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Reconditioning of Wash Water for the Fresh-Cut Industry

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Abstract

Large volumes of water are used in the fresh-cut produce industry affecting the generation of wastewater and the need for recycling. The present study evaluated different treatments for the reconditioning of wash water. Suitable technologies were examined to reduce the organic matter and the content of chlorate as the most critical chlorine disinfection by-product. Results showed that the reconditioning of wash water from the fresh-cut produce industry represents a challenge due to the high content of dissolved organic matter. Coagulation-flocculation treatment with a tannin-based agent, Tanfloc™ was effective in reducing the turbidity but not the organic matter. Cross-flow ultrafiltration by 15 kDa ceramic membrane retained the particulate organic matter, reducing above 85% the turbidity and the total suspended solids, but it decreased by only 25% the organic matter. Heterogeneous TiO2-mediated photocatalysis combined with Ultraviolet Light-Emitting Diodes (UV-LEDs) treatment at 365 nm after ultrafiltration did not improve organic matter reduction. However, granular activated carbon adsorption removed organic matter and chlorate, although the carbon mass turned out exhausted. This study shows that ultrafiltration and activated carbon adsorption are promising options for wash water reconditioning for the fresh-cut industry.

Keywords: Active carbon adsorption; Disinfection by-products; Chlorate; Coagulation-flocculation; Photocatalysis; Ultrafiltration

Introduction

The fresh-cut industry is one of the food industries with significant resources needs because of the large volumes of water and energy required in the washing process of fresh-cut products. As a result, large quantities of potable water are used, and equally large amounts of wastewater are generated [1,2]. Water reuse is a top priority area in primary production, and several actions have been proposed for the substantial reduction of water needs [3]. In the processing of fresh-cut, reconditioning of wash water is also an option to reduce water consumption and water discharge. However, reconditioning is not a common practice now, but authorities are controlling the water used to reduce water demand, making water use more efficient.

Water from the washing tank can be collected and treated to eliminate any plant and human pathogens as well as the chemical and physical contaminants and reused it again, avoiding any food safety risk [4]. Chemical disinfection has been commonly used to minimize the potential of cross-contamination from wash water to produce [5]. The quality characteristics of wash water can fluctuate depending mainly on the type of product, but it is generally characterized by large amounts of organic substances which are measured as Chemical Oxygen Demand (COD) as well as there are an accumulation of Disinfection By-Products (DBPs) [6,7]. The wastewater discharged can cause severe environmental problems. Thus, there is a strong motivation to develop methods and technologies for water reconditioning even if they require a high cost for treatments. The main target in the reconditioning of wash water is the reduction of the organic matter as much as possible to reduce the disinfectant demand and the formation of DBPs that can be uptaken by the fresh produce [8,9]. Industrial application of water treatments such as coagulation, flocculation, filtration, in combination or not with other treatments such as adsorption and oxidation, has been devoted to wastewater. The information on the efficacy of these technologies for water reconditioning in the fresh produce industry is limited [10], and it is even more restricted in the fresh-cut industry with few commercial applications [11].

Coagulation-flocculation has been considered as the most common and economically feasible process to remove Natural Organic Matter (NOM). It is widely used in wastewater from the food industry to precipitate particulate and dissolved matter [8,12]. However, the toxicity of the mineral substances frequently used as coagulants (e.g., alum, polyaluminum chloride, and synthetic polymers) have several environmental and human health consequences [8]. For these reasons, natural organic coagulants and flocculants have been considered as biodegradable and usually non-toxic alternatives. A tannin-based coagulant-flocculant (Tanfloc™) obtained from *Acacia mearnsii* de Wild. has been used for drinking water and wastewater as well as in industrial sectors [13-15]. Membrane filtration technologies are promising alternatives for the removal of suspended and dissolved solids from wastewater [10,16]. Membrane-Based Separation Processes (MBSPs) include Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) [17]. These technologies are increasingly used nowadays for potable water and food processing applications [16,18]. The combination of different membranes, together with Advanced Oxidation Processes (AOPs) are among the most frequently used approaches to remove pollutants for water reuse in potable water [16] and wastewater [19].

TiO_2 has been developed to be the most widely used catalyst in photocatalytic disinfection AOPs involve different methods of generation and activation of oxidizing agents such as H_2O_2 and O_3. They include the combination with irradiation such as Ultraviolet Light (UV), and TiO_2 as catalyst support with the potential for the total mineralization of organic compounds [19]. Previous studies in a tomato processing plant and citrus juice industry showed that the application of AOPs improved the biodegradability of wastewater, reducing the content of organic and inorganic constituents [20,21]. Furthermore, activated carbon adsorption is one of the best wastewater treatment technologies because it is easy to operate, with a simple design that can be easily coupled to other systems such as coagulation-flocculation [12]. Granular Activated Carbon (GAC) is an effective barrier against a wide range of organic contaminants, such as dissolved organic matter and DBPs [22]. Based on these previous findings, the objective of the present study was to evaluate the effect of different technologies, including a tannin-based agent for coagulation-flocculation, ceramic membranes for ultrafiltration, TiO_2 photocatalysis as AOP and granular activated carbon as an adsorption process for water reconditioning. Wash water obtained periodically from washing fresh-cut lettuce in a commercial processing plant was selected for this study because it represents the most common but complex composition wash water.

