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Integrated Treatment of Refinery Wastewater using Oxidized Cotton Waste (H_2O_2/NaOH/CW) as Adsorbent and Photodegradation

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ABSTRACT

A new environmentally acceptable method for manufacturing high carboxyl content (CC) oxidized cotton waste (OCW) utilizing H_2O_2/NaOH has been developed to enhance the surface and pore size of the prepared material by removing hemicellulose, lignin, and impurities, and then treated chemically to produce free radicals from oxidized waste cotton by hydrogen peroxide. The structure and morphology of the resulting OCW were meticulously considered using various techniques, including titration, EDX, XRD, FTIR, TGA, and FE-SEM. It was observed that the degree of polymerization, yield, and crystallinity of OCW were influenced by the NaOH concentration and exhibited variations in different directions. FTIR analysis indicated successful selective oxidation of the hydroxide groups of CW. XRD and FE-SEM results revealed thorough oxidation penetration throughout the waste cotton, disrupting its consistency and length while preserving its crystal structure. This paper presents a straightforward green approach for fabricating OCW with high crystallinity and specific surface area. The resulting OCW holds promise for applications such as adsorption and photodegradation of organic pollutants in refinery wastewater (RWW), contributing to environmental sustainability.

Introduction

Water is essential for sustaining all life forms and plays a pivotal role in maintaining the integrity and sustainability of Earth's ecosystems [1]. However, in recent years, the availability and accessibility of fresh water have emerged as critical issues. Water contamination has become a significant threat to humanity, with domestic households contributing to the discharge of oily wastewater that pollutes seas, rivers, groundwater, and lakes [2]. This contamination originates from various sources, including oil refineries, dyes, paper mills, textile dyes, detergents, surfactants, pesticides, herbicides, insecticides, and pharmaceutical manufacturers [3]. The proliferation of contaminated water poses a serious challenge as it renders water unfit for daily consumption and use [4]. Addressing this issue is imperative to protect both human well-being and the environment [5]. Therefore, wastewater should be treated before being discharged into the soil or the aquatic systems by using practical treatment methods [6].

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Many previous studies have investigated the ability of various treatment processes to eliminate pollutants from wastewater and to address the crisis of continuous freshwater demands worldwide, in accordance with stringent environmental regulations [7]. Wastewater treatment encompasses a range of techniques, including physical, chemical, and biological methods such as sorption [8], coagulation [9], precipitation [10], ion exchange [11], electrochemical treatment [12], membrane filtration, and biodegradation [13]. However, traditional biological and chemical methods often need to catch up due to the non-biodegradable nature of many pollutants. Moreover, conventional wastewater treatment processes are costly or ineffective, merely transferring pollutants between phases rather than eliminating them [14]. Despite membrane filtration's ability to produce high-quality water, its susceptibility to fouling adds to operational expenses [15].

To address these challenges, the adsorption process emerges as an efficient and economical means of removing organic, pigments, and other colorants from wastewater. Activated carbons are commonly utilized due to their high adsorption capacity and microporous structure [16]. However, commercial activated carbon is cost-prohibitive, prompting the search for alternative low-cost adsorbents [17]. Cotton, comprising over 90% cellulose, is a promising candidate due to its widespread availability, affordability, renewability, durability, and biodegradability. Surface chemical modifications of cellulosic nanomaterials have been explored by incorporating various inorganic and organic functional groups to enhance adsorption capabilities [18, 19]. Combining adsorption with chemical processes can effectively remove organics from solutions and achieve higher maximum adsorption capacities [20]. Hydrogen peroxide is a green and inexpensive oxidant for fabricating oxidized cellulose, offering advantages over oxidizing agents like periodate and permanganate [21]. This study focuses on fabricating CW with high carboxyl content using a two-step method involving the preparation of H_2O_2/NaOH/CW. It evaluates its efficacy for organic removal in refinery wastewater through physical and chemical processes. Optimization of parameters such as cotton waste type, reaction time, pH, temperature, and UV light exposure will be conducted to determine the optimal conditions for batch technical applications.

Experimental

Chemical and Instrumentation Test

A sample of refinery wastewater containing organic pollutants discharged from an oilfield refinery plant in Iraq was stored in a polypropylene container at 4°C for treatment using adsorption and oxidation technologies, as listed in Table 1. The chemical compounds utilized in this investigation were of analytical grade. H_2SO_4 and NaCl were purchased from Scharlau, Spain. Hydrogen peroxide (45% wt), as well as NaOH (99% purity) and carbon tetrachloride, are organic pollutants in wastewater, according to the lecture [22].

Eq. 1 was used for organic removal:

$$\mathrm{Y}_{\mathbf{OCRE}} = \frac{\boldsymbol{A_{\circ}-A_t}}{\boldsymbol{A_{\circ}}} \times \mathbf{100\%} \qquad (1)$$

where Y_{OCRE} is the organic elimination, Ao and At are the organic concentrations before and after treatment (mg organic/L), respectively.

Table 1. Refinery wastewater specification

No.	Limit	Concentration (mg/L)
1	Oil content	165.3 (mg/L)
2	COD	265 ppm
3	Turbidity	24.79 NTU
4	Dissolved oxygen content	0.032 (mg/L)
5	Specific gravity	0.9965
6	Conductivity	51000 us/cm
7	TDS	326400 (mg/L)
8	Viscosity	1.0103 m Pa/s
9	TSS	15.2 (mg/L)

Preparation of H_2O_2/NaOH/CW

The waste cotton was washed with hot water to remove impurities and then added to a NaOH solution to prepare NaOH/CW, as described by the author [23], with some modifications. The CW with NaOH was then desiccated at 75 °C in an oven for 24 hours to produce NaOH/CW. Next, the alkali-treated cotton waste was added to a solution containing 2% acetic acid and 7% hydrogen peroxide, as shown in Fig. 1. The alkali-treated cotton waste was then added to 2% acetic acid and 9% hydrogen peroxide under UV light for 19 hours [24], meeting specific requirements.

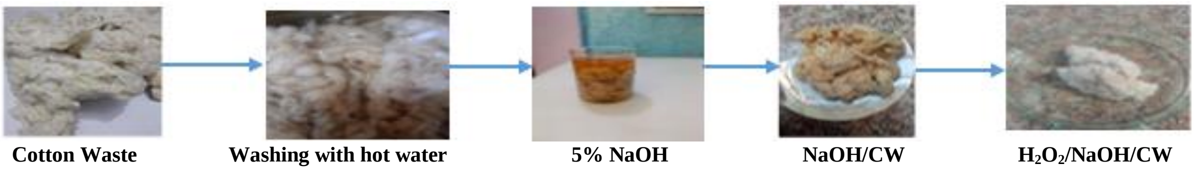


Fig. 1. Preparation of H_2O_2/NaOH/CW

Residual of Hydrogen Peroxide

The residual amount of H_2O_2 is quantified using a method that involves a slightly acidified potassium iodide (KI) solution in the presence of a certain amount of ammonium molybdate, serving as a catalyst. In this process, the hydrogen peroxide oxidizes the potassium iodide, liberating iodine in the solution. The unconventional iodine is titrated with a thiosulfate solution, with starch acting as an indicator [25].

