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Integration of Ion Exchange—AOP—Biological System for the Treatment of Real Textile Wastewater

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Abstract: Real textile wastewater (RTWW) poses significant environmental challenges. RTWW typically contains high levels of organic compounds, such as dyes, as well as inorganic substances like salts. These contaminants can harm aquatic life when released into water bodies without appropriate treatment. RTWW was subjected to a series of sequential treatments: exchange resins for removing ions, advanced oxidation with bicarbonate-activated peroxide to degrade organic matter, and a biological treatment based on the Zahn–Wellens test to remove remaining chemical oxygen demand (COD) The advanced oxidation process based on the activation of H_2O_2 with $NaHCO_3$ (catalyzed with cobalt impregnated on a pillared clay, Co/Al–PILC)) was optimized using central composite design (CCD) and response surface methodology (RSM). After the process integration, reductions in ion concentrations, chemical oxygen demand (COD), and total organic carbon content (TOC) were achieved. Reduced hardness (99.94%) and ions (SO_4^{2-} and acid black 194 dye of 99.88 and 99.46%, respectively), COD (96.64%), and TOC (96.89%), guaranteeing complete treatment of RTWW, were achieved. Additionally, the biodegradability index of RTWW increased from 0.28 ± 0.01 to 0.90 ± 0.01, and phytotoxicity was reduced, going from a phytotoxic that inhibited the germination of lettuce seeds to a phytostimulant after biological treatment with activated sludge.

Keywords: textile wastewater; process integration; ion exchange; bicarbonate-activated peroxide; CCD–RSM; Zahn–Wellens; biodegradability index; COD; phytotoxicity

1. Introduction

The textile industry is among the global industries with the highest water use [1,2]. The production of textiles results in a significant amount of wastewater, which is often highly polluted with dyes and other chemical components such as alkalis, acids, bleaching, resins, and surfactants [3,4]. If not properly treated, this wastewater can have severe environmental impacts and cause harm to aquatic life. Textile wastewater treatment typically involves several physical, chemical, and biological stages. However, there is no universally applicable treatment solution for textile effluents [5,6]. The most effective strategy is often to combine several treatment techniques. Treating complex, high-strength textile wastewater will be more successful if physical, chemical, and biological approaches are used in tandem [6,7].

Ion exchange is a water treatment process that uses resins to replace unwanted ions in the water with desired ions [8,9]. Ion exchange resins are commonly used to treat textile wastewater due to their ability to remove heavy metals, dyes, and other contaminants [10–12]. One of the main advantages of using ion exchange resins in textile

wastewater treatment is their high efficiency in removing specific pollutants. However, there are also some disadvantages to consider, given that they can be expensive and require frequent regeneration or replacement depending on the level of contamination in the wastewater [11–13]. The textile industry generates wastewater that often contains high concentrations of specific ions (e.g., SO_4^-, Cl^-, etc.), such as those from dyes and other chemicals used in textile processing. Ion exchange can effectively remove these ions, replacing them with less harmful ones [6,10].

Advanced oxidation processes (AOPs) are a set of chemical treatment procedures designed to remove organic and sometimes inorganic materials in water and wastewater by oxidation through reactions with radicals [14,15]. AOPs are particularly effective at degrading recalcitrant organic contaminants in wastewater (such as colored water effluents) [15]. In contrast, biological treatment processes (BTPs) use microorganisms (aerobic and anaerobic treatment), enzymes, and plants (phytoremediation) to break down and remove pollutants from wastewater [16]. These processes are often used in conjunction with AOPs to facilitate the mineralization of contaminants [17].The integration of AOPs with biological processes can significantly enhance efficiency, achieve complete mineralization, and reduce the cost of the overall water treatment process [18]. The combination of AOPs and biological processes in industrial textile wastewater treatment is an emerging field with promising results [17,19]. This method harnesses the strengths of both AOPs and biological processes to effectively eliminate pollutants from wastewater [17].

Although integrated AOP/biological systems generate by-products that can be non-hazardous, implementing these technologies can be expensive [19]. Several challenges need to be addressed for their large-scale applications, such as cost-effectiveness in terms of energy and chemicals, the use of non-toxic reagents, the activity and recyclability of catalysts, and the design of more efficient coupled systems (exploring new oxidation and biological treatment systems) [17–19].

The bicarbonate-activated hydrogen peroxide (BAP) system is a novel advanced oxidation process that has gained attention recently due to its efficiency and environmental friendliness [20]. This system operates under slightly alkaline pH conditions and is based on applying hydrogen peroxide (H_2O_2), a powerful oxidizing agent [21]. The activation of hydrogen peroxide with bicarbonate leads to the formation of reactive species such as hydroxyl radicals ($\bullet OH$), peroxymonocarbonate ion (HCO_4^-), superoxide anion ($O_2^{\bullet -}$), and carbonate radical anion ($CO_3^{\bullet -}$) which are capable of degrading a wide range of pollutants [20,21].

One application of the BAP system is wastewater treatment, particularly from the textile industry and colorants [20–22]. Textile wastewater contains various organic pollutants, including dyes, which are considered refractory compounds that are difficult to degrade using conventional chemical and biological methods [1–6]. The BAP system has been demonstrated to be a clean and efficient technology for dye degradation in both homogeneous and heterogeneous media [20,21,23].

In a previous study, the BAP system catalyzed with cobalt ions in solution (Co^{2+}) was used to optimize the degradation of textile wastewater contaminated with the azo dye acid black 194 (AB-194) [24]. (AB-194) is a 1:2 symmetric metal–complex dye with a central chromium (III) atom coordinated with two organic ligand molecules (Figure S1, Supplementary Materials). The study found that complete decolorization ($\geq 99.40\%$), 32.20% mineralization, and 52.02% chemical oxygen demand removal were achieved under optimal conditions. Additionally, the acute toxicity of the textile wastewater was significantly reduced after treatment with the Co^{2+}–BAP system [24]. In another study, cobalt impregnated in a pillared clay (Co/Al–PILC) was used as a catalyst for azo-dye degradation, with the BAP system as the oxidizing agent [25]. Although the BAP system is efficient in removing color from wastewater, it does not achieve complete mineralization [24–28], so a coupling with a biological system may be desirable, contributing to the development of sustainable and green technologies.