Methods

Wash Water

Process wash water from a commercial processor of leafy vegetables was sampled on different days to carry out the various experimental tests. The processing line was exclusively dedicated to the production of shredded iceberg lettuce washed in chlorinated water. Water (40 L) was collected from the washing tank and transported to the lab within 30 min under refrigerated conditions. Wash water was filtered through sediment filter cartridges of 50 µm and 20 µm installed in series to simulate the industrial process of water reconditioning. Then, the wash water was pumped back into the washing tank. The physicochemical characteristics of the water sampled for the different experimental tests are shown in (Table 1). The COD level was about 4000 mg O_2 L^{-1} in coagulation-flocculation trials, while in the tests performed for ultrafiltration, photocatalysis and GAC adsorption treatments, COD was lower (1000-2000 mg O_2 L^{-1}). These differences in the COD were due mainly to the improvements in the processing conditions carried out by the processor, such as the set up of a new cutter to reduce product damage. For the different batches of industrial wash water evaluated in this study, the initial content of dissolved COD (CODd) represented 95.6 % of total COD (Table 1) and above 96.8% after filtered. The pH varied between 7.5-7.9, but it was adjusted to 5.5-6.0 with phosphoric acid in the coagulation-flocculation and GAC adsorption trials. The ultrafiltration separation processes and the TiO_2 photocatalytic treatments were carried out at the Technology Center for Energy and the Environment (CETENMA, Cartagena, Spain), while the coagulation-flocculation and GAC adsorption tests were carried out at CEBAS-CSIC institute (Murcia, Spain).

Sample	COD (mg L^{-1})	CODd (mg L^{-1})	UV254	Turbidity (NTU)	Total dissolved solids (g L^{-1})	Total suspended solids (g L^{-1})	Free chlorine (mg L^{-1})	Combined chlorine (mg L^{-1})	Chlorate content (mg L^{-1})
Wash Water	1188 ± 10	1159 ± 15	0.420± 0.001	26.5 ± 1.4	1.65 ± 0.03	0.024 ± 0.006	0.8 ± 0.2	3.8 ± 0.2	0.89 ± 0.05
Permeate	944 ± 10**	936 ± 15**	0.314 ± 0.002***	2.9 ± 0.4***	1.52 ± 0.02**	0.003 ± 0.000**	0.2 ± 0.0**	0.7 ± 0.1***	0.80 ± 0.05ns

Values are the mean ± standard deviation of two replicates. Student t-test comparing permeate and wash water. For significant differences: ** ($p < 0.01$); ***($p < 0.001$); ns, not significant.

Table 1: Physicochemical characteristics of the wash water from a commercial fresh salad processing line used in the different experimental tests, including Chemical Oxygen Demand (COD), dissolved COD (CODd), absorbance at 254 nm (UV254), turbidity, total dissolved solids, total suspended solids, free chlorine, combined chlorine and chlorate content.

Reconditioning Treatments for Wash Water

Coagulation-Flocculation

The experimental trials for coagulation-flocculation were performed using the jar test described by Van Haute, et al. [8] with some modifications. Three different batches of water with different COD levels were prepared by the dilution with tap water to reach COD of about 500, 1300 and 2600 mg O_2 L^{-1}, named as COD 500, COD 1300, and COD 2600 respectively. Tanfloc™ (TANAC, Brazil) developed for drinking water was used as a coagulant [14]. Four concentrations of Tanfloc™ were studied; 25, 75, 150, and 300 mg L^{-1}, named as T 25, T 75, T 150, and T 300, respectively. During the experiments, one jar per wash water (0.7 L) and coagulant concentration was stirred for 3 min at 150 rpm in a conventional jar test apparatus. Then, the water samples were stirred again for an additional 10 min at 30 rpm, after which the formed flocs were settled after 20 min. Volumes of 300 mL from the upper part were withdrawn from the jars using a pipette and vacuum filtered through filter paper Whatman No. 41. The temperature was controlled at 7˚C to simulate the washing conditions of a processing line. Physicochemical parameters, including pH, turbidity and COD, were measured in two replicates per sample.

Cross-Flow Filtration by Ceramic Membranes

Membrane filtration studies were carried out in the CETENMA pilot plant, which was equipped with laboratory-scale equipment reproducing industrial applications for cross-flow filtration by tubular membranes. This equipment allows the control of the operating variables such as the type of membrane, temperature in the feed tank, Transmembrane Pressure (TMP) and cross-flow velocity. The filtration system included a vane pump for water circulation, 10 L stainless steel tank with temperature control, pressure pipe for the tubular membrane coupling, needle valve for the TMP regulation, pressure gauges and valve for flow regulation. Two ultrafiltration tubular membranes with Molecular Weight Cut-Off (MWCO) of 1 and 15 kDa were studied. Each membrane consisted of a multichannel tubular membrane with an outer diameter of 1 cm, a length of 25 cm and 7 inner channels (Inside Céram, Tami Industries, Nyons Cedex, France).