Carboxyl Content Determination

The carboxyl content in oxidized cotton waste was determined using a titration technique described by Saida et al. [26]. 50 mL of a 2% calcium acetate solution contained 0.4 g of the H_2O_2/NaOH/CW and was titrated with 0.1 N NaOH solution.

$$\text{Carboxyl group} = \frac{\boldsymbol{Nx(Vc-Vb)xMcooH}}{\boldsymbol{OWC(mg)}} \text{x100\%} \tag{2}$$

Batch Adsorbent and Photodegradation Experiments

The adsorption/photodegradation experiments were conducted in a 250 mL batch oxidation reactor equipped with a UV light source. The intensity of UV light was maintained at 0.5 mW/cm^2. A stirring velocity of approximately 200 rpm was used to agitate the RWW at different times, ranging from 30 to 120 minutes. Before adding reagents, the pH of the solutions was adjusted using dilute solutions of sodium hydroxide or sulfuric acid. Various amounts of oxidized cotton waste (ranging from 0.5 to 1.5 grams) were utilized in the experiments, as shown in Fig. 2.

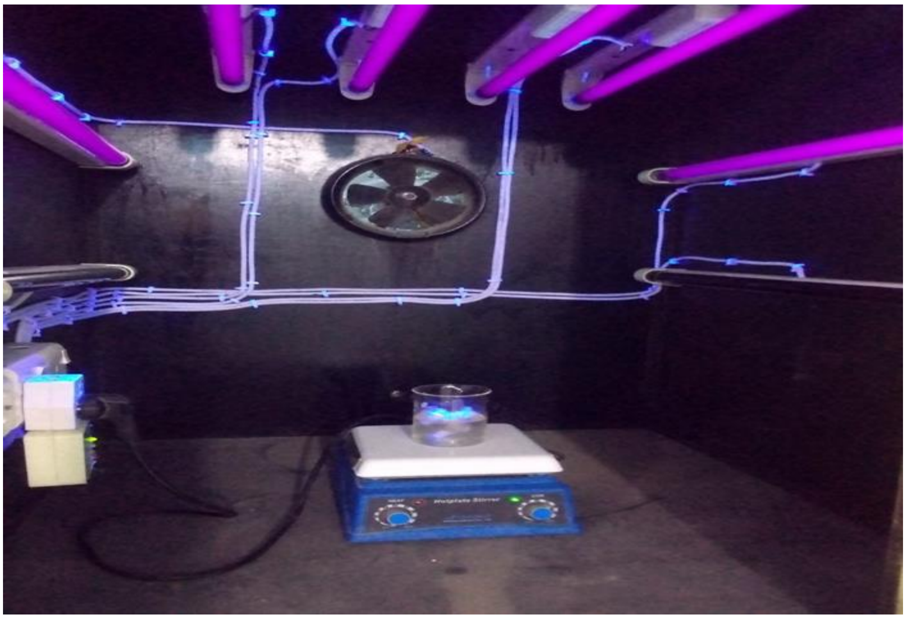


Fig. 2. Adsorption and photodegradation treatment

Experimental Design

This work demonstrated the optimization of untried conditions for the mineralization and removal of pollutants from refinery wastewater using adsorption and photodegradation treatment. Design Expert Minitab-17 program with Box-Bingham design is used for graphical depiction, arithmetical analysis, and quadratic model removal with time (30-120 min), pH (3-9), Dose (0.5-1.5 gm), temperature (25-70), and UV light (2-8).

Results and Discussion

Effects that Affect Oxidized Groups

A comprehensive study was conducted to investigate the impact of various limitations on the growth of carboxyl groups in CW. The untried circumstances for the different examples were as follows: Fig. 3a presented the slow effect of H2O2, Fig. 3b showed the temperature effect with varying agent concentration; Fig. 3c presented the effect of pH, and Fig. 3d investigated the impact of time. The study's findings showed that various working conditions had a similar influence on the production of carboxyl content in prepared materials. The addition of H2O2 significantly influenced the quantity of OCW. Increasing the agent concentration leads to an increase in the carboxyl groups, reaching a highest of 9% as shown in Fig. 3a. However, H_2O_2 must be added in restraint to produce carboxyl content on cotton waste. [27, 28]. The pH of the solution influenced the oxidation reaction by affecting the release rate of reactive hydroxyl radicals. Higher initial pH values resulted in a higher carboxylate content, indicating a more significant oxidation outcome under basic conditions [29]. With increasing pH, the carboxyl groups rose slowly until they reached a peak at pH 9.0. Shorter times led to imperfect oxidations and reduced functional groups [30].

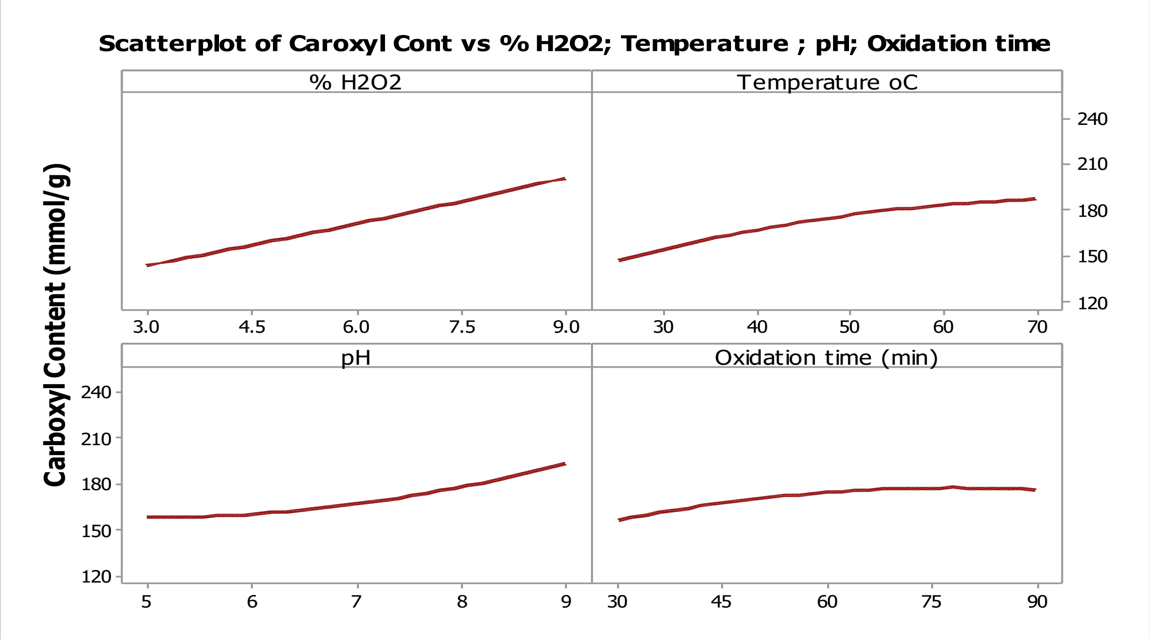


Fig. 3. Parameters that affect the carboxyl content on (a) hydrogen peroxide, (b) temperature, (c) pH, and (d) oxidation time

The Mechanism of Oxidation

Fig. 4 proposes and exemplifies the CW oxidation technique. The vicissitudes in cotton structures over time are presented in Fig. 4a. The crystal structure first undergoes vicissitudes from cellulose I to cellulose II, followed by infiltration by alkaline solution. This increased accessibility facilitates the number of hydroxyl groups in the solid-liquid reaction system by H_2O_2 [30]. The oxidation mechanism of H_2O_2 is illustrated in Fig. 4b. Under UV light, H_2O_2 decomposes to generate free radicals. This hydroxyl radical binds to the carbon atom at the C-6 position, facilitated by the inductive effect of the adjacent hydroxyl group [31].