The coupling of different treatment methods in textile wastewater treatment can enhance the overall efficiency of the process. Combining physical, chemical, and biological treatments makes it possible to target a wider range of pollutants in the wastewater. For example, coupling advanced oxidation processes and biological systems can help degrade toxic contaminants in the wastewater [17,29].

In this research, an integrated real textile wastewater treatment system consisted of exchange resins to eliminate ions, AOP with hydrogen peroxide activated by bicarbonate to degrade organic matter, and a biological treatment based on the Zahn–Wellens test to eliminate biodegradable organic matter and reduce toxicity. The improvements of each treatment on degradability and phytotoxicity were evaluated by analyzing the biodegradability index (BOD_5/COD) and the germination index in lettuce seeds, respectively.

2. Materials and Methods

2.1. Reagents

The reagents utilized for the catalyst synthesis ($AlCl_3 \cdot 6H_2O$, NaOH, and $Co(NO_3)_2 \cdot 6H_2O$) and oxidation reaction ($NaHCO_3$, H_2O_2) were of high purity, obtained from Merck KGaA (Darmstadt, Germany). A previous investigation described the details of the catalyst synthesis, which used cobalt impregnated (1.0 wt%) in pillared clay (Co/Al–PILC) [25].

Two resins, a strongly acidic cationic (Lewatit® MonoPlus S 108, Lanxess, GmbH, Cologne, Germany) and a strongly basic anionic (Lewatit® MonoPlus M 500, Lanxess, GmbH, Germany), were used for the ion exchange.

The reagents used to prepare the mineral medium (KH_2PO_4, K_2HPO_4, $Na_2HPO_4 \cdot 2H_2O$, NH_4Cl, $CaCl_2$, $MgSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$) in the biological tests were analytical grade supplied by Loba Chemie Pvt. Ltd. (Mumbai, India).

2.2. Real Textile Wastewater Sample

The real textile wastewater (RTWW) corresponded to industrial effluent from a textile factory located in the Colombian coffee region (Manizales-Caldas, Colombia, South America) [30]. Sampling, initial characterization of the textile wastewater, and optimization of the coagulation-flocculation (CF) treatment were performed at the GI–PRISMA Research Group of the Universidad Nacional de Colombia Sede Manizales [31]. The physicochemical characteristics of the sample after CF were determined by following the American Public Health Association (APHA) procedures [32]. The RTWW–CF sample was stored at 4 °C before use in the experiments.

2.3. Treatment with Ion Exchange Resins

The RTWW after the coagulation-flocculation process (RTWW–CF) presents high concentration of ions [31], which interfere with the application of the advanced oxidation process based on the activation of H_2O_2 with $NaHCO_3$. To guarantee adequate removal of the total hardness (Ca^{2+}, Mg^{2+}) in RTWW–CF, a strongly acidic cation (SAC) exchange resin was used. In contrast, a strongly basic anion (SBA) exchange resin was applied to remove SO_4^{2-} and Cl^- ions. A summary of the resins utilized (Lewatit®, Lanxess, GmbH, Germany) with the functional group, exchange capacity, and operating pH range is shown in Table 1.

Table 1. Properties of ion exchange resins used for pretreatment of textile wastewater.

Resin	Functional Group	Resin Matrix	Exchange Capacity	Mean Particle Size (mm)	Density (g/mL)	pH Range
Lewatit® MonoPlus S 108 Strongly acidic	Sulfonic acid	Styrene–DVB copolymer	2.2 eq/L	0.62 ± 0.05	1.30	2–14
Lewatit® MonoPlus M 500 Strongly basic	Quaternary ammonium type 1	Styrene–DVB copolymer	1.3 eq/L	0.62 ± 0.05	1.08	0–12

DVB = divinylbenzene.

All ion exchange (IE) tests with the resins were performed in batch mode and triplicate. The volume of resin required to treat a specific volume of wastewater is a function of the concentration of ions present in the sample. Since textile wastewater is a complex matrix, tests were carried out to analyze the effect of resin volume (Lewatit® MonoPlus S 108 and Lewatit® MonoPlus M 500) and contact time on the removal of hardness, sulfates, chlorides, and color in the RTWW–CF. The tests were performed in Erlenmeyer flasks, maintaining the temperature of the textile wastewater at 25 ± 1 °C and constant magnetic stirring at 180 rpm. Before being used, the resins were washed twice with distilled water.

The hardness (2340 C, EDTA titrimetric method) and concentrations of sulfates (4500 SO_4^{2-} E, turbidimetric method) and chlorides (4500 Cl^- B, Argentometric method) in the textile wastewater were determined according to standard methods [32]. The concentration of the anionic dye acid black 194 (AB-194) was obtained from an absorbance vs. concentration curve at 572 nm in a UV–Vis spectrophotometer (Genesys 150, Thermo Scientific, Madison, WI, USA). Considering that ion removal can affect the organic matter content in the textile wastewater sample, total organic carbon (TOC) and chemical oxygen demand (COD) concentrations were measured once the ion exchange treatment with the resins was completed. The TOC concentration was quantified in a Multi N/C 3100 equipment (Analytik Jena, Jena, Germany), and tube test kits (Nanocolor® COD160/1500, Macherey-Nagel, Munich, Germany) were used to measure the COD concentration.