The filtration trials were carried out in two phases. In the first phase, the optimum operating TMP was arranged. Temperature and flow velocity were maintained at 5˚C and 2.22 ms^{-1}, respectively, and for each membrane 3 TMP conditions were assessed: 2, 4 and 6 bar for the 15 kDa membrane and 4, 7 and 10 bar for the 1 kDa membrane. The fractions obtained (both the permeate and retentate) were recirculated to the feed tank. During the experiments, the permeate flux (J) ($L\ h^{-1}\ m^{-2}$) was regularly measured until the variation with time was negligible. Then, a small sample of the permeate fraction was sampled and analyzed for COD. A schematic drawing of the experimental set up is shown in Supplementary information (SI.1A). In the second phase, the membrane selected was evaluated under operating conditions chosen in the previous phase. This experimental test was carried out at 5˚C in an open-loop mode with a continuous permeate production and the retentate was recirculate to the feed tank (SI.1B). Samples of the permeate were analyzed for COD at a different level of water recovery (20, 40, 60 and 80% of recovery) to establish the optimum recovery percentage. Wash water and the permeate were analyzed in triplicate for pH, turbidity, COD, CODd, absorbance at 254 nm (UV25), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Free Chlorine (FC) and Total Chlorine (TC) as described below. In all trials, membranes were characterized for their pure water flux (J0) in the conditions of each experiment. The membranes were chemically cleaned after each test.

Heterogeneous Photocatalysis

The permeate obtained after cross-flow filtration of the wash water was treated by titanium dioxide (TiO_2) photocatalysis under the conditions selected from the previous trials: ceramic tubular membrane of 15 kDa, TMP of 6 bar, flow velocity of 2.22 ms^{-1} and water recovery of 80% at 5˚C. The TiO_2 photocatalytic treatment was carried out in the CETENMA pilot-plant using laboratory-scale equipment that included a centrifuge pump for water circulation, 10 L stainless steel tank with temperature control, pressure valve for flow regulation and a 0.8 L concentric stainless steel reactor with a length of 48 cm and an inner diameter of 6 cm (SI.2). Light Emitting Diodes (LEDs) strip of 365 nm wavelength (Lighting Will, Shenzhen, China) (UV-LED) with a maximum power of 14 W were incorporate into a quartz tube inside the reactor and used as the irradiation source. Two forms of TiO_2 (Sigma-Aldrich, Madrid, Spain) for the photocatalytic applications were evaluated: TiO_2 P25 (CAS 13463-67-7) <25 nm particle size and TiO_2 325 mesh of large particle size (CAS 1317-70-0). A concentration of 0.1 g L^{-1} TiO_2 was evaluated for TiO_2 P25, and two concentrations, 0.1 and 0.3 g L^{-1} for TiO_2 325 mesh. The TiO_2 was incorporated suspended in water. The experiments were carried out in a closed recirculation system in a continuous process at 5˚C with a flow rate of 50 L h^{-1} and irradiance of 17.4 W cm^{-1}. The experiments were carried out along 5 h, and samples of treated water were collected at different times. Samples were settled for 30 min and then filtrated through 0.45 µm syringe nylon filters (Fisherbrand-Fisher Scientific, Waltham, USA) to remove TiO_2 before the analysis of COD.

Adsorption Treatment by Granular Activated Carbon

The adsorption tests were carried out in a laboratory-scale dynamic column system, which consisted of an acrylic column of 25 mm diameter mounted vertically in downflow plug mode. During the tests, wash water as the influent solution was continuously stirred in a reservoir glass beaker (2 L), and then pumped to the packed bed column by a peristaltic pump. The effluent of the column was collected in amber flasks (SI.3). In these experiments, a coal-based Granular Activated Carbon (GAC) (Norit GAC 1240, Acros Organics, Geel, Belgium) was used. This commercial GAC was characterized by a thermal activation method and a particle size between 12-40 mesh, a total surface area (BET) of 1150 m^2

g^{-1} and a total pore volume of $0.83\ cm^3\ g^{-1}$. Previously, the GAC sample was washed with deionized water, dried in an oven at 105°C for 12 h, and stored in a desiccator until the experiments. A GAC sample was packed in the column (approximately 22 g) with a height of 10.5 cm and a bed volume of 51.5 mL. Three layers of polyamide mesh of 0.5 mm pore size were inserted in the column below and above to support the GAC bed. A flow rate of $42\ mL\ min^{-1}$ was established with a hydraulic loading rate throw column of $5\ m\ h^{-1}$ based on the dimensions of the column, simulating the operating conditions suggested for water treatments [23]. Effluent samples of 50 mL, as GAC bed volume, were collected after regular intervals of 3 h. The throughput of GAC column was measured as cycles or bed volumes treated (BV) defined as the relation between the total volume treated and the volume of GAC bed [22]. The temperature was maintained at 5-8°C. Several physicochemical parameters, such as COD, CODd, pH, absorbance at 254 nm (UV254), Free Chlorine (FC) and Total Chlorine (TC), as well as the content of chlorate as the main DBPs, were analyzed in duplicate in the wash water (the influent) and the effluent samples at each evaluating time.

