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ORIGINAL PAPER

Treatment of embroidery wastewater containing poly(vinyl alcohol) by electrooxidation process

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Abstract

Embroidery industry wastewater contains high levels of polyvinyl alcohol (PVA), making it resistant to biodegradation and conventional treatment methods such as coagulation and adsorption. Chemical oxidation processes have been successfully used to treat PVA-containing effluents, but the high chemical demand raises significant environmental and sustainability concerns. Recent studies are focused on finding innovative and efficient chemical approaches to effectively treat PVA-containing effluents. This work used an electrooxidation process (EO) with boron-doped diamond electrodes to treat wastewater containing PVA for the first time in the literature. The effects of pH (2.0–8.0), temperature (25–45 °C), current (3.0–6.0 A), electrolyte concentration (NaCl of 3.0–8.0 g/L), and oxidation time (0–6000 min) on the removal of total organic Carbon (TOC) were investigated. The pollutant removal mechanism of the process was elucidated using high-performance size exclusion chromatography, Fourier-transform infrared, Ultraviolet–visible, and Fluorescence Spectroscopy methods. The results showed that TOC concentrations significantly dropped from 6584 to 159.10 mg/L after 10 h of treatment at 6.0 A, pH 5.01, and 25, with an estimated 97.6% removal efficiency. Characterization studies showed that much of the wastewater's PVA is broken down, and the halogens are bound to the degraded part of the polymer. The raw wastewater used contained a wide range of pollutants (10^3–10^{10} Da). The results showed that the pollutants in the wastewater were successfully removed by EO irrespective of the molecular size. These results demonstrate the superiority of EO over treatment techniques that exhibit selectivity for pollutants with different molecular weights.

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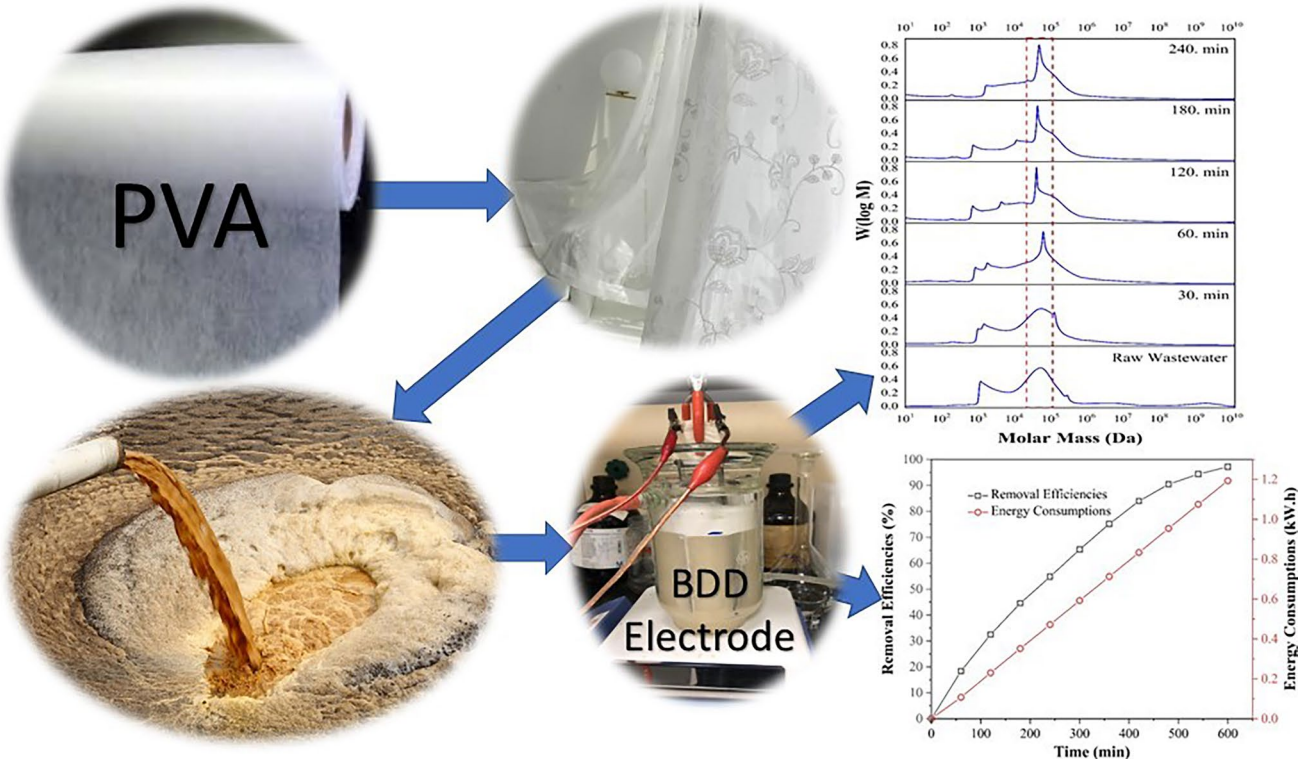
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Graphical abstract