2.4. Bicarbonate-Activated Peroxide (BAP)—Catalytic Tests

In this study, the optimization of textile wastewater oxidation after CF and ion exchange (RTWW–CF–IE) was performed using the response surface methodology (RSM) based on a central composite design (CCD). The objective was to analyze the effect of H_2O_2 and $NaHCO_3$ concentrations on TOC and COD removals. The catalyst used for oxidation with bicarbonate-activated peroxide (BAP) was cobalt (1.0 wt%) impregnated on a clay pillared with aluminum (Co/Al–PILC, 2.0 g/L), which are efficient for dye degradation [25,27]. The details of the synthesis and characterization (XRD, N_2 adsorption–desorption isotherm and point of zero charge—pH_{PZC}) of the catalyst were previously published [27]. Table 2 lists the factors considered in the experimental design and their respective levels. The DCC obtained randomly with the Design Expert software (version 8.0, StatEase, Inc., Minneapolis, MN, USA) considered 25 runs, which included 5 replicates in the central points, duplicates in the factorial points, and triplicates in the axial.

Table 2. Experimental and code values in CCD design.

Factor	Name	Units	Coded Value				
			−1.4142	−1	0	+1	+1.4142
X_1	H_2O_2	mM	108.3	150	300	450	491.7
X_2	$NaHCO_3$	mM	28.9	40	80	120	131.1

All oxidation tests of the experimental design were performed at a laboratory scale. Oxidation reactions were carried out in a batch glass reactor connected to a thermostatic bath regulated at 25 ± 0.2 °C. The reactor was charged with 200 mL of textile wastewater (RTWW–CF–IE), a predetermined amount of $NaHCO_3$, and 400 mg of the catalyst (equivalent to a dose of 2 g/L), and the suspension was magnetically stirred at 300 rpm for 15 min. Then, H_2O_2 was added, and the reaction started (t = 0). At the end of the reaction time (t = 5 h), aliquots were filtered with 0.45 μm cellulose membranes to separate the catalyst and quantify the final concentrations of TOC and COD. TOC and COD removals were determined by the following equations:

$$\text{TOC removal}(\%) = \frac{\text{TOC}_i - \text{TOC}_f}{\text{TOC}_i} \times 100 \tag{1}$$

$$\text{COD removal}(\%) = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100 \tag{2}$$

where TOC_i, TOC_f, COD_i, and COD_f are the TOC and COD concentrations at the beginning and end of the reaction, respectively.

The relationship between the factors and response variables was analyzed by fitting a quadratic function [33]. The significance and precision of the models were then evaluated through variance analysis (ANOVA), and the fitness of the models was expressed using the coefficients of determination (R^2, R^2 adjusted, and R^2 predicted) [33,34]. The concentrations of H_2O_2 and $NaHCO_3$ that maximize TOC and COD removals were optimized using a multi-objective approach with the desirability function. The responses predicted by the model for multi-objective optimization were validated with additional experimental tests.

2.5. Aerobic Biological System (AES)—Assay Using Zahn–Wellens Test

The biodegradability of pollution present in textile wastewater post-oxidation was evaluated with an aerobic biological assay using a methodology based on the Zahn–Wellens test [35]. The activated sludge used in the biological tests was collected at the Colombian coffee region's municipal wastewater treatment plant (WWTP) (Colombia, South America). The WWTP effluent has a $BOD_5 < 25$ mg/L, and the BOD and COD removals are 95.8 and 93.7%, respectively, characteristics that make the sludge appropriate for use in the Zahn–Wellens test.

A sludge inhibition test was performed before the biological test with the pollutant sample. The reactor was charged with 500 mL of activated sludge and 1.5 L of mineral medium (aqueous solution of KH_2PO_4, K_2HPO_4, $Na_2HPO_4 \cdot 2H_2O$, NH_4Cl, $CaCl_2$, $MgSO_4 \cdot 7H_2O$, and $FeCl_3 \cdot 6H_2O$), and the post-oxidation contaminant sample was gradually added. In the first 3 days, 200 mg/L of glucose was added, and from Day 4 to 27, between 1 and 30 mL of the post-oxidation sample was added. Biomass growth and CO_2 production were monitored during the 28-day inhibition test. As a blank of the inhibition test, a control was carried out for 28 days in which only glucose was added as a nutrient.

Two biological tests were performed with the post-oxidation wastewater sample; 450 mL of adapted activated sludge and 112.5 mL of pollutant sample (4:1 sludge:pollutant ratio) were added to each reactor, and the volume (2 L) was completed with the mineral medium. Two additional assays were performed as controls: inoculum blank containing 450 mL adapted activated sludge and 1550 mL of mineral medium and reference blank containing 450 mL of adapted activated sludge, glucose (which is highly biodegradable), and 1550 mL of mineral medium. The four reactors were kept under constant agitation (200 rpm) and aeration during the tests.

The biodegradation process was monitored by determining COD in filtered samples taken at a specific time interval. The ratio of eliminated COD, corrected by the inoculum blank, to the initial DOC value, was referred to as the biodegradation percentage at the sampling time [36]. The percentage of biodegradation (D_t) at time t was determined with the following equation:

$$D_t(\%) = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}} \right] \times 100 \tag{3}$$

where C_A and C_{BA} are the COD (mg/L) in the test with the polluting sample and in the inoculum blank, measured 3 h $\pm$ 30 min of incubation, and C_t and C_B are the COD (mg/L) in the test with the polluting sample and in the inoculum blank, measured at the sampling time t [35]. The biodegradability in the Zahn–Wellens test is the D_t value after 28 days, or less if the tested sample is completely biodegradable [37].

2.6. Phytotoxicity Tests

Phytotoxicity experiments were conducted using lettuce seeds to evaluate the impact of ion exchange treatment, advanced oxidation process based in bicarbonate-activated peroxide, and the aerobic biological system on plant growth and development. *Lactuca sativa* L. seeds were purchased from a local seed market (Manizales, Colombia) and for

each experiment, 10 lettuce seeds of similar size and shape were selected. They were evenly distributed on Whatman No. 3 paper impregnated with 5 mL of the test water sample (treatment) and sealed with cling film to prevent evaporation of the solution. Petri dishes were then incubated in the dark at 20 ± 1 °C for 120 h [38,39]. All tests were carried out in triplicate, and the control sample was distilled water [40]. Finally, the germinated seeds were counted, and root elongation was measured. With these data, the relative seed germination (RSG), the relative root growth (RRG), and the germination index (GI) were determined using the following equations [41]:

$$RSG(\%) = \frac{No.seeds\ germinated\ (treatment)}{No.seeds\ germinated\ (control)} \times 100 \qquad (4)$$

$$RRG\ (\%) = \frac{Mean\ root\ length\ (treatment)}{Mean\ root\ length\ (control)} \times 100 \qquad (5)$$

$$GI(\%) = \frac{RSG \times RRG}{100} \qquad (6)$$

3. Results and Discussion

3.1. Physicochemical Characterization of the Real Textile Wastewater

The physicochemical characterization of textile wastewater polluted with acid black 194 dye was recently published [30]. The values of the physicochemical parameters of the RTWW–CF reported in Table 3 were obtained by this research and are within the range of the characterizations carried out by the GI–PRISMA Research Group of the Universidad Nacional de Colombia Sede Manizales [31].