Physicochemical Characteristics of Wash Water

Turbidity was measured using a turbidimeter (Turbiquant 3000 IR, Merck). Chemical Oxygen Demand (COD), total dissolved solids (TDS), and total suspended solids were determined by the standard methods [24]. COD was measured by the photometric method using the Spectroquant NOVA 60 photometer. Dissolved COD (CODd) was the COD measured after filtration through 0.45 µm syringe nylon filters (Fisherbrand-Fisher Scientific, Waltham, USA). Free chlorine and total chlorine were measured by the N,N-Diethyl-P-Phenylendiamine (DPD) colorimetric method using the Spectroquant NOVA 60 photometer (Merck, Darmstadt, Germany) [24]. Combined chlorine was calculated by subtracting the results of total chlorine and free chlorine. For UV254 measurement, wash water was filtered through 0.45 µm syringe nylon filters (Fisherbrand-Fisher Scientific, Waltham, USA), and the absorbance at 254 nm measured using a UV-VIS spectrophotometer (Jasco V-630, Tokyo, Japan). pH was measured using a portable multimeter sensION+ MM150 (Hach, Loveland, Colorado, USA).

Chlorate Content

The content of chlorate was measured following the detailed protocol described by Garrido, et al. [25] based on the improved methodology of Anastassiades, et al. [26]. Before analysis, water samples (10 mL) were filtered through a 0.22 µm filter (Sartorius Minisart PES; Sartorius, Gottingen, Germany) and diluted (1:10) with acidified methanol fortified with an Internal Standard (IS) of ClO_3^- at a final concentration of $0.1\ \mu g\ mL^{-1}$. For quantification, a calibration curve with the internal standard was prepared in acidified methanol. For the LC-MS/MS analysis, the conditions performed were those described previously [27] and modified in the multiple reaction monitoring mode. The transitions of $^{35}Cl^{16}O_3^-$ (m/z 83) into $^{35}Cl^{16}O_2^-$ (m/z 67) and $^{35}Cl^{18}O_3^-$ (m/z 89) into $^{35}Cl^{18}O_2^-$ (m/z 71) were used for quantifying the chlorate and the IS, respectively; and transitions of $^{37}Cl^{16}O_3^-$(m/z 85) into $^{37}Cl^{16}O_2^-$ (m/z 69) were monitored to ensure that the abundance ratio of $^{35}Cl/^{37}Cl$ was within an acceptable range (2.31 to 3.85). The results of chlorate content in water samples were expressed as $mg\ L^{-1}$.

Statistical Analysis

All data were analyzed using PASW Statistics 25 for Windows (SPSS Inc., Chicago, IL, USA). Student t-test (independent two-sample t-test) with a significant level at $P < 0.05$ was carried out for comparing treated and not treated wash water samples. Bilateral correlations were performed by Pearson's correlation with a confidence interval established at 95%. Regression analysis was carried out using nonlinear regression analysis with Sigma Plot 14.0 Systat Software, Inc. (Addilink Software Científico S.L., Barcelona, Spain). The confidence intervals of the estimated data were established with a confidence interval of 95%.

Results and Discussion

Coagulation-Flocculation

Depending on the wash water characteristics and the amount of coagulant added, the effect of Tanfloc™ was different (Figure 1). Only in wash water with the intermediate COD level, T 25 and T 75 reduced COD in about 7%. For the other wash water samples, Tanfloc™ had no impact or showed a negative effect on increasing the COD significantly, particularly when added at high concentrations (Figure 1A). Regarding turbidity, Tanfloc™ showed different results depending on the type of wash water, and the concentration added. In wash water with the low COD level, turbidity increased when Tanfloc™ was added (Figure 1B). However, in wash water with the intermediate and high COD levels, turbidity significantly decreased when Tanfloc™ was added at T 25 and T 75, but it increased at concentrations > T 150. Additionally, Tanfloc™ decreased the pH as the concentration was increased, particularly in wash water with the low COD level (Figure 1C). Previous studies suggest that the dominant flocculation mechanism of Tanfloc™ is charge neutralization, bridging or path flocculation [15]. However, as Tanfloc™ is a tannin-based product, it represents a complex combination of polyphenols with a considerable variation in the composition [15].