Keywords Poly(vinyl alcohol) wastewater · Electrooxidation · Boron doped diamond electrode

Introduction

Approximately 930 kilotons of poly(vinyl) alcohol (PVA) are manufactured annually in more than 20 countries worldwide (Zhu and Ge 2021). This quantity is used in manufacturing a broad array of items across many sectors. It is employed as a thickening or coating agent in the paper and food industries and in paints, glues, meat packing, and pharmaceuticals. PVA is also commonly used as a protective film for laundry and dish detergents, as well as a sizing and finishing agent in the textile industry (Rolsky and Kelkar 2021).

Embroidery is the art of creating decorative designs on fabric, leather, or paper. It is also known as chemical or Schiffli lace. In this lace-making method, a pattern is formed on a sacrificial fabric. The sacrificial fabric, usually PVA, is then chemically dissolved. When PVA is selected as the sacrificial fabric, the chemical solvent is water, resulting in the production of a large volume of wastewater. Due to a variety of operations in the embroidery textile industry (finishing, bleaching, mercerization, etc.), the wastewater produced contains significant amounts of organic and colorful substances, including PVA.

PVA is non-biodegradable and cannot be broken down by natural processes. Therefore, the discharge of effluents containing PVA into aquatic ecosystems will result in a its gradual buildup in our water bodies. Although PVA is generally considered non-toxic, some studies suggest that it can have adverse effects on aquatic systems and organisms, especially at high concentrations (Dong et al. 2019; Yan et al. 2020). If not treated with a high-efficiency removal method, PVA forms a massive foam layer on the surface of the aquatic ecosystems where it is released. The foam layer hinders the penetration of sunlight in the aquatic environment and thus affects the photosynthetic process. Consequently, the oxygen concentration in the water decreases, and anaerobic conditions occur. Furthermore, the hydrophilicity property of PVA has been particularly found to favor heavy metals and antibiotics accumulation in the aquatic environment (Sun et al. 2017; Rolsky and Kelkar 2021). This, along with the widespread production and usage of this chemical across a wide range of industries worldwide, raises serious ecological and environmental concerns. A substantial portion of total global PVA production ends up in the environment, generally in aquatic systems, through industrial wastewater discharges. Yet, its presence in the environment remains largely

under-monitored, making PVA an important environmental problem.

In recent years, the potential of different waste treatment technologies for PVA treatment has been thoroughly researched (Zhang et al. 2011; Hamad et al. 2021). Biological treatment methodologies stand out due to their low cost in comparison to other approaches in wastewater treatment. However, the BOD–COD ratio of PVA is quite low (BOD_5/COD < 1). This implies that conventional biological systems are unable to catalyze the decomposition of PVA since the requisite quantity of oxidation is not present (Hamad et al. 2014; Song et al. 2021). A study found that only about 40% of the PVA was mineralized after a 48-day incubation period in mixed cultures acclimated to PVA solution (Solaro et al. 2000). The 48-day treatment period is rather lengthy and inefficient when 800–1000 m^3 of wastewater is produced daily. During PVA treatment with biological methods, a foam is formed on the equipment, makeing it difficult to obtain operating stability and acceptable treatment efficiencies (Yu et al. 1996; Solaro et al. 2000; Chou et al. 2010). High treatment efficiencies have been obtained with the salting method; however, the process requires high chemical consumption (Zimmermann and Schindler 1979). Furthermore, PVA is neutrally charged and highly hydrophilic with a high concentration of –OH groups. The neutral charge of this polymer particularly renders it irresponsive to treatment by coagulation (Pan et al. 2020).