Table 3. Physicochemical characteristics of real textile effluent after coagulation-flocculation and ionic exchange.

Parameter	RTWW		
	CF	CF–IE SAC Resin	CF–IE SBA Resin
pH	8.9 ± 0.1	1.6 ± 0.1	7.8 ± 0.1
Conductivity (μS/cm)	7040 ± 99	4892 ± 64	61.6 ± 1.0
Total hardness (mg/L)	1170 ± 62	<1.0	<1.0
Sulfates (mg/L)	2679 ± 52	2679 ± 52	<2.1
Chloride (mg/L)	137 ± 2.0	137 ± 2	18.1 ± 1.2
Total alkalinity (mg/L)	93 ± 1	<10.0	<10.0
COD (mg/L)	1428 ± 84	917 ± 42	826 ± 50
BOD_5 (mg/L)	397 ± 31		302 ± 23
TOC, mg/L	1832 ± 63	1755 ± 57	1625 ± 98
Acid Black 194, (mg/L)	29.6 ± 1.6	29.6 ± 1.6	0.16 ± 0.08
Apparent color, (Pt-Co)	2360 ± 35	780 ± 18	14 ± 1

Textile wastewater is a complex matrix, as evidenced by the data in Table 3. The RTWW after the CF process is characterized by high COD levels due to organic compounds, elevated concentrations of hardness and sulfates, and intense coloration, highlighting the need for effective treatment methods [31]. Understanding these physicochemical characteristics is essential for treating textile wastewater to minimize its environmental impact.

3.2. Treatment of Textile Wastewater Using Ion Exchange Resins

The RTWW–CF presented high conductivity and concentration of hardness (Ca^{2+}, Mg^{2+}) and SO_4^{2-} and Cl^- ions, which interfered with the application of the AOP. The addition of $NaHCO_3$ for H_2O_2 activation (oxidation reaction) led to the formation of precipitates, confirmed by XRD analysis to be sulfates ($CaSO_4$, $MgSO_4$, and $NaSO_4$), and carbonates ($CaCO_3$ and $MgCO_3$). To remove the total hardness (Ca^{2+}, Mg^{2+}) in RTWW–CF,

a strongly acidic cation (SAC) exchange resin was used, followed by a strongly basic anion (SBA) exchange resin to remove SO_4^{2-} and Cl^- ions.

Given the RTWW–CF sample's complex composition, the effect of resin volume on ion concentration was studied. For cation exchange tests (Table 4), a SAC resin/sample volume ratio of 0.05 guarantees a complete removal ($\geq$99.9%) of the hardness (Ca^{2+}, Mg^{2+}). In contrast, the anion exchange resin (Table 5), apart from removing SO_4^{2-} and Cl^- ions, can also eliminate the acid black dye 194 (AB-194), a premetallized acid dye. With an SBA resin/sample volume ratio of 0.14, the removal of more than 99.5% of SO_4^{2-} and AB-194 dye and 86.8% of Cl^- ions were obtained. As AB-194 is an anionic dye (Figure S1 of the Supplementary Materials), SBA resin can remove it. Additionally, Tables S1 and S2 of Supplementary Materials show the effects of the volume of SAC and SBA resins on ions removal, respectively.

Table 4. Effect of resin volume on ions concentration.

Cation Exchange Resin		Anion Exchange Resin			
SAC Volume (mL)	Hardness (mg/L)	SBA Volume (mL)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NA–194 (mg/L)
0.0	1170	0.0	2679	137	29.6
1.0	81.8	2.5	309.5	82.4	12.0
2.0	25.0	5.0	23.1	73.6	2.8
3.0	22.4	9.0	5.0	48.9	2.6
4.0	15.0	11.0	4.6	36.5	1.2
5.0	<1.0	14.0	<2.1	18.1	0.16

Conditions: V_{sample} = 100 mL, T = 25 $\pm$ 1 °C, stirring speed = 180 rpm, and contact time = 2 h.

Table 5. Effect of contact time on ions concentration.

Cation Exchange 25 mL SAC Resin		Anion Exchange 70 mL SBA Resin			
Time (min)	Hardness (mg/L)	Time (min)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NA–194 (mg/L)
0.0	1170	0.0	2679	137	29.6
1.0	160	1.0	118	120.2	5.85
5.0	45	5.0	5.0	89.0	3.53
15.0	3.4	15.0	4.7	60.3	2.32
30.0	1.2	30.0	<2.1	42.4	1.48
60.0	<1.0	60.0	<2.1	21.6	0.77
120.0	<1.0	120.0	<2.1	18.1	0.16

Conditions: V_{sample} = 500 mL, T = 25 $\pm$ 1 °C, stirring speed = 180 rpm.

The total exchange capacity (TEC) of resin is usually expressed as eq/L and corresponds to the maximum theoretical quantity of equivalent ions that can be held in 1 L of resin. Only 26.8% and 29.1% of the TEC reported in the datasheet (Table 1) were utilized to remove the ions of interest (Tables 4 and 5). The low useful exchange capacity (UEC) values could be associated with the RTWW–CF sample's chemical composition since the typical UEC of strongly acidic and strongly basic resins is 40 to 70% of their TEC.