The hydroxyl group oxidizes to aldehyde groups as a consequence of the unbalanced structure, which is shared with carbon. The augmented OH concentration then saves the aldehyde groups oxidized to carboxyl groups. The ionization of carboxyl content throughout this oxidation procedure causes the pH of the solution to drop. Additionally, the amorphous portion of CW is hydrolyzed, resulting in upsurges in crystallinity, which consequently lead to reductions in yield. Deprived of altering the crystal structure of H_2O_2/NaOH/CW [32].

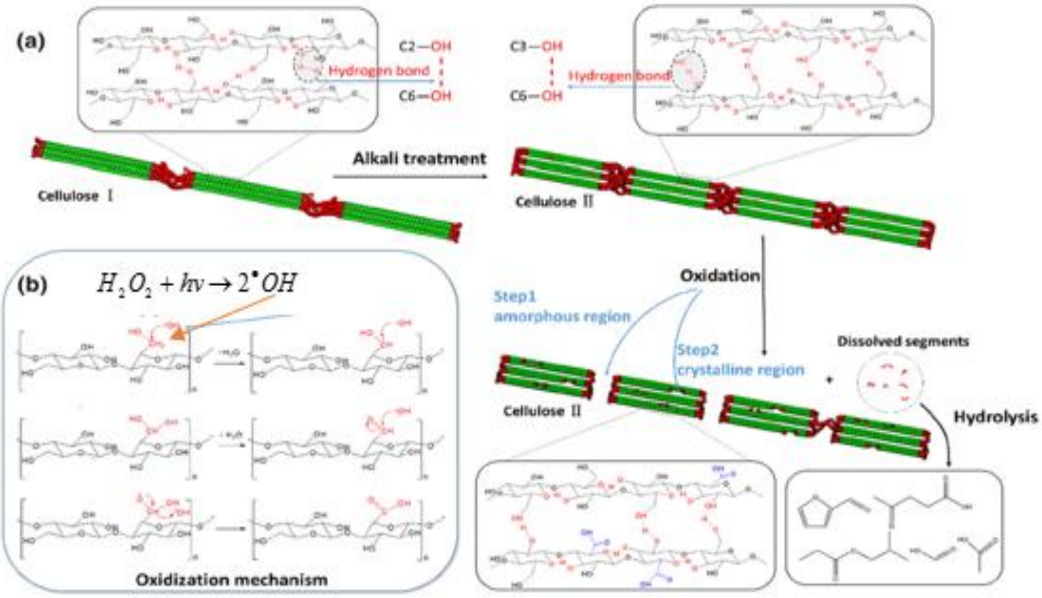


Fig. 4. Structure alteration of (a) cellulose, and (b) the oxidation mechanism

The Characteristics of H_2O_2/NaOH/CW

The oxidation reaction induces structural changes in the macromolecules of cotton waste. To investigate the changes in the chemical composition of treated CWs, FT-IR spectroscopy was used. The spectra for CW, NaOH/CW, and H_2O_2/NaOH/CW are shown in Fig. 5, respectively. Following treatment, there was a noticeable decrease in relative intensities at 3600–3000 cm^{-1}, which corresponds to –OH stretching vibrations mainly from the presence of hydroxyl groups in cotton waste. This reduction demonstrated a noteworthy decline in the number of hydroxyl groups following treatment, indicating a partial disruption of hydrogen bond structures in waste cotton and, consequently, a reduction in the mechanical properties of waste cotton, which was observed with increasing degrees of oxidation and oxidized group content. This shift is attributed to the formation or incorporation of aldehyde and carboxylate groups during the oxidation degumming. Additionally, the FT-IR spectrum of treated cotton waste revealed distinctive absorption peaks, including O–H stretching at around 3420 cm^{-1}, CH_2 symmetric bending at approximately 1420 cm^{-1}, and C–O–C stretching at about 1060 cm^{-1}. These intensities displayed subtle alterations due to the oxidative impact of hydrogen peroxide [33].

Fig. 6 shows the XRD spectra of oxidized cotton waste with varying CC. Sharp peaks are observed at $2\theta = 22.59$, indicating the typical pattern of type I cellulose for CW. The crystallinity of the samples exhibits diverse variations. The crystallinity of cotton waste reductions after pretreatment with alkali was initially attributed to the destruction of hydrogen bonds in the cellulose I crystals during the alkali treatment process [34].

This reduction in crystallinity occurs because the regular arrangement of cellulose molecular chains is disrupted. However, the crystallinity significantly increases upon oxidation, nearly reaching 100.0% for OCW. This increase in crystallinity is attributed to several factors. The destruction of hydrogen bonds during alkali pretreatment increases the accessibility of waste cotton, making hydroxyl groups more susceptible to oxidation by hydrogen peroxide; primary hydroxyl groups in the amorphous region are preferentially oxidized to carboxyl groups during the oxidation process, and oxidation results in the formation of water-soluble fragments and a decline in the molecular weight of cellulose. Consequently, the region of amorphous cotton waste is mainly removed, leaving only the crystalline region behind. As a result, the crystallinity of oxidized cotton waste increases to 100.0% and stabilizes with the increase in carboxylate content. This indicates a transformation from amorphous to crystalline structure, driven by oxidation and the consequent elimination of amorphous regions. In high content (OCW High) images, more intense defibrillation is observed with fewer unaffected fibers than with alkali-treated waste cotton. Notably, only a tiny portion of the total cotton waste fraction was approved through a 1-micron membrane filter, and the amount was nearly the same for cotton waste and OCW. The fractionation work indicated that only a tiny portion of the processed cotton fell within the size range of OCW. Figs. 6a-f depicts the structural differences between CW and OCW [35].

In Fig. 7b, alkali pretreatment induces crystal transformation, reducing crystallinity and resulting in volume variations for cotton waste, compared with CW in Figs. 7c, e, and f as presented in the lecture [36]. The images show cotton waste entangled to form bundle-like structures with smooth surfaces and straight shapes. Conversely, in Fig. 7c, the surfaces of OCW with different carboxylate contents appear coarser than that of waste cotton, with a few cracks visible on the cotton surface. Also, the roughness of the cotton surface increases with higher CC [37]. This phenomenon is likely caused by etching from the oxidant, as observed in the images. Fig. 7 also illustrates that hydrogen peroxide can penetrate the entire waste cotton, ensuring the oxidation reaction occurs within the cotton. Consequently, the partial dissolution of OCW in water generates cavities within the cotton structure [38].

This observation indicates the effectiveness of H_2O_2 in facilitating the oxidation process throughout the cotton waste. Energy-dispersive X-ray (EDX) analysis was used to verify the purity of the prepared composite samples. The samples consisted of C and O elements, as seen in Fig. 8a. Furthermore, no impurity peaks are visible, indicating that the sample is pure [39].

Fig. 8b demonstrates the TGA of the CW. TGA was used to inspect the weight loss and thermal stability of the examples as the temperature increased to 200 °C. A 5.75% initial weight loss was observed, which was attributed to the evaporation of volatile materials contained in the moisture and CW. After the prepared sample was heated from 285 to 380 °C, a significant 78% weight loss occurred. Generally, when compared to the published investigation, the prepared oxidized cotton waste exhibited moderately similar thermal characteristics [40].