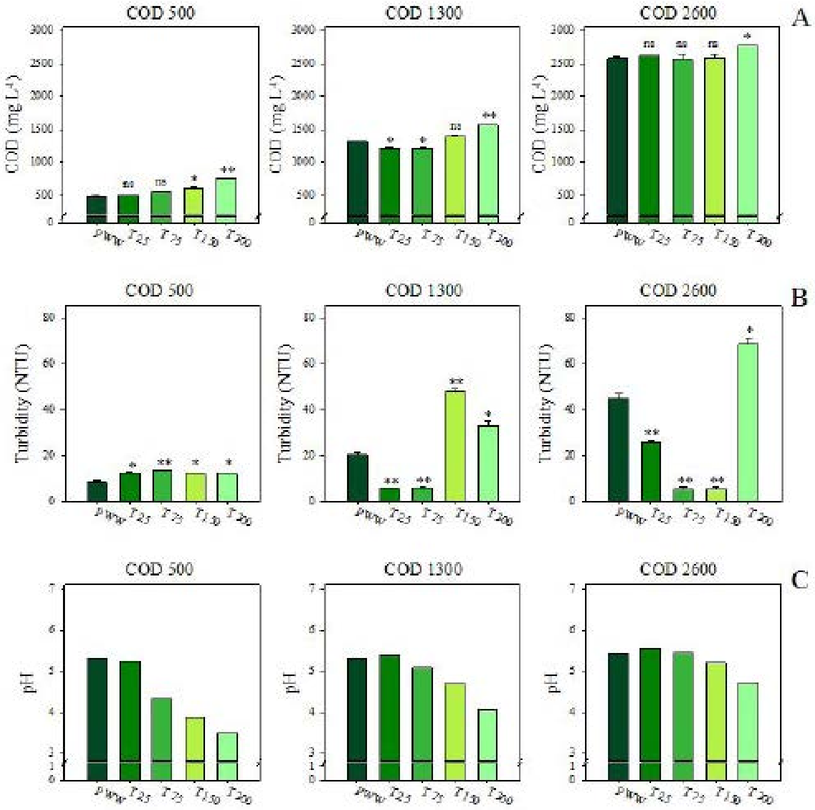

Figure 1: Effect of Tanfloc™ as a coagulant-flocculant agent on the changes in the Chemical Oxygen Demand (COD) (A), turbidity (B) and pH (C) of wash water (PWW) with initial COD levels of 500, 1300 and 2600 mg L^{-1} (COD 500, COD 1300 and COD 2600) treated with 25, 75, 150 and 300 mg L^{-1} of Tanfloc™ (T 25, T 75, T 150 and T 300, respectively). Bars are the mean ± standard deviation of 2 replicates for COD and turbidity and only one replicate for pH. Student t-test comparing each treatment with the PWW. For significant differences: * ($p < 0.05$); ** ($p < 0.01$); ns, not significant.

The beneficial effect of Tanfloc™ in reducing COD and turbidity has been reported in municipal wastewater with similar efficacy to mineral coagulants such as alum and polyaluminium chloride [13-15]. In the present study, despite the high reduction in the turbidity observed in some cases, the effect on COD reduction was restricted to some wash water and Tanfloc™ concentrations. Previous studies agree with the limited efficacy of some coagulants such as chitosan due to the mineral and organic nature that were not able to remove the Dissolved Organic Matter (DOM) [6,8]. The effect observed on turbidity reduction may be related to a decrease in particulate COD. Moreover, similar to other coagulants, when Tanfloc™ was added in excess, the dispersion of colloidal molecules occurred, and the turbidity and COD level increased again due to the presence of the coagulant and its organic nature.

Cross-Flow Filtration by Ceramic Membranes (UF)

In the close-loop mode, the permeate flux was always higher in 15 kDa than in 1 kDa membrane and increased when increasing TMP (Figure 2). For both membranes, the permeate flux showed the typical decline curve over time caused by the accumulation of particles on the membrane surface until approached a steady-state. The normalized flux (J/J0) showed the performance of the filtration concerning ideal conditions (pure water), indicating the energetic pumping cost and the maintenance cost due to the cleaning of fouled membranes. The mean values of normalized fluxes for 15 kDa membrane were 0.38, 0.39 and 0.24 for 2, 4 and 6 bar respectively and 0.14 for 1 kDa membrane and all the TMP analyzed. After filtration by 15 kDa membrane, the reduction of COD was about 27, 30, 31% for 2, 4 and 6 bar, respectively. In the case of 1 kDa membrane, COD reduction was 32, 38, 31% for 4, 7 and 10 bar, respectively. Thus, despite the differences between both membranes in pore size, the efficiency on COD removal was very similar. Therefore, for further test, ultrafiltration with 15 kDa membrane and 6 bar TMP was selected based on the permeate flux.