With a contact time for ion exchange of 120 min and SAC resin/sample and SBA resin/sample volume ratios of 0.05 and 0.14, respectively, high removals of hardness, sulfates, chlorides, and AB-194 dye were obtained (Figure S2). After five cycles of using the resins (Tables S3 and S4, and Figure S3, Supplementary Materials), the removal of hardness and anions (sulfates, chlorides, and AB-194) decreased by 33.2 and 16.6%, respectively. These results indicate that the ion exchange resins have outstanding reuse performance, with a slight decrease in pollutant removal.

In addition to removing ions and the AB-194 dye, at the end of the treatment with the SAC and SBA resins, TOC removals of 11.29% and COD removals of 42.15% were achieved. Ion exchange resins can remove specific organic pollutants, such as anionic surfactants [42]

in RTWW. The electrostatic interaction between the functional groups of the resin and the organic matter present in the sample, such as carboxylic acids, can explain the removal of organic substances by ion exchange resins [43].

3.3. Oxidation Tests Using H_2O_2-Activated $NaHCO_3$—Experimental Design

Batch experiments were performed to study the degradation of real textile wastewater after coagulation–flocculation and ion exchange (RTWW–CF–IE) treatments using bicarbonate-activated peroxide and RSM-based CCD. The design matrix and the responses (TOC and COD removal) are shown in Table 6.

Table 6. Independent variables (factors) and response for the AOP of textile wastewater.

Std	Run	Factors Values				Response Variables—Removal	
		Codified		Experimental (mM)		TOC (%)	COD (%)
		X_1	X_2	X_1	X_2	Y_1	Y_2
9	1	0	$-\alpha$	300	28.9	4.67	25.62
20	2	0	$-\alpha$	300	28.9	4.77	23.61
14	3	-1	$+1$	150	120	6.97	17.57
5	4	$+\alpha$	0	491.7	80	6.96	36.85
11	5		0	491.7	80	7.50	39.94
8	6	0	$-\alpha$	300	28.9	4.78	26.35
18	7	0	0	300	80	13.22	38.58
25	8	0	0	300	80	12.99	37.87
23	9	0	0	300	80	13.16	38.12
16	10	$+\alpha$	0	491.7	80	7.03	38.94
17	11	0	0	300	80	12.31	37.67
2	12	$+1$	$+1$	450	120	14.58	42.17
10	13	$+1$	-1	450	40	0.56	31.97
21	14	$-\alpha$	0	108.3	80	4.59	10.02
1	15	$-\alpha$	0	108.3	80	4.75	12.77
15	16	0	$+\alpha$	300	131.1	15.03	31.21
22	17	-1	-1	150	40	5.28	11.01
13	18	0	$+\alpha$	300	131.1	15.67	33.28
6	19	$+1$	-1	450	40	0.50	33.52
3	20	0	0	300	80	13.29	37.25
7	21	-1	$+1$	150	120	7.82	16.04
24	22	0	$+\alpha$	300	131.1	15.07	34.79
19	23	-1	-1	150	40	5.25	13.87
12	24	$-\alpha$	0	108.3	80	4.58	11.74
4	25	$+1$	$+1$	450	120	15.04	41.87

A multiple regression analysis was conducted, and response functions were fitted to a second-order polynomial model (as suggested by the software), obtaining the following equations for the TOC and COD removals:

$$\begin{aligned} Y_1(\%) = &-8.9977 + 0.0792X_1 + 0.12795X_2 + 5.0625 \times 10^{-4}X_1X_2 \\ &-1.9020 \times 10^{-4}X_1^2 - 1.1068 \times 10^{-3}X_2^2 \end{aligned} \tag{7}$$

$$\begin{aligned} Y_2(\%) = &-35.0111 + 0.2542X_1 + 0.50931X_2 + 2.0458 \times 10^{-4}X_1X_2 \\ &-3.2928 \times 10^{-4}X_1^2 - 3.0614 \times 10^{-3}X_2^2 \end{aligned} \tag{8}$$

In the quadratic Equations (7) and (8), the sign reflects the particular factor's effect (positive or negative) on the response, while the magnitude of the coefficient indicates the intensity. When a factor has a positive influence, the response improves as the level of the factor increases. Likewise, a negative effect of the factor is reduced when the factor level increases [44]. ANOVA technique was applied to the regression models (Equations (7) and (8)), and the significance of each term is presented in Tables 7 and 8.

Table 7. ANOVA results for TOC removal.

Parameter	Sum of Squares	Degrees Freedom	Mean Square	*F*-Value	*p*-Value
Model	559.28	5	111.86	996.72	<0.0001 [a]
X_1	12.7	1	12.70	113.15	<0.0001 [a]
X_2	300.54	1	300.54	2678.06	<0.0001 [a]
$X_1 X_2$	73.81	1	73.81	657.71	<0.0001 [a]
X_1^2	172.23	1	172.23	1534.68	<0.0001 [a]
X_2^2	29.49	1	29.49	262.79	<0.0001 [a]
Residual	2.13	19	0.11		
Lack of fit	0.57	3	0.19	1.96	0.1602 [b]
Pure error	1.56	16	0.097		
Cor total	561.42	24			

R^2 = 0.9962, R^2_{adj} = 0.9952, R^2_{pred} = 0.9933, CV = 3.87%, Adeq. Precision = 89.644, [a] significant at *p*-value < 0.05, [b] non-significant at *p*-value > 0.05.

Table 8. ANOVA results for COD removal.

Parameter	Sum of Squares	Degrees Freedom	Mean Square	*F*-Value	*p*-Value
Model	2885.15	5	577.03	297.24	<0.0001 [a]
X_1	2132.20	1	2132.20	1098.33	<0.0001 [a]
X_2	186.19	1	186.19	95.91	<0.0001 [a]
$X_1 X_2$	12.05	1	12.05	6.21	<0.0001 [a]
X_1^2	516.19	1	516.19	265.90	<0.0001 [a]
X_2^2	225.62	1	225.62	116.22	<0.0001 [a]
Residual	36.88	19	1.94		
Lack of fit	10.07	3	3.36	2.00	0.1542 [b]
Pure error	26.81	16	1.68		
Cor total	2922.03	24			

R^2 = 0.9874, R^2_{adj} = 0.9841, R^2_{pred} = 0.9777, CV = 4.82%, Adeq. Precision = 42.758, [a] significant at *p*-value < 0.05, [b] non-significant at *p*-value > 0.05.