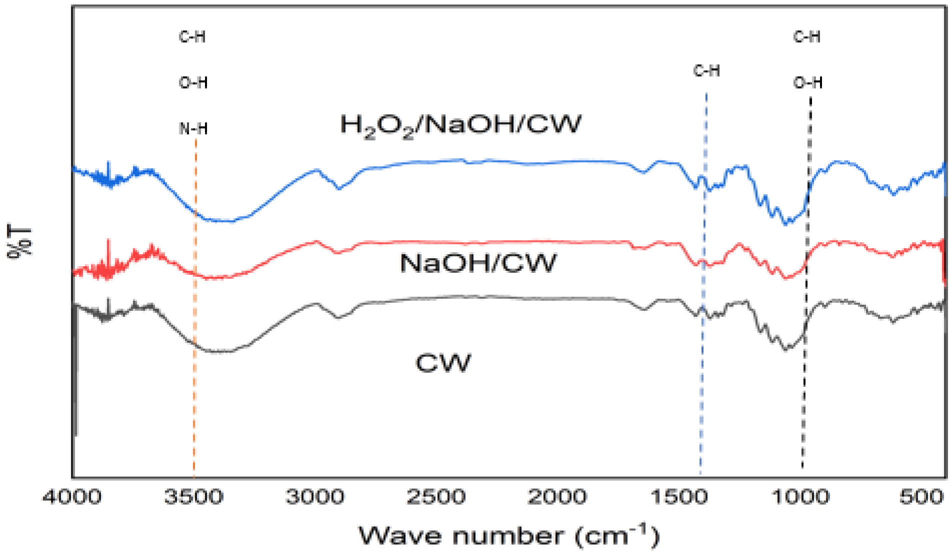


Fig. 5. FTIR of CW and composites

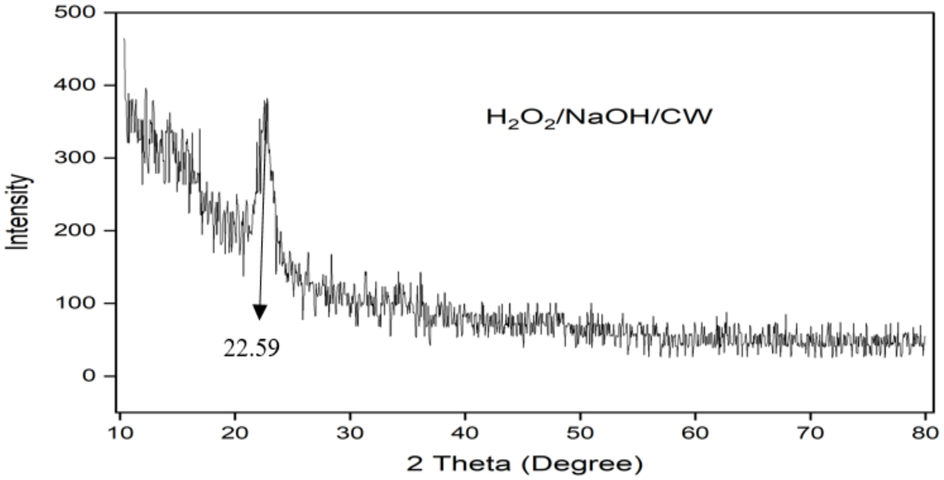
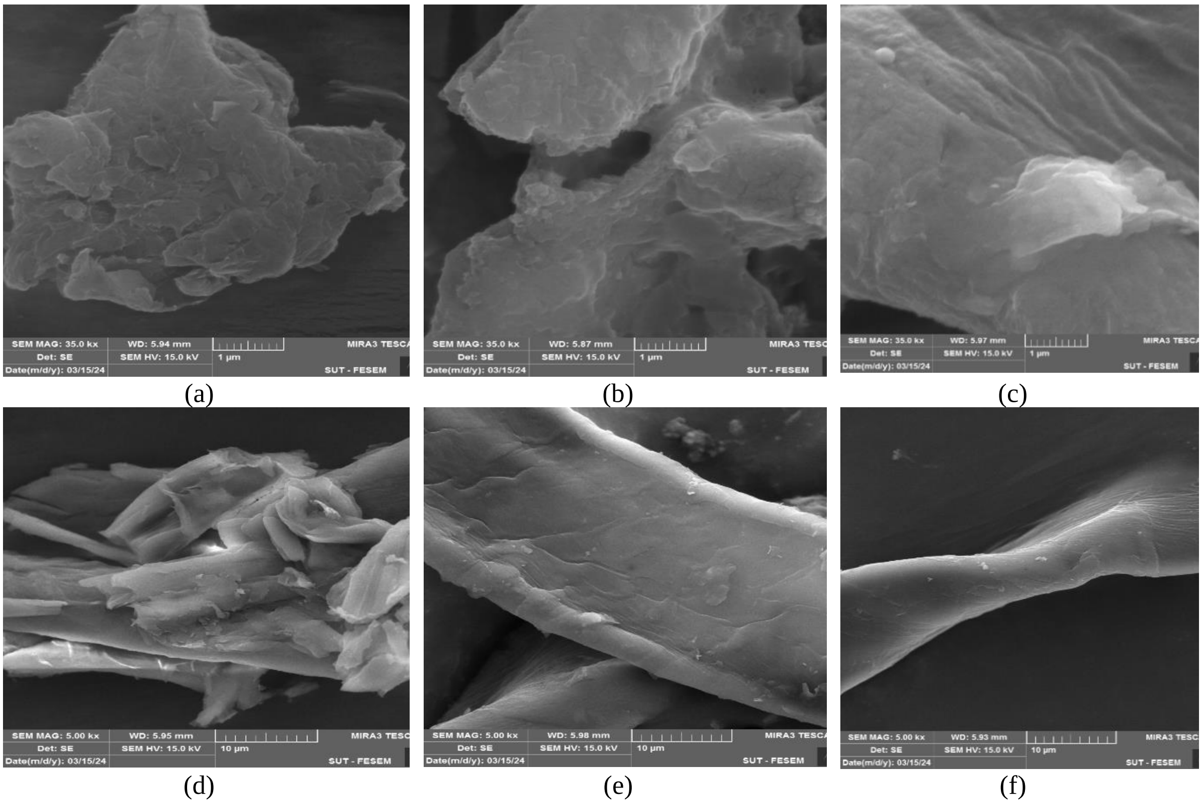