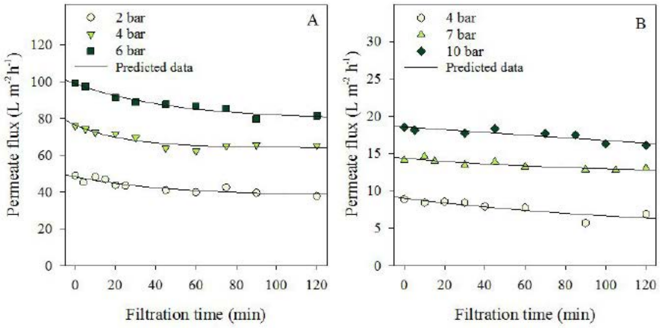

Figure 2: Effect of ultrafiltration by15 kDa (A) and 1 kDa (B) ceramic membranes on the permeate flux using transmembrane pressure conditions of 2, 4, and 6 bar in a close loop mode. Filtration process was carried out at 5˚C for 120 min with a flow velocity of 2.22 m s^{-1}. The solid line represents the best-fitted equation generated by non-linear regression analysis.

In the open-loop with membrane of 15 kDa and TMP of 6 bar, the permeate flux at the steady-state reached a value of 59.3 L m^{2} h^{-1} with a normalized flux (J/J0) of 0.2. Permeate samples were evaluated at different recovery levels (20, 40, 60 and 80%). Results showed that the COD reduction was similar among the recovery levels assessed with a mean value of 21%. Thus, the increase in the COD level of the feed water along time did not influence the efficacy of UF on COD removal. The characterization of the permeate at a recuperation level of 80% indicated that the cross-flow filtration led to a clarification of wash water with a significant reduction of 89, 88 and 72% in turbidity, total suspended solids and particulate COD, respectively (Table 2). Regarding the effect of cross-flow filtration on dissolved compounds removal, there was only a reduction of 26, 19 and 8% for UV254, CODd, and total dissolved solids, respectively. Moreover, combined chlorine decreased significantly by UF, showing a reduction of 82%, while the content of chlorate remained unaffected (Table 2).

Sample	COD (mg L^{-1})	CODd (mg L^{-1})	UV254	Turbidity (NTU)	Total dissolved solids (g L^{-1})	Total suspended solids (g L^{-1})	Free chlorine (mg L^{-1})	Combined chlorine (mg L^{-1})	Chlorate content (mg L^{-1})
Wash Water	1188 ± 10	1159 ± 15	0.420± 0.001	26.5 ± 1.4	1.65 ± 0.03	0.024 ± 0.006	0.8 ± 0.2	3.8 ± 0.2	0.89 ± 0.05
Permeate	944 ± 10**	936 ± 15**	0.314 ± 0.002***	2.9 ± 0.4***	1.52 ± 0.02**	0.003 ± 0.000**	0.2 ± 0.0**	0.7 ± 0.1***	0.80 ± 0.05ns

Values are the mean ± standard deviation of 3 replicates. Student t-test comparing permeate and wash water. For significant differences: ** ($p < 0.01$); ***($p < 0.001$); ns, not significant.

Table 2: Physicochemical characteristics of wash water from a commercial fresh salad processing line and the permeate obtained after ultrafiltration. Chemical Oxygen Demand (COD), dissolved COD (CODd), absorbance at 254 nm (UV254), turbidity, total dissolved solids, total suspended solids, free chlorine, combined chlorine, and chlorate content. Permeate was obtained by ultrafiltration with a ceramic membrane (15 kDa) at 5˚C with a flow velocity of 2.22 m s^{-1} in open loop mode at a recuperation level of 80%.

Most of the constituents present in the wash water from washing leafy vegetables include polyphenols, free sugars, and organic acids [8]. The ultrafiltration membranes range from 4-30 kDa effectively retain high molecular weight wash water compounds such as tannins, chlorophylls, and high molecular weight polyphenol. On the contrary, tight UF membranes of 1-3 kDa are highly useful to retain low molecular weight compounds such as low molecular weight polyphenols, sugars, and peptides [28]. In the present study, 1kDa membrane did not achieve higher COD reduction than 15 kDa contrary to our expectations. However, in the conditions of our study, no differences in COD removal were observed between both membranes. Typically, UF membranes reject all suspended solids, while organic constituents both soluble and colloidal forms can be partially removed with and achieved rejection that can vary widely (10-85%) [16]. Moreover, UF has been reported to be successful in removing emerging pollutants in wastewaters [17]. These findings are partially in agreement with our results regarding the clarification effect of COD reduction and combined chlorine removal but not for chlorate removal. Our results showed the potential application of UF as a pre-treatment for the reconditioning of wash water.