From Tables 7 and 8, it is clear that the models are significant and can adequately explain the relationship between responses and independent variables [33], as indicated by their *F*-values (996.72 and 297.24 for TOC and COD removals, respectively), corresponding *p*-values < 0.0001, and high sum of squares (SS of 559.28 and 2885.15 for TOC and COD removals). The linear, interaction, and quadratic coefficients were significant for both models. ANOVA study suggested that the concentration of $NaHCO_3$ has the most important effect on TOC removal, while the concentration of H_2O_2 presented the most significant effect on COD removal. The obtained R^2, R^2_{adj}, and R^2_{pred} values for TOC and COD removals were greater than 0.9777, which indicates the adequacy of the suggested quadratic models. Adequate precision is a signal-to-noise ratio that compares the range of the predicted values, the design points, and the average prediction error [45]. The adequate precision values obtained for TOC and COD removals were 89.644 and 42.758, respectively, and values larger than 4 indicate that the model is able to navigate the design space [46]. The coefficient of variation (CV) values for TOC and COD removals were between 3.87 and 4.82%, respectively, and the models are considered acceptable when the CV is less than 10% [47,48].

Figure 1 shows the 3D surfaces for the TOC and COD removals in oxidation del RTWW with the BAP system as a function of independent variables. The analysis of the red areas in Figure 1a,b allowed us to establish that medium–high concentrations of H_2O_2 (300–450 mM) and $NaHCO_3$ (80–120 mM) favor the degradation of RTWW–CF–IE.
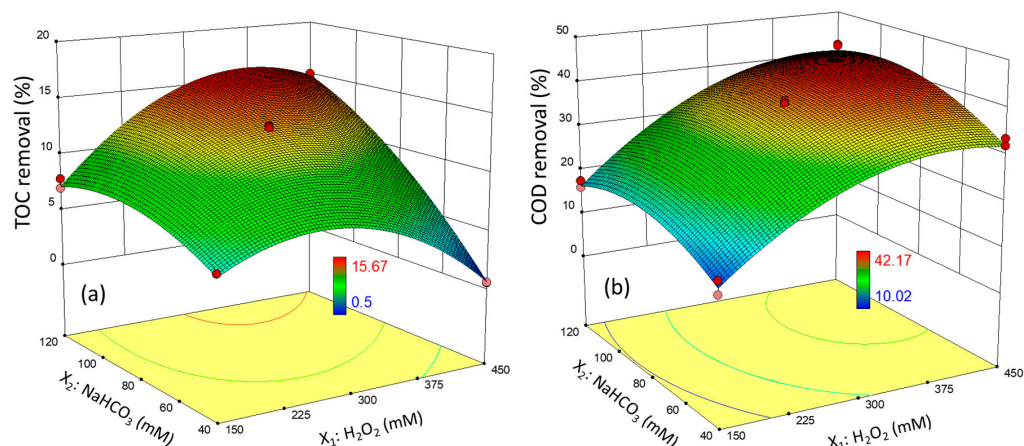
Figure 1. Three-dimensional response surface plots for real textile wastewater oxidation using BAP system. (**a**) TOC removal; (**b**) COD removal.

Figure 2 shows the relationship between actual and predicted values of TOC (Figure 2a) and COD (Figure 2b) removal during the oxidation of RTWW–CF–IE. The actual data are the measured removals of TOC and COD, estimated experimentally using Equations (1) and (2). On the other hand, predicted values were generated using Equations (7) and (8). The data distribution around the straight-line X = Y in a narrow zone indicates that the models proposed for the TOC and COD removals adequately approximated the experimental values.
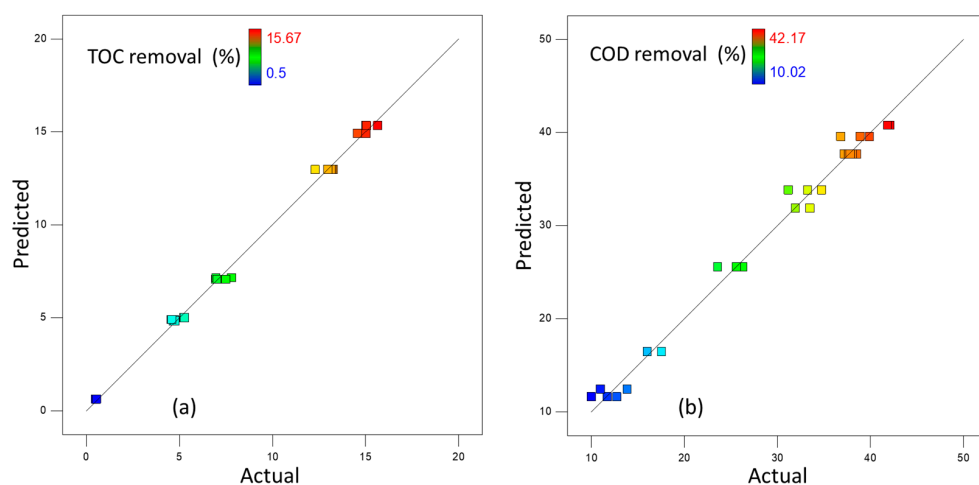
Figure 2. Plots of predicted vs. actual values for real textile wastewater oxidation using BAP system. (**a**) TOC removal; (**b**) COD removal.

Numerical optimization was carried out to obtain the optimum concentration of H_2O_2 and $NaHCO_3$ that maximizes the TOC and COD removals from real textile wastewater by desirability function. The highest TOC and COD removals with the multi-objective optimization approach and desirability of 0.95 were obtained at 393.3 mM H_2O_2 and 114.3 mM $NaHCO_3$ concentrations, corresponding to 15.67 and 41.44% removals, respectively. The experimental removals of TOC and COD for the optimization conditions were 14.77 and 38.86%, respectively, values slightly lower than those predicted by the models.

