellulose and 45% polyester) revealed a medium response in adsorption of ADBAC, but similar antimicrobial effectiveness to W1, whereas the plasma-treated ones displayed an increased adsorption effect due to the hydrophilic nature of the plasma-generated species on the polyester component. However, the antimicrobial performance of plasma-treated W2 showed an opposite behavior compared to the untreated sample because of the different adsorption mechanisms of the disinfectant that depending to the type of wipe material or N-alkyl chains length of ADBAC which adsorption can be ruled by electrostatic or hydrophobic interactions. W3 (100% cellulosic material) achieved the major adsorption of ADBAC resulting in the highest values of concentration reduction (C_R). Despite plasma treatment significantly reduced the ADBAC adsorption of about 50%, both untreated and plasma-treated samples showed the lowest antimicrobial efficacy due to the high adsorption and negative interaction of ADBAC with the OH groups in cellulose. It is important to note that liquor ratio (fabric mass in gram/liquid volume in mL) and immersion time in the first 30 minutes, has a relatively substantial impact on the investigated variables. A small liquor ratio can yield to low C_R , high C_Q and R_W leading to the higher available disinfectant active ingredient in the wipe. On one hand, this work confirms once again the negative impact of cellulose in the efficacy of QACs for disinfection. On the other hand, plasma treatment applied to polyester-containing wipes reveals to be an effective way to improve QACs concentration on the wipe surface for improved antimicrobial efficacy. This work opens the way for a new class of wiping

materials with improved antimicrobial efficacy using a low-cost and environmental-friendly plasma technique.

ASSOCIATED CONTENT

Supporting Information.

Figures illustrating the developed method, figures of the high-resolution deconvoluted XPS spectra, tables of the absorption and adsorption results, additional images of the laser scanning microscopy, tables of the ANOVA analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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X.S. wrote the manuscript, performed the main analysis and data collection. U.C and P.S. performed the XPS data analysis. L.V. supervised the antimicrobial analysis and performed data interpretation. A.Z. supervise all works, performed the XPS deconvolution analysis and finalize the manuscript.

Funding Sources

This work was funded by European Regional Development funds (FEDER) through the Competitiveness and Internationalization Operational Program (POCI) – COMPETE and by National Funds through Fundação para a Ciência e Tecnologia (FCT)—under the project POCI-01-0145-FEDER-007136 and UID/CTM/00264/2019. Xinyu Song (SFRH/BD/130028/2017) acknowledges FCT, Portugal, for its doctoral grant financial support. Andrea Zille also acknowledges financial support of the FCT through an Investigator FCT Research contract (IF/00071/2015) and the project PTDC/CTM-TEX/28295/2017 financed by FCT, FEDER and POCI in the frame of the Portugal 2020 program.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was funded by European Regional Development funds (FEDER) through the Competitiveness and Internationalization Operational Program (POCI) – COMPETE and by National Funds through Fundação para a Ciência e Tecnologia (FCT)—under the project POCI-01-0145-FEDER-007136 and UID/CTM/00264/2019. Xinyu Song (SFRH/BD/130028/2017) acknowledges FCT, Portugal, for its doctoral grant financial support. Andrea Zille also acknowledges financial support of the FCT through an Investigator FCT Research contract (IF/00071/2015) and the project PTDC/CTM-TEX/28295/2017 financed by FCT, FEDER and POCI in the frame of the Portugal 2020 program.

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