Cross-Flow Filtration Combined with Heterogeneous Photocatalysis

For this test, the TiO_2 photocatalysis was studied after the ultrafiltration of wash water with the selected conditions previously described of 15 kDa membrane and 6 bar TMP. In the open-loop, a permeate flux of 39.2 m^2 h^{-1} and a COD reduction of 14.5 % was achieved at the steady-state. The lower filtration performance and inferior COD reduction obtained in this test compared with the previous one was due probably to the higher COD level (34.5%) of the wash water used in this test. Results showed that the TiO_2 photocatalysis UV LED (365 nm) did not promote a higher COD reduction of the permeate after 5 h treatment, for any type of TiO_2 (P25 and 325 mesh) or concentration (0.1 and 0.3 mg L^{-1}) evaluated (Table 3). Some studies have reported the efficacy of AOPs in reducing the organic matter in process water from the fruit and vegetable industry. Thus, Beltrán et al. [20] reported that the combination of ozone and UV-LED (254 nm) reduced COD at about 90% in tomato wastewater. Caudo, et al. [21] described that copper-pillared clays catalyzed with peroxide oxidation led a Total Organic Carbon (TOC) reduction of about 50% in the wastewater of citrus juice production with initial COD above 4000 mg L^{-1}. In wash water from fresh-cut products, Selma, et al. [29] showed that TiO_2 combined with UV radiation (254 nm) reduced 20% of the COD level in the lettuce wash water. However, the same treatment was ineffective for other types of wash water such as those from washing cut escarole, carrot and diced onions. In the present study, LED light sources were examined as they are inexpensive and provide high current-to-light conversion efficiency with little heating [30]. One main characteristic required for water treatments is to maintain a low temperature in the washing tank (4°C). Izadifard, et al. [30] reported that the application of UVA-LED in combination with different types of TiO_2 led to a reduction in NOM and emerging contaminants in drinking water. However, our results showed that UV-LED (365 nm) did not affect the NOM content of the wash water in the conditions performed in this study.

Evaluation time (h)	**COD (mg L^{-1})**		
	TiO_2 P25 0.1 g L^{-1}	**TiO_2 325 mesh 0.1 g L^{-1}**	**TiO_2 325 mesh 0.3 g L^{-1}**
1	1395	1400	1398
2	1390	1384	1348
3	1320	1380	1436
4	1352	1381	1392
5	1384	1400	1390

Table 3: Effect of TiO_2 photocatalysis UV-LED (365 nm) at 5°C on the changes in the Chemical Oxygen Demand (COD) of wash water after 1 h treatment for 5 h period. Two particle size and concentrations of TiO_2 were compared: P25 at 0.1 g L^{-1}, and TiO_2 325 mesh at 0.1 and 0.3 g L^{-1}.

Adsorption by Granular Activated Carbon

The results of the adsorption tests using GAC presented the typical breakthrough curves between the outlet Concentration (C) and the influent concentration (Co) (Figure 3). As the water flowed down through the GAC, the levels of COD and CODd in the effluent decreased as well as the UV254 value and the content of chlorate. As the adsorption continued, GAC became exhausted, and then, the concentration of the substances in the effluent rinsed with time [23]. As described, the breakthrough point for the compounds removed by adsorption in GAC columns is achieved when the ratio C/Co is 0.9, as the operating limit of the column [31]. In our study, even though an initial reduction of 100 % was observed, the ratio C/Co for COD reached a level of 0.9 after 75 cycles measured as bed volumes treated (Figure 3A). As CODd expressed in absolute concentration represented about 96% of the total COD, the changes of CODd showed the same trend as the COD with a similar breakthrough point (Figure 3A). There was a significant correlation between COD and CODd (Pearson's correlation coefficient of 0.999 at $p < 0.001$). However, the level of particulate COD (CODp) in the treated wash water showed an initial relative concentration (C/Co) of 0.6, which was maintained during the experiment. Results regarding the UV254 decrease in the wash water showed the same trend as observed for COD and CODd although for UV254 the relative level (C/Co) did not exceed 0.43 at the end of the experiment (Figure 3A). Significant correlations were also found between the levels of UV254 and COD (Pearson's correlation coefficient of 0.695 at $p < 0.001$) and CODd (Pearson's correlation coefficient of 0.575 at $p < 0.05$).

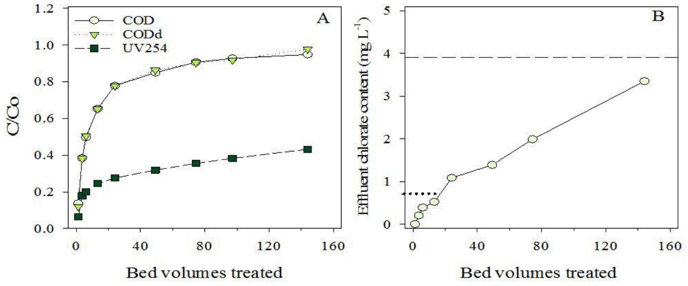

Figure 3: Effect of Granular Activated Carbon (GAC) adsorption tests in a column over cycles (number of bed volumes treated) on the changes in the Chemical Oxygen Demand (COD), dissolved COD (CODd) and absorbance at 254 nm (UV254) (A) expressed as the ratio between the outlet concentration and the influent concentration (C/Co) and the content of chlorate in the effluent (B) of treated wash water. Dash line in graph B represents the content of chlorate in the influent water, and the dotted line represents the maximum residue limit (MRL) allowed for chlorate in drinking water (0.7 mg L^{-1}).