Advanced oxidation processes (AOPs) have demonstrated great prospects in treating PVA-containing wastewaters and improving their biodegradability (Sun et al. 2012). Some of the widely encountered AOPs are the wet oxidation process (Zhang et al. 2021), the Fenton process (Zhu and Ge 2021), a persulfate-Fe system (Oh et al. 2009), Peroxymonosulfate (Zhai et al. 2021), and the use of ionizing radiation (Sun et al. 2015). These have collectively surfaced as cutting-edge technologies that rely on the generation of reactive substances, including hydroxyl radicals, hydroperoxyl radicals, superoxide radicals, and sulfate radicals. These potent reactive species play a pivotal role in dismantling organic pollutants through degradation. However, further research on the treatment of PVA-containing wastewater with AOPs is needed due to some limitations and gaps in the literature. For instance, the Fenton method alone cannot be used to effectively mineralize high concentrations of PVA; it is particularly promising at pretreatment. During the Fenton process, the long-chain PVA molecules break up and the abundant hydroxyl groups are partially oxidized to COOH or –C=O groups. This enhances the biodegradability of the wastewater or, through the charged groups, makes it responsive to coagulation (Guo et al. 2016; Pan et al. 2020).

Finding ways to treat PVA-containing wastewater with minimal chemical and energy use are of great interest to the scientific community (Pan et al. 2020). The electrooxidation (EO) process has promising possibilies owing to its ability to completely mineralizes pollutants in a short oxidation time with little chemical demand. The EO process achieves the treatment of the pollutants through indirect and direct oxidation pathways. In indirect oxidation, oxidizing reagents such as chlorine, hypochlorous acid, hypochlorite, hydrogen peroxide, and ozone are formed on the electrode surface and oxidize pollutants. On the other hand, electron transfer from the anode surface to pollutants and/or the formation of hydroxyl radicals is possible during direct oxidation (Wu et al. 2014; Särkkä et al. 2015). The chosen electrode is an important factor that determines the success of electrooxidation. A wide variety of anode electrodes have been used in both direct and indirect oxidation, but Ti/IrO_2-RuO_2, SnO_2, PbO_2, and boron-doped diamond (BDD) electrodes have come to the fore with their high efficiencies (Panizza and Cerisola 2001; Prabhakaran et al. 2009; Soni et al. 2020; Arslan et al. 2023; Chaabene et al. 2022; Yao et al. 2022).

Since the BDD electrode is an inactive anode, it is very effective in the treatment of wastewater. The formation of hydroxyl radicals, one of the highest oxidizing reagents, on the BDD surface has been reported as the main removal mechanism (Özcan et al. 2008; Prabhakaran et al. 2009; Brycht et al. 2016; Soni et al. 2020; Arslan et al. 2023; Chaabene et al. 2022; Yao et al. 2022). BDD has an inert surface, and this inert surface causes low physisorption of hydroxyl radicals. Complete mineralization of pollutants in wastewater can be achieved due to these physisorbed hydroxyl radicals (Reaction 1 and 2, R: organic pollutants in wastewater) (Scialdone 2009; Sires et al. 2014).

$$M + H_2O \rightarrow M(HO^{\cdot}) + H^+ + e^- \quad (1)$$

$$M(HO^{\cdot}) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \quad (2)$$

In this study, the electrooxidation method was employed to reduce pollutants from wastewater discharged by the embroidery industry to acceptability limits. Based on the existing literature, this is the first study on the electrooxidation treatment of embroidery wastewater. To do this, PVA-containing wastewater was obtained from a textile company in Turkey in 2022 and tested using BDD electrodes. The optimal pH, temperature, current, electrolyte concentration, and operating duration in the electrooxidation process were determined for this purpose.