Experimental validation was carried out to guarantee the reliability and prediction of the mathematical models obtained, as shown in Table 9. The test conditions were the same as those proposed for the design: T = 25 °C, P = atmospheric pressure (78 kPa), catalyst dose = 2 g/L, and reaction time = 5 h. The values predicted by the second-order models for TOC and COD removals are similar to those obtained experimentally, with errors between 1.54 and 6.64%.

**Table 9.** Validation of the experimental design—comparison of predicted and experimental results.

Conditions	TOC Removal (%)		COD Removal (%)	
	Predic.	**Exper.**	**Predic.**	**Exper.**
[H$_2$O$_2$] = 393.3 mM [NaHCO$_3$] = 114.3 mM	15.67	14.77	41.44	38.86
[H$_2$O$_2$] = 150 mM [NaHCO$_3$] = 100 mM	7.93	7.81	19.09	19.40
[H$_2$O$_2$] = 300 mM [NaHCO$_3$] = 100 mM	14.57	14.17	38.06	36.91

In all the CCD oxidation tests and the validation tests, the leaching of the active cobalt phase in the catalyst (Co/Al–PILC) was less than 0.01 mg/L (atomic absorption spectrometry, Thermo Scientific iCE 3000), which indicates a high stability of the activate phase in the reaction medium.

3.4. Aerobic Biological System (AES)

In the blank of the Zahn–Wellens assay with the reference substance (glucose), the COD removals at 21 and 28 days were 89.29% and 95.42%, respectively. For the glucose assay to be valid, a minimum COD removal of 70% is required on Day 14 [35], and for this test, it was obtained between Days 11 (65.21%) and 13 (73.70%), which guarantees the quality of the activated sludge for the degradation of organic matter. In the inhibition test, where glucose is initially added to the reactor and then the contaminant sample, a slight decrease in biomass growth was observed between Days 21 and 28 (reduction in the sludge volume index—SVI). The COD removal in the inhibition test was 76.51%, which suggests that microorganisms can grow in the textile wastewater and degrade organic matter.

The monitoring of biodegradation over time or biodegradation curve for Tests 1 and 2 post-oxidation are shown in Figure 3. The two post-oxidation samples showed an improvement in biodegradability, reaching 70% at 14.3 days. After day 21 of the tests, biodegradability tends to stabilize, and at 28 days, an average percentage of biodegradation (D$_t$) of 96.38% was obtained, a highly satisfactory condition for the AOP/biological coupling at the laboratory level for the RTWW sample under study. Additionally, the average TOC removal for the post-oxidation tests was 95.88 $\pm$ 0.04%, indicating that almost all organic matter was degraded in the biological system.
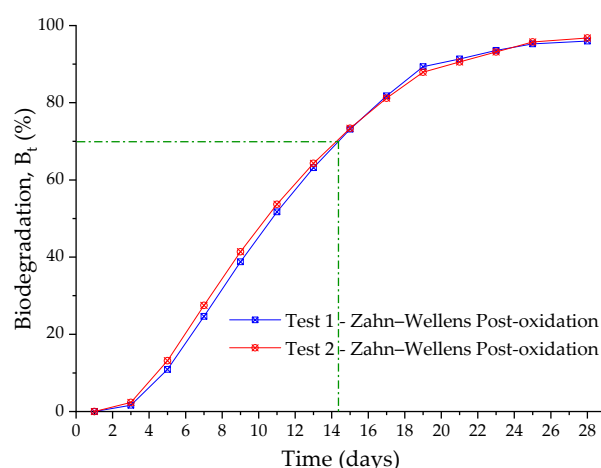
Figure 3. Biodegradation curves of post-oxidation textile wastewater using activated sludge inoculum—Zahn–Wellens essay.

3.5. Effect of RTWW Treatments on Phytotoxicity

Table 10 summarizes the results of the relative seed germination (RSG), the relative root growth (RRG), and the germination index (GI) during the different RTWW treatments.

Removing ions using exchange resins and the AOP with bicarbonate-activated peroxide reduced the phytotoxicity of textile wastewater to moderate levels. With the aerobic biological system, a GI $\geq$ 100% was obtained, which is associated with the assimilation of nutrients from the mineral medium in which the Zahn–Wallens assay was carried out and the byproducts of biodegradation, which favored germination and development of lettuce seedlings, confirming that the sample does not contain phytotoxic substances. GI values > 100% have been obtained in seeds of cucumber (Cucumis sativus), barley (Hordeum vulgare), wheat (Triticum aestivum), soybeans (Glycine max), watercress (Nasturium officinale), and tomato (Licopersicon esculentum) subjected to testing with piggery wastewater (dilution 1:20) treated with microalgae, where the suspensions presented a biostimulant activity for the growth of the different seeds [49].

Table 10. Summary of RSG, RRG, and GI during the different RTWW treatments.

Sample/Treatment	RSG (%)	RRG (%)	GI (%)	Interpretation [50–52]
Control (Distilled water)	100	100	100	GI $\geq$ 80, no-phytotoxic
RTWW–CF	0	0	0	GI = 0, phytotoxic that inhibits germination
RTWW–CF–IE	30.8 $\pm$ 6.7	14.1 $\pm$ 4.9	4.2 $\pm$ 1.5	GI $\leq$ 50%: highly phytotoxic
RTWW–CF–IE–BAP	61.5 $\pm$ 6.7	84.5 $\pm$ 16.9	52.0 $\pm$ 11.3	GI between 50–80%, moderately phytotoxic
RTWW–CF–IE–BAP–ABS	100	233.8 $\pm$ 12.9	233.7 $\pm$ 18.7	IG $\geq$ 100%, phytonutrient or phytostimulant effect

CF: coagulation-flocculation, IE: ion exchange, BAP: bicarbonate-activated peroxide, ABS: aerobic biological system.