Regarding the efficacy of GAC adsorption, reducing the content of chlorate, results showed that chlorate content was removed from the wash water initially. Still, the content in the effluent rapidly exceeded the Maximum Residual Limit (MRL) allowed for potable water of 0.7 mg L^{-1} after 17 BV [32] (Figure 3B). At the end of the tests, which corresponded to 144 BV, the content of chlorate in the effluent was 3.35 mg L^{-1}, representing a C/C0 of 0.85, which was very close to the operating limit of 0.9 established in this study (Figure 3B). The results in the case of combined chlorine showed an initial reduction of 98.4% confirmed by the content in the effluent of 0.2 mg L^{-1} at the end of the experiment. The results of this study also showed that there were some changes in the pH of the treated wash water, as the pH of the effluent drastically changed from 5.6 (influent wash water) to 9.7 (effluent water) after 1BV. Still, it decreased again when the volume of the treated wash water increased and remained about 6.5 after 24 BV.

Previously, it has been reported the largest NOM adsorption capacity of Norit GAC 1240 compared with other GAC for drinking water and surface water [33]. Our results showed that the adsorption capacity of Norit GAC 1240 was able to completely remove dissolved organic matter (DOM) measured as CODd as well as chlorate. For GAC treatments, the relation between UV254 and the content of dissolved organic carbon has been previously reported [22,34). Moreover, the UV254 reduction has been related to the removal of organic micropollutants [34]. In our study, the results confirmed the potential application of Norit GAC 1240 for the removal of chlorate as the main inorganic DBPs. Despite the reduction observed in DOM and chlorate, the adsorbent mass rapidly becomes exhausted. The rate at which GAC is exhausted and when to replace/regenerate must be determined [23]. In terms of the adsorption capacity of GAC in a fixed bed column, the Carbon Usage Rate (CUR) is known as the mass of activated carbon required per unit volume of water treated until breakthrough. The typical CUR described for GAC ranges from 0.29-1.04 kg m^{-3} for the physicochemical treatment of municipal wastewater and 0.12-0.23 kg m^{-3} for tertiary treatment [23]. In the present study, the CUR of Norit GAC 1240 at the operating limit of the column established in 0.9 C/Co was 5.99 kg m^{-3} for COD removal and 3.09 kg m^{-3} for chlorate removal. The operation of columns in series could allow for recirculating wash water to achieve the quality required for the reuse in the washing tank. However, given the performance of GAC for COD removal, the cost of reposition of this adsorbent could make this treatment economically unfeasible.

The results of this study remarked the potential of GAC for chlorate removal despite the limitations of GAC treatment for reconditioning of wash water. Chlorate is the main inorganic DBPs presented in wash water derived from the use of chlorine-based antimicrobials as water disinfectant during the washing of fresh produce. The accumulation of chlorate in the fresh product during the washing process may constitute a health risk for consumers as exposition to chlorate ions have been shown to be harmful to erythrocytes and can also interfere with thyroid function. [27,35]. The adsorption capacity of chlorate by GAC treatment has been reported for drinking water [36]. Recently, the use of activated carbon has been shown to reduce the concentration of DBPs in water significantly, leading to a lower concentration of chlorate in the washed produce [37]. Currently, there is not a standardized process for chlorate removal, and once that is formed, it is difficult to eliminate; thus, the control of the accumulation is preferable than the removal. As known, the competition from background DOM reduces the adsorption capacity of the GAC for target organic compounds [22]. However, there is no information about the possible competition between DOM and chlorate for adsorption sites in GAC, so the effectiveness of GAC should be higher in matrices with lower DOM. Future studies about chlorate removal by GAC may be interesting for water reconditioning. Our results showed that wash water obtained from washing fresh-cut vegetables constitutes a challenging matrix for reconditioning due to the difficulty of DOM removal.

Conclusions

Even though Tanfloc™ has been used as a natural organic coagulant-flocculant in drinking water and wastewater, it is not adequate as a reconditioning treatment for water used for washing fresh-cut salads due to the high prevalence of DOM. Moreover, when Tanfloc™ is added in excess, it contributes to the adverse effect of increasing turbidity and COD level. Ultrafiltration positively contributes to the clarification of wash water by the removal of suspended organic solids above 90% and a COD reduction of about 30%. However, TiO_2 photocatalysis UV-LED (365 nm) does not improve the COD reduction of the permeate obtained after ultrafiltration. This study shows that ultrafiltration can be a suitable reconditioning treatment. However, the combination with other treatments that allow the total removal of DOM would be needed for the reconditioning of wash water from the fresh-cut salad industry. Adsorption by activated carbon led to the complete removal of COD and chlorate, but it may be economically inadvisable because the carbon mass rapidly became exhausted. This study shows the potential use of active carbon for chlorate removal as a potential treatment once accumulated in the wash water. Treatments for wash water recycling must be capable of treating high volumes of water of high variability in quality. The water quality characteristics are specific of the product type, cutting size and equipment design apart from the processing operations, which make that "One size does not fit all" and each case will require the selection of the appropriate treatment technology.

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