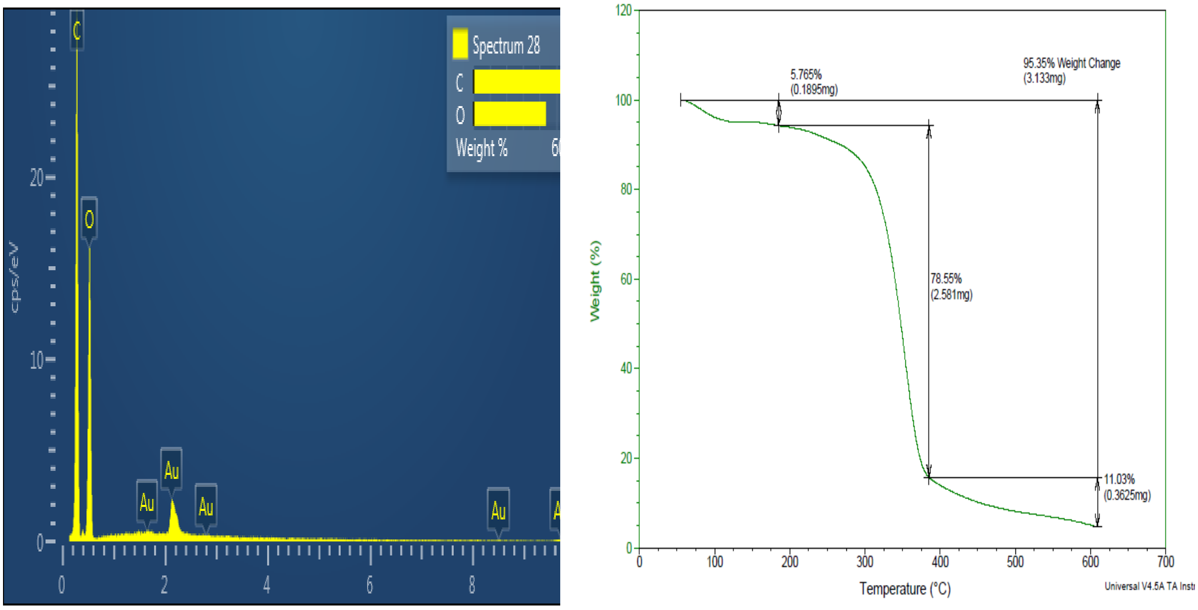
Fig. 6. XRD analysis for H_2O_2/NaOH/CW



(a) (b) (c)

(d) (e) (f)

Fig. 7. FE SEM photographs of (a) cotton waste at 10 µm, (b) Alkali CW at 10 µm, (c) OCW at 10 µm, (d) cotton waste at 1 µm, (e) Alkali CW at 1 µm, and (f) OCW at 1µm



(a) (b)

Fig. 8. H_2O_2/NaOH/CW analysis of (a) EDX and (b) TGA

Modeling of Adsorption/Photodegradation

Various parameters, including time, pH, dose, temperature, and the use of UV lamps, during the oxidation of cotton waste, influence the recovery of organic matter through functional oxidation. This is illustrated in the following equations for CW, NaOH/CW, and H_2O_2/NaOH/CW, respectively.

$$Y_{CW} = 8.9 + 0.109 X_1 + 4.96 X_2 + 5.2 X_3 - 0.026 X_4 - 2.22 X_5 - 0.000334 X_1^2 - 0.326 X_2^2 - 1.21 X_3^2 + 0.00023 X_4^2 + 0.108 X_5^2 - 0.0019 X_1X_2 - 0.0267 X_1X_3 + 0.00115 X_1X_4 + 0.0007 X_1X_5 + 0.35 X_2X_3 - 0.0170 X_2X_4 + 0.269 X_2X_5 + 0.084 X_3X_4 + 0.38 X_3X_5 + 0.0281 X_4X_5 \quad (3)$$

$$Y_{NaOH/CW} = 14.1 + 0.063 X_1 + 5.13 X_2 + 41.5 X_3 + 0.370 X_4 + 0.14X_5 - 0.352 X_2^2 - 9.51 X_3^2 - 0.00182 X_4^2 + 0.041 X_5^2 + 0.0057X_1X_2 - 0.029 X_1X_3 + 0.00106 X_1X_4 - 0.0009 X_1X_5 + 0.22 X_2X_3 - 0.0229 X_2X_4 + 0.275 X_2X_5 - 0.147 X_3X_4 - 1.23 X_3X_5 + 0.0332 X_4X_5 \quad (4)$$

$$Y_{H2O2/NaOH/CW} = 12.8 + 0.020 X_1 + 4.17 X_2 + 38.6 X_3 + 0.356 X_4 - 0.47 X_5 + 0.000031 X_1^2 - 0.342 X_2^2 - 8.58 X^2 - 0.00183 X_4^2 + 0.116 X_5^2 + 0.0080 X_1X_2 - 0.022 X_1X_3 + 0.00118 X_1X_4 - 0.0043 X_1X_5 + 0.53 X_2X_3 - 0.0198 X_2X_4 + 0.329 X_2X_5 - 0.148 X_3X_4 - 1.35 X_3X_5 + 0.0329 X_4X_5 \quad (5)$$

where X_1 is the oxidation time, X_2 is the pH, X_3 is the dose, X_4 is the temperature, and X_5 is the UV Lamps.

As shown in Fig. 9, the main belonging plots demonstrate the perfect set of vital limits for attaining the obligatory oxidation presentation for OCW. The best set of parameters for a given adsorption and photodegradation presentation is shown in each plot [19].

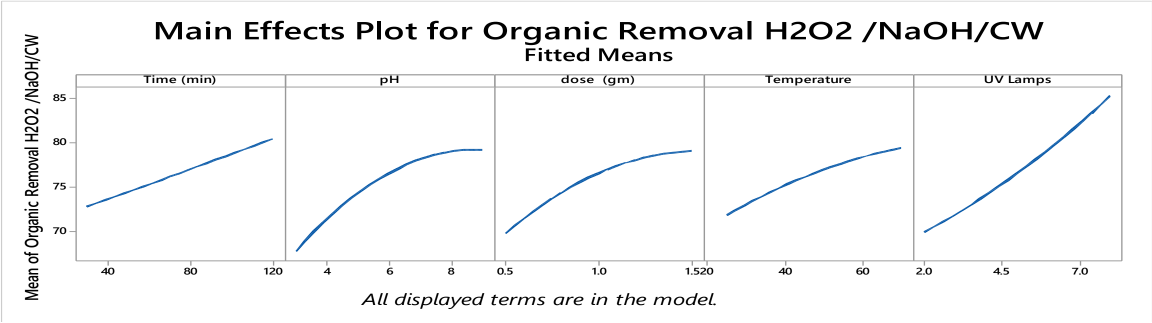


Fig. 9. Main effects plot for organic removal

The consequences exposed in Fig. 10, for all oil pollutants with OCW values, show that the efficiency of the removal response recovers with time throughout the reaction. In these circumstances, the reaction material's incomplete surface area tends to cause a drop at a specific spot, making it more challenging to achieve a moderately high elimination ratio [41].