Materials and methods

The experimental set-up

The wastewater was obtained at the entrance of an embroidery plant treatment system. The temperature, pH,

conductivity, turbidity, and TOC of the sample wastewater were measured to be 60 °C, 4.76, 804 µS/cm, 46.9 NTU, and 6584 mg/L, respectively. In the initial trials of the study, the conductivity was increased by adding NaCl because the initial conductivity of the raw sample was relatively low. In addition, the effects of temperature on the EO process was investigated due to the high temperature of the raw wastewater from the production process.

In the EO process, experiments were carried out in a double-walled reactor with a volume of 600 mL. A 15 cm × 6 cm × 0.2 cm BDD by DiaCCon GmbH was used as the anode, and a stainless-steel plate as the cathode. For each sample volume of 500 mL, the active surface area of a single plate was 60 cm^2. The electrodes were placed vertically and parallel to each other, and the distance between the plates was fixed at 2 cm. The electrodes were connected to a digital DC power supply (Agilent 6675A model; 30 V, 6 A) that operated in galvanostatic mode, and the current was held constant at desired value for each run. During the treatment, 3 samples of 1 mL were taken from the reaction media at regular intervals. The electrical energy consumption (ENC, kWh) of the EO process was calculated with Eq. 3:

$$ENC = U \times i \times t_{EC} \tag{3}$$

where U is cell voltage (V), I is current (A), and t is operating time (s) (Palahouane et al. 2015).

Analytical methods and characterization

TOC levels were determined by combustion of the samples at 680 °C using a non-dispersive IR source (Shimadzu, TOC-L model) (Gengec et al. 2018; Karatas et al. 2022).

A Hach 2100Q turbidimeter was used for measuring the turbidity, a Varian Agilent Cary Clipce instrument for obtaining fluorescence spectra, and a PG Instruments T80 + UV/VIS spectrophotometer for the UV/VIS spectrum. The FT-IR analysis was used to measure sample spectrum. The Fourier Transform Infrared (FT-IR) method is an analysis method used to analyze vibrations that occur in the chemical bonds of matter. FT-IR allows infrared light to be passed through a sample to obtain the absorption spectrum in the infrared region of the sample. Fourier transforms infrared (FTIR) spectrum of the wastewater was recorded in the range 4000–650 cm^{-1} on a Bio-Rad FTS 175 C spectrophotometer.

The molecular weight distribution (MWD) of the pollutants in the wastewater was determined using a high-performance liquid chromatography instrument (Hewlett-Packard HPLC 1260 series) with a refractive index detector (RID). In this system, two ultra hydrogel columns [PL aqua gel-OH 30 (100–60,000 MW) and PL aqua gel-OH MIXED-H (6000–10,000,000 MW)] and polysaccharide (Pollulan) standards with different molecular weights (186, 100, 58, 48, 23.7, and 12.2 kDa) were used. Ultrapure water was chosen as the mobile phase and used at a flow rate of 1 mL/min. 100 µL of sample was injected into the system for MWD measurement (Gengec and Kobya 2013; Gengec 2015; Kac et al. 2017).

Experiments and TOC analyses were conducted in triplicates and reported in average terms. The accuracy of the measured TOC values was estimated at around 1.0%. The standard deviations were also calculated and the error bars were plotted.

A one-way analysis of variance (ANOVA) was performed to examine the statistical significance of the data sets. The data analysis was performed using Origin (version 9.6, Originlab) at of 0.05 significance level, meaning the difference between the treatments was deemed significant at a p-value (P) of < 0.05.

Results and discussion

The effect of operational parameters on removal efficiencies

Initial pH effect

A vast body of research demonstrates that pH affects the efficiency of treatment technologies (Gengec et al. 2013; Gengec and Kobya 2013; Gengec 2017; Ergan and Gengec 2020), and the effects vary considerably based on the system and wastewater type.