3.6. Improvement in the Biodegradability of Real Textile Wastewater

The BOD_5/COD ratio or biodegradability index (BI) is considered an accurate measurement of wastewaters biodegradability [53]. With the different treatments to which the RTWW was subjected, an increase in the BI was obtained (Figure 4). The RTWW had a BI of 0.20 $\pm$ 0.01 [30], and after coagulation-flocculation and ion exchange with resin, this parameter increased to 0.28 $\pm$ 0.01 and 0.37 $\pm$ 0.01, respectively. However, the BOD_5/COD ratio < 0.4 and the sample (RTWW–CF–IE) are considered non-biodegradable [54]. After oxidation with the bicarbonate-activated peroxide system, the textile wastewater presented a BI of 0.59 $\pm$ 0.01, which indicates that the sample is biodegradable and can be treated through a biological process [54,55]. With the aerobic biological system, it was possible to increase the BI up to 0.90 $\pm$ 0.03 and considerably reduce the organic matter concentration.
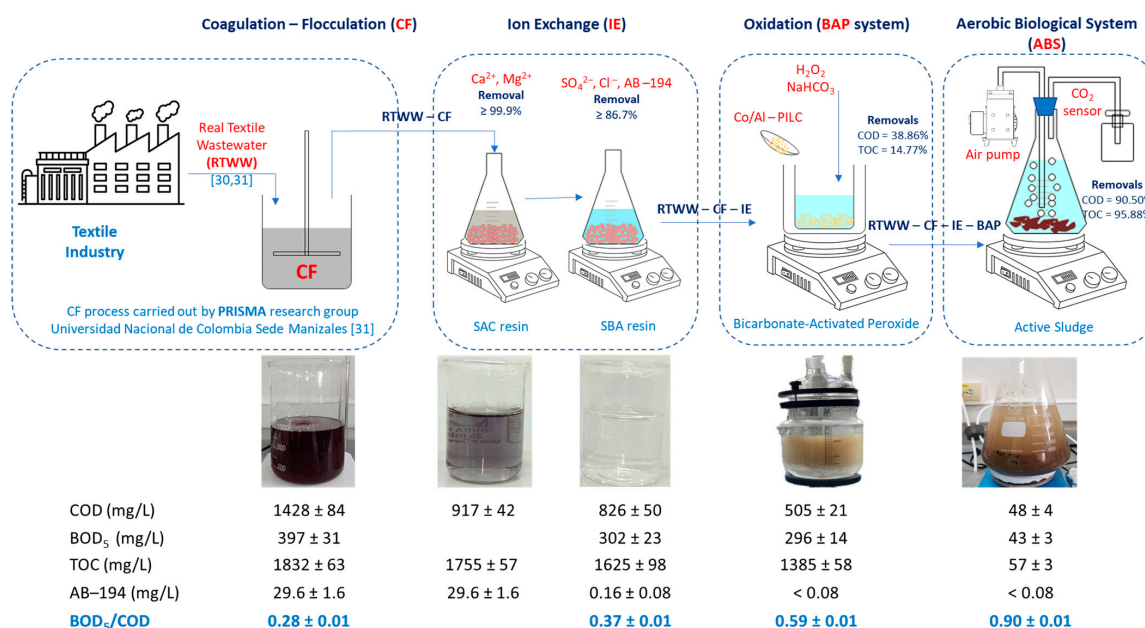

	Coagulation – Flocculation (CF)	Ion Exchange (IE)		Oxidation (BAP system)	Aerobic Biological System (ABS)
COD (mg/L)	1428 $\pm$ 84	917 $\pm$ 42	826 $\pm$ 50	505 $\pm$ 21	48 $\pm$ 4
BOD_5 (mg/L)	397 $\pm$ 31		302 $\pm$ 23	296 $\pm$ 14	43 $\pm$ 3
TOC (mg/L)	1832 $\pm$ 63	1755 $\pm$ 57	1625 $\pm$ 98	1385 $\pm$ 58	57 $\pm$ 3
AB–194 (mg/L)	29.6 $\pm$ 1.6	29.6 $\pm$ 1.6	0.16 $\pm$ 0.08	< 0.08	< 0.08
BOD_5/COD	**0.28 $\pm$ 0.01**		**0.37 $\pm$ 0.01**	**0.59 $\pm$ 0.01**	**0.90 $\pm$ 0.01**

Figure 4. Scheme of treatments carried out at RTWW and improvement of biodegradability.

4. Conclusions

With the ion exchange scheme, SAC resin/sample and SBA resin/sample volume ratios of 0.05 and 0.14, and a contact time of 120 min, greater than 99% removals of hardness, sulfates, and AB-194 were achieved in the wastewater textile. The elimination of the ionic charge influenced the removal of organic matter, allowing reductions in TOC and COD of 11.29 and 42.15%, respectively. The removal efficiency of AB-194 by the SBA resin was attributed to the dye's ionic structure. Therefore, ion exchange pretreatment is an alternative for textile effluents contaminated with anionic dyes and a high concentration of salts.

Although in the optimal RTWW–CF–IE oxidation conditions the $NaHCO_3$-activated H_2O_2 system, low removals of TOC and CDO were obtained (14.77 and 38.86%, respectively), the wastewater became easily biodegradable, which allowed the subsequent application of a biological treatment.

The integration of the ion exchange processes, oxidation with $NaHCO_3$-activated H_2O_2, and aerobic biological treatment based on the Zahn–Wellens assay improved the biodegradability index of the real wastewater under study, going from 0.28 ± 0.01 (RTWW–CF) to 0.37 ± 0.01 (after ion exchange), 0.59 ± 0.01 (after AOP), and 0.90 ± 0.01 at the end of biological treatment.

Additionally, the integration of the treatments reduced the phytotoxicity of textile wastewater, going from inhibiting the germination of lettuce seeds and being phytotoxic (RTWW–CF) to favoring their germination and development (phytostimulant effect), where the components present in the sample after the aerobic biological process acts as phytonutrients.

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