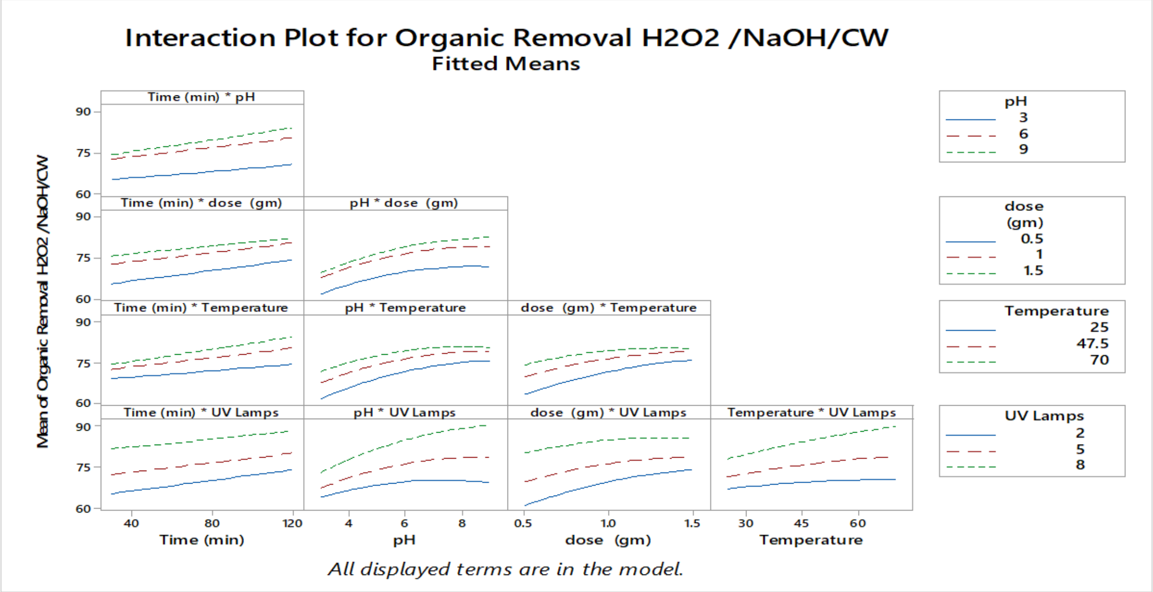


Fig. 10. Interaction plot of parameters

The Adsorption and Photodegradation

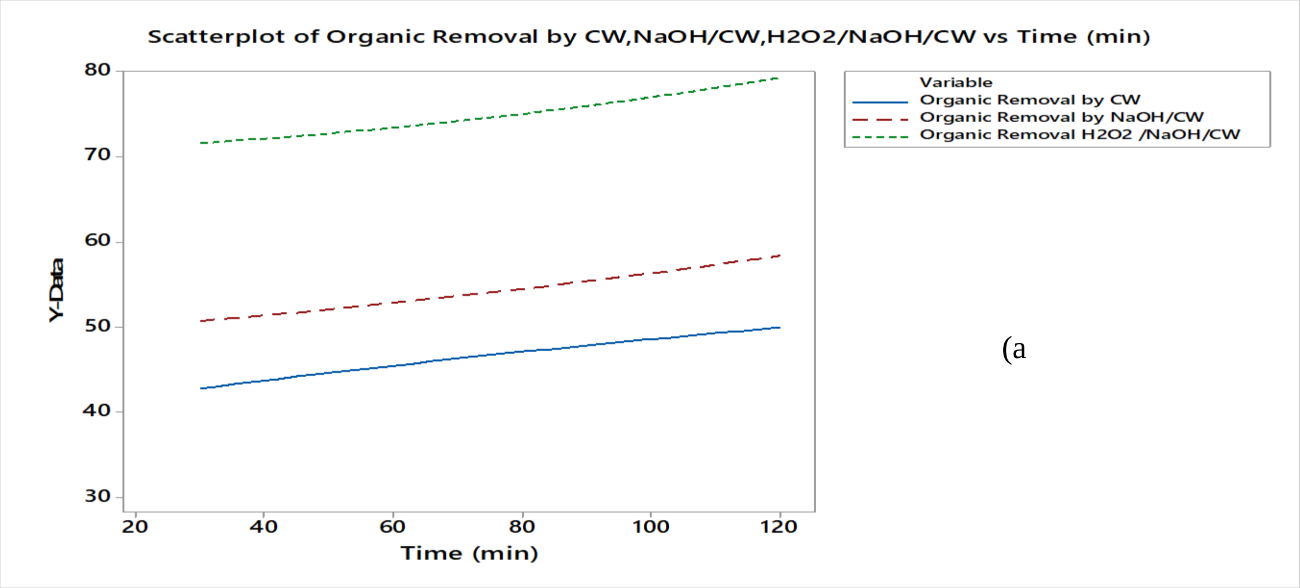
To determine how the oxidation time variable affected the adsorption and oxidation treatment, as well as its effectiveness in removing organic pollutants from RWW, a purposeful analysis of the variable was conducted. For this work, other variables were kept constant. Based on photo-oxidation principles, the formation of free radicals with high oxidizing capacity occurs during the process. These free radicals oxidize the organic pollutants, leading to the breakdown of ions within a short time [42]. Fig. 11a illustrates the relationship between organic removal efficiency and time (adsorption and oxidation) throughout the combined process. Experiments were conducted to determine the optimal time for achieving maximum adsorption and oxidation efficiency in removing organic matter from wastewater. With increased time, the elimination efficiency is enhanced [43].

An upsurge in organic removal has been linked to the oxidation of pollutant material by free radicals. The consequences were in line with another study that found spreading the oxidation period to the recovery process competence, as reported by [44]. The pH in adsorption and oxidation systems is a crucial factor influencing the uptake of organic pollutants, as it controls the surface charge of solid particles, the types of potentially determining ions, and the extent of ionization and speciation of the adsorbed species [45]. Utilizing a pH range of 3 to 9 and a contact time of 120 min, all trials were conducted to inspect the influence of pH on the adsorption of organic pollutants by CW using H_2O_2 and NaOH. The highest adsorption and oxidation competencies for 46.9.3, 57.9, and 77.8% at pH 9 for CW, NaOH/CW, and OCW were corresponding, as shown in Fig. 11b [46].

Fig. 11c demonstrates that the quantity of organic oxidation upsurges rapidly with the dose of CW [47], the removal efficiency has increased with the total amount of adsorbent, and that is enhanced adsorption and oxidation treatment (47.1, 56.8, and 76.3 % for CW, NaOH/CW, and H_2O_2/NaOH/CW, respectively). A higher amount of adsorbent increases the probability of solid particle collision and, thus, particle aggregation. As the number of particles increases, the adsorption effectiveness improves. This is because of the increased surface area for adsorption [48].

The temperature of the reaction is another crucial limit that significantly influences the degradation process. This study employed different temperatures, ranging from 25 to 70 °C, while maintaining the amounts of reagents. Fig. 11d illustrates the removal efficiency of organic pollutants for experiments conducted at various temperatures. The influence of temperature on the removal efficiency is evident as a positive effect on wastewater treatment. The removal rate increases significantly as the temperature rises from 25 to 70 °C. For instance, at 25 °C, the removal efficiency is 41.2%, 51.5%, and 71% for CW, NaOH/CW, and H_2O_2/NaOH/CW, respectively. However, at 70 °C, the removal efficiency increases to 48.5%, 58.6%, and 78% for the same treatments, representing the enhanced efficiency at higher temperatures. This positive correlation between temperature and removal efficiency can be attributed to the faster reaction rates at high temperatures [49]. The increase in temperature promotes the oxidation process, leading to higher levels of oxidized group content. However, it is crucial to maintain the temperature within certain appropriate limits to prevent excessive damage to the cotton structure and to achieve optimal cotton waste efficiency [50].

The last limiting factor controlling the rate of the oxidation process is the intensity of light exposure. To investigate the impact of UV light on the effectiveness of cotton waste oxidation to remove organic pollutants from wastewater, each with an intensity of 0.5 mW/cm² and a wavelength of 365 nm [51]. Different configurations of UV lamps (2, 4, and 8) were tested in the batch oxidation process to assess their influence on the organic elimination efficiency of waste cotton, NaOH-treated cotton waste, and H2O2-treated cotton waste, while keeping all other parameters and quantities constant. Fig. 11e presents the results of the number of lamps on the organic efficiency targeting wastewater. The results indicate that the efficiency was enhanced with an increasing number of cumulative UV-A lamps, ranging from one to three. This observation is consistent with previous findings [47].