In chloride-mediated reactions, the pH level plays a crucial role in influencing the oxidation rate due to its effect on the predominant active chloro species present in the effluent. In the process of indirect oxidation, chlorine evolution transpires at the anode (Eq. 4). When the pH value is below 3.3, the primary active chloro species is Cl_2. However, at higher pH values, the diffusion of Cl_2 away from the anode is coupled with its disproportionation reaction, leading to the formation of HClO at pH < 7.5 (Eq. 5), and ClO^- at pH > 7.5 (Eq. 6). In principle, operating under strongly acidic conditions is considered favorable since chlorine is the most potent oxidant, followed by HClO. Nevertheless, the typical system configuration employed in the electrochemical oxidation of wastewater promotes the desorption of chlorine, impeding its effectiveness as an oxidizing agent. Consequently, higher pH values theoretically enhance the electro-oxidation of pollutants, as HClO and ClO^- are relatively unaffected by gas desorption and can function as oxidizing reagents throughout the entirety of the wastewater volume (Anglada 2009).

$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^- \tag{4}$$

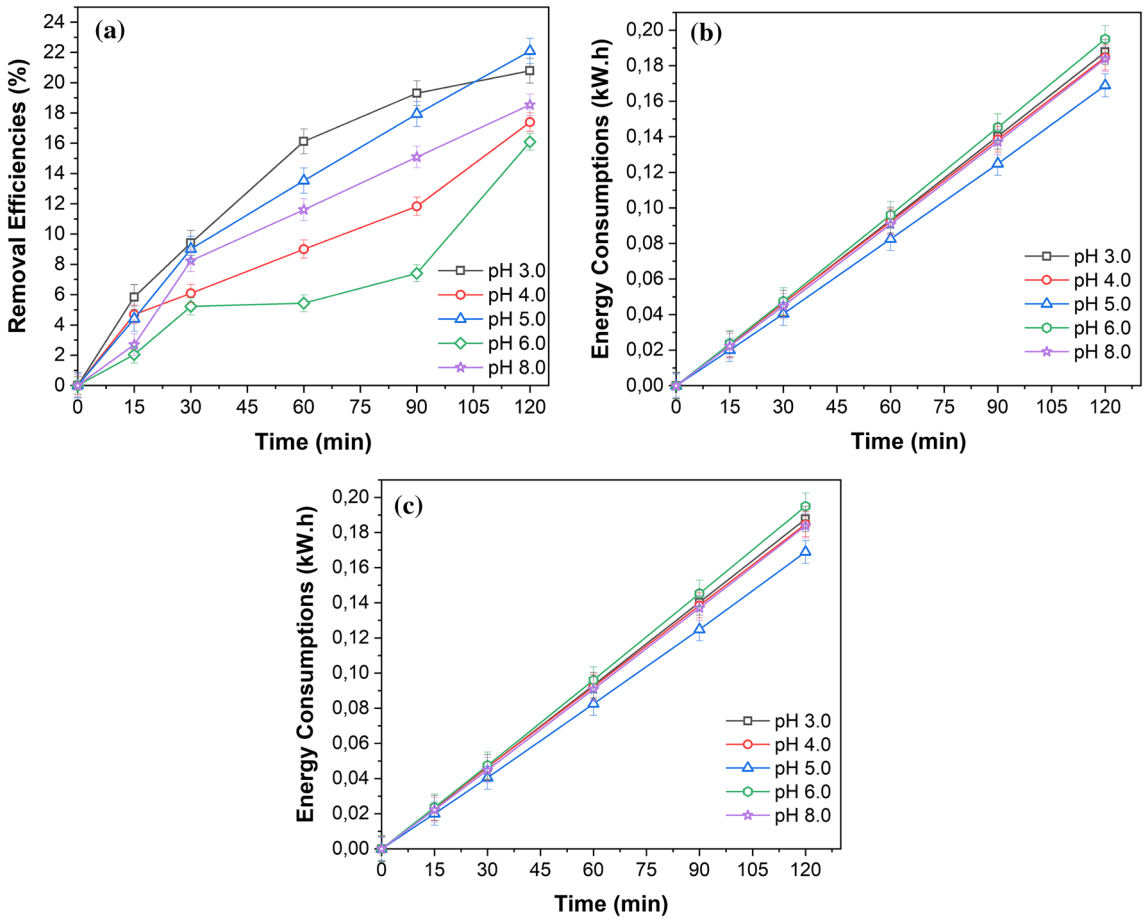


Fig. 1 TOC removal and energy consumption at different initial pHs (25 °C, 3.0 Amper, 120 min, and 3.0 g/L of NaCl)

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (5)$$

$$HOCl \rightarrow OC^- + H^+ \quad (6)$$

For this reason, the effect of pH on treatment efficiency was examined at the beginning of the study. The initial pH of the wastewater was adjusted to between 3.0 and 8.0, and the removal efficiency at 3 A was monitored for 120 min.