Scatterplot of Organic Removal by CW,NaOH/CW,H2O2/NaOH/CW vs Time (min)
Y-Data
80
70
60
50
40
30
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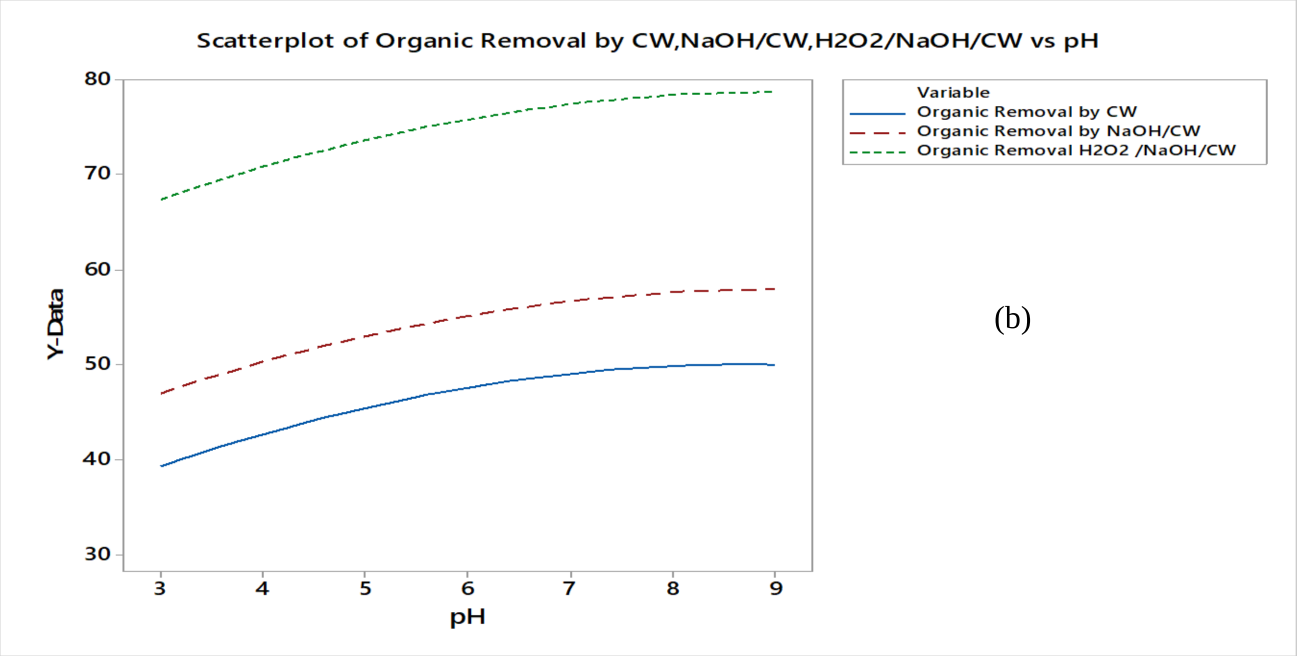
Organic Removal by CW
Organic Removal by NaOH/CW
Organic Removal H2O2 /NaOH/CW

(a


Scatterplot of Organic Removal by CW,NaOH/CW,H2O2/NaOH/CW vs pH
Y-Data
80
70
60
50
40
30
3
4
5
6
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8
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pH
Variable
Organic Removal by CW
Organic Removal by NaOH/CW
Organic Removal H2O2 /NaOH/CW

(b)

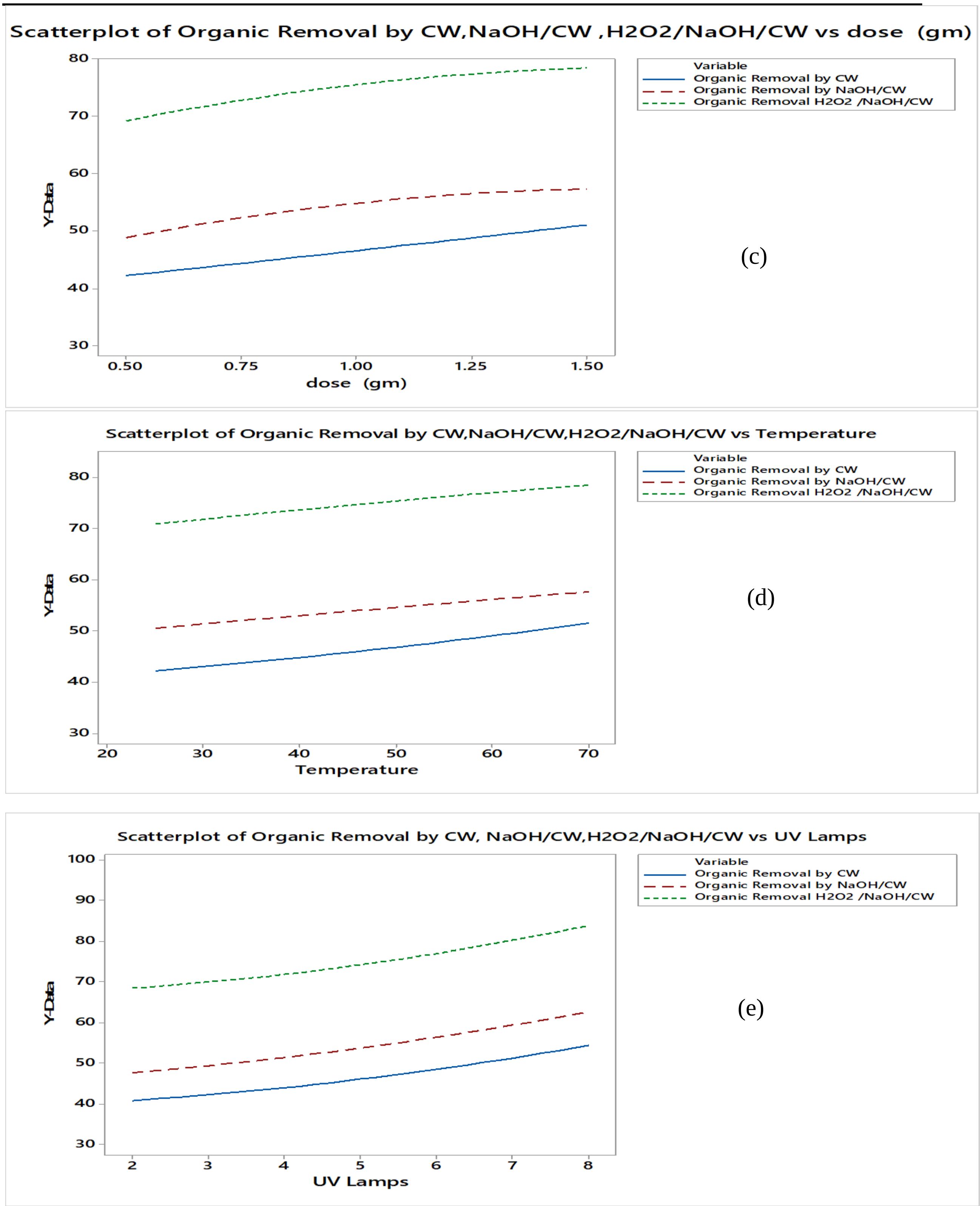

Fig. 11. Effect of the working parameters on organic removal (a) time, (b) pH, (c) dose, (d) temperature, and (e) UV light

Optimization of Operational Parameters

The optimal working limits, including the prepared oxide dose, pH, irradiation time, temperature, and UV lamps, are determined under ideal experimental conditions, focusing on the cotton waste and prepared oxide material. Fig. 12 illustrates the optimal organic removal using Minitab software. When associated with similar studies in Table 2, the present work is compared with those studies.