Similar to our previous study (Gengec 2017; Can et al. 2019; İskurt et al. 2022), very small differences were observed in the TOC removal efficiency after 120 min at different initial pHs (Fig. 1.). These results showed that the BDD electrode is not pH sensitive and demonstrates superiority over other processes that require pH adjustment (Gengec 2017; Kuchtová et al. 2020). It was observed that TOC value to 5025 mg/L pH 5.0 which is very close to the original pH value of wastewater. Thus, the optimum pH value was selected as pH 5.0. The energy consumption (EC) was also monitored for 120 min during the experiment, the lowest EC value of 0.1699 kWh (Fig. 1b) was obtained at pH 5.0. During the EO process with BDD, it was observed thatthe pH always tended to shift to between 4 and 6, regardless of the starting pH (Fig. 1c).

Initial electrolyte effect

The type and concentration of electrolyte used in the EO process have been found to be important to the color, COD, TOC removal, and current efficiency (Gengec 2017; Zou et al. 2017). NaCl was used as an electrolyte because it shows higher removal efficiency than other electrolytes (He et al. 2016). In the EO process, the removal of pollutants usually occurs with the formation of hydroxyl radicals. At the same time, the presence of catalytic components such as chlorine in wastewater causes the production of active chlorine by electro-generation (Eq. 7, 8). The active chlorine formed plays a role in the disintegration of pollutants, which is referred to as indirect EO (He et al. 2016).

$$Cl^- + H_2O \rightarrow ClO^- + H^+ + e^- \quad (7)$$

$$Organics + ClO^- \rightarrow Intermediates \rightarrow CO_2 + Cl^- + H_2O \quad (8)$$

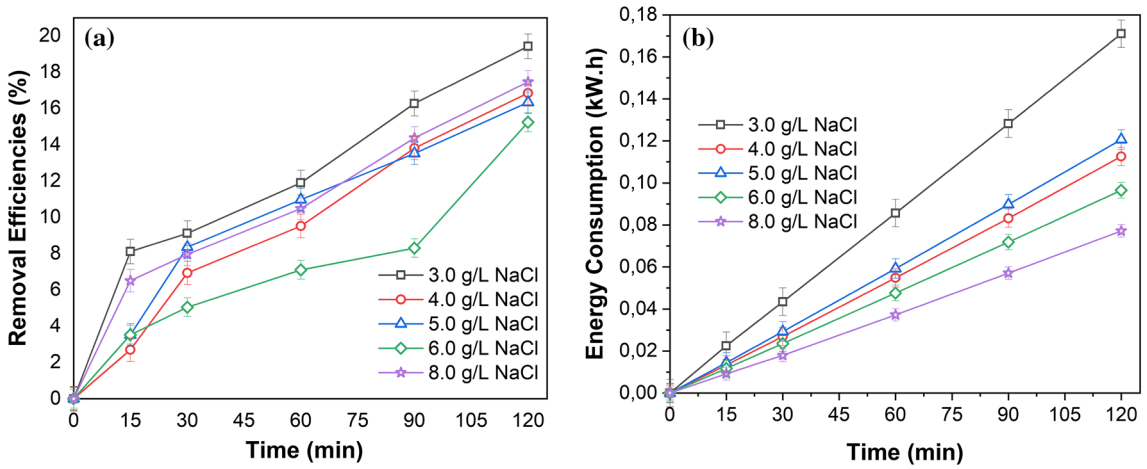


Fig. 2 TOC removal and energy consumption at different electrolyte concentrations (25 °C, 3.0 Amper, 120 min, and pH 5.0)

When the concentration of NaCl electrolyte varied between 3.0 and 8.0 g/L, the lowest TOC value was obtained at 4779 mg/L at a 3.0 g/L NaCl concentration. It was found that increasing the NaCl concentration did not increase the removal efficiency. The addition of electrolytes resulted in a decrease in treatment efficiency, which is attributable to the increased ion concentration. Neto and Andrade (2009) reported similar results. A decrease in oxidation efficiency was observed above 3 g NaCl/L. The study hypothesized that the increase in Cl_2 led to the formation of more oxidizable species (HClO, ClO^-). Also, the formation of chlorate (ClO_3^-) at high current density and high chloride concentration were considered as another possibility (Neto and Andrade 2009). The greatest advantage of electrolyte production is that it reduces energy consumption by increasing wastewater conductivity. In this study, variations in NaCl content of 3.0, 4.0, 5.0, 6.0, and 8.0 g/L resulted in energy consumption variations of 0.17102, 0.11257, 0.12064, 0.09647, and 0.07717 kWh, respectively. Although adding more electrolytes reduces electricity consumption, it increases chemical use and costs excessively without significantly enhancing treatment efficiency (Fig. 2). Therefore, the study continued with a concentration of 3.0 g/L NaCl. In addition, the results in Fig. 2 showed that increase in time has a positive effect on treatment efficiency at all NaCl concentrations.

Initial temperature effect

The influence of temperature on the overall efficiency of the electro-oxidation process has received limited attention in academic research. It is widely recognized that temperature has negligible impact on direct oxidation processes. However, it has been observed that mediated oxidation processes, involving inorganic electrogenerated reagents such as active chlorine and peroxodisulfate, exhibit enhanced performance as temperature rises (Anglada et al. 2009).

Until this stage of the study, the experiments were carried out at 25 °C. Subsequently, temperature effects on pollutant removal efficiency were investigated at constant temperatures of 25 °C, 35 °C, and 45 °C. The experiments were carried out under following conditions: 500 A/m^2 (3.0 A), 3 g/L of NaCl, and initial pH of 5.0. The findings showed that the highest removal efficiency was obtained at 25 °C, with the TOC levelreduced from 6587 to 4777 mg/L, which is approximately 19.48% TOC removal (Fig. 3a). The effect of temperature variation on EC was also investigated and presented in Fig. 3b. The results showed increased in sample conductivity with temperature (Fig. 3b). This can be attributed to the increased in mobility of molecules in the wastewater as temperature rises. The increased in sample conductivity resulted in low energy demand, which explains the decreased energy consumption observed (Fig. 3b). Increasing operating time was found to have a significant positive effect on treatment efficiency (Fig. 3a).

Current effect

One of the most important parameters in EO is current. Previous studies have shown that current has a direct effect on the removal of COD and TOC (Hurwitz et al. 2014; He et al. 2016; Zou et al. 2017; Kuchtová et al. 2020). The effect of currents of 3.0 A (500 A/m^2), 4.5 A (750 A/m^2), and 6.0 A (1000 A/m^2) on efficacy of EO was studied at a constant temperature of 25 °C. The TOC levels after the experiment were measured to be 4782 mg/L at 3.0 A, 4610 mg/L at 4.5 A, and 3867 mg/L at 6.0 A, with lowest TOC level recorded at the highest current (Fig. 4a). Treatment time was found to have a significant effect on the removal efficiency at all currents. The energy consumptions were calculated as