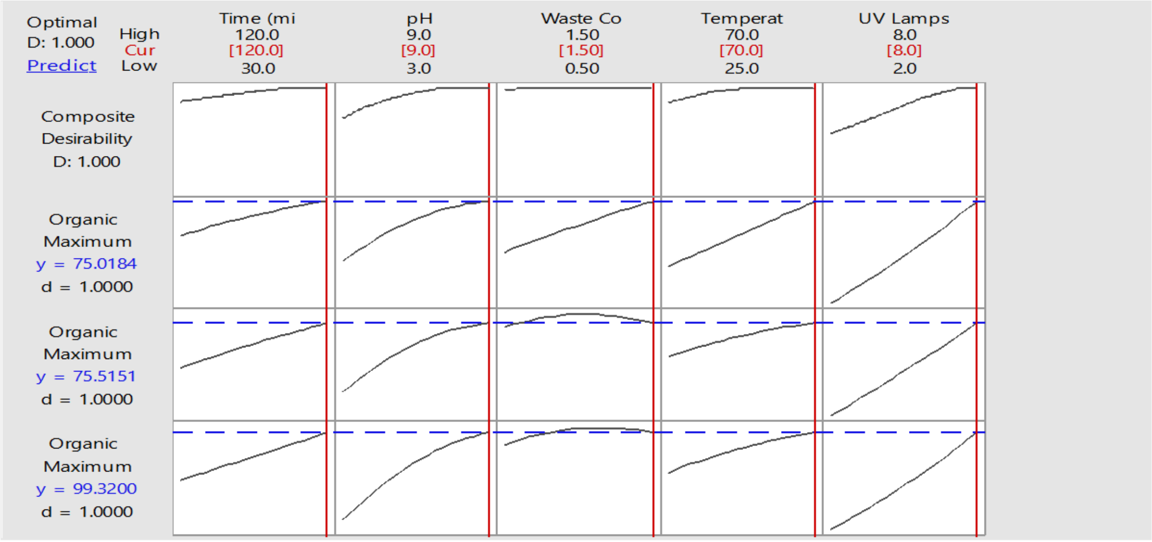

Fig. 12. Finest employed variables on refinery wastewater

Table 2. Comparison of the current study with other described studies

Photocatalyst	Organic Pollutants	Irradiation Type	Time (min)	Degradation Efficiency	Ref.
ZnO, TiO_2 and Al_2O_3	Organic pollutants	Solar	120	95.2 % and 92.11%, 80.7% for ZnO, TiO_2 and Al_2O_3	[52]
TiO_2/ bentonite	Hydrocarbons	UV	120	93%	[53]
ZnO/Cellulose Acetate	Dyes	UV	20	75%	[54]
H_2O_2/NaOH/CW	Organic pollutants	UV	120	96.3%	This work

Kinetic Model for Oxidation

The effect of H_2O_2 addition on the photodegradation of organic pollutants over NaOH/CW. The adsorbent was investigated under specific conditions: a 1-gm dose, a 50-min reaction time, and a pH of 7. The results showed that as agent concentrations increased, more free radicals were formed, which facilitated the reaction of organic pollutants and accelerated oxidation. Nonetheless, there was a slight increase in organic oxidation, rising from 94.5% to 96.3%, when the hydrogen peroxide concentration was increased from 7% to 9%. Considering cost-effectiveness, the 7% H_2O_2 was deemed suitable for further study [55]. The first-order model is expressed as:

$$\ln\left[\frac{C_O}{C}\right] = K_1 t \tag{6}$$

where C_O and C_t are the initial concentration of organic mg/l (before and after treatment), t is time in minutes, and K_1 is the first-order rate constant (min^{-1}).

The best correlation between oxidation time and the left side of Eq. 6 was observed in the kinetics investigation for OCW, as shown in Fig. 13. This suggests a pseudo-first-order kinetic model. When the agent concentration was kept at 7%, the prepared oxide showed a first-order degradation coefficient (k_1) value of 0.077 min^{-1}.

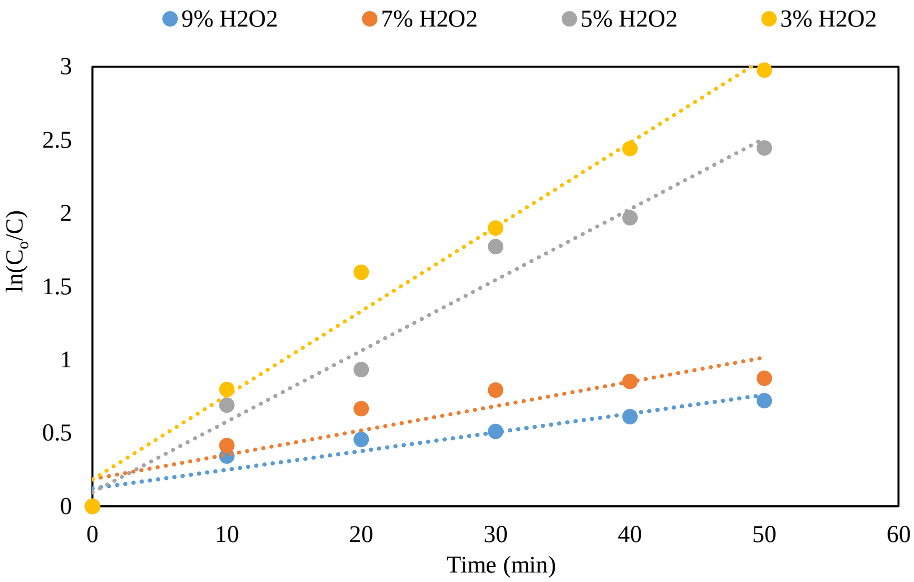

Fig. 13. Plot of –ln (C/Co) vs. time for the organic photodegradation

Conclusion

The oxidation competence is notably enhanced by pretreating cotton waste with NaOH solution, which increases its accessibility to the oxidizing agents. Optimized reaction conditions were determined to achieve high CC in OCW through a green and convenient method involving NaOH pretreatment followed by H_2O_2/UV oxidation. This approach can also change usual carbohydrates into furfural and other soluble organic compounds using the H_2O_2 oxidant system. The study demonstrates high removal efficiencies when employing H_2O_2/NaOH/CW for organic removal in RWW across all dosages. Even at lower dosages, H_2O_2/NaOH/CW exhibits superior removal efficiencies compared to NaOH/CW and CW alone, with efficiencies increasing to 96.3%, 73.1%, and 64.8%, respectively, at higher dosages. Furthermore, the oxidation pretreatment results in an OCW product containing a higher proportion of small, well-fibrillated particles, as evidenced through fractionation and scanning electron microscopy analysis, compared to alkali and other pretreatment methods studied. This indicates the effectiveness of the proposed method in producing OCW with desirable characteristics for various applications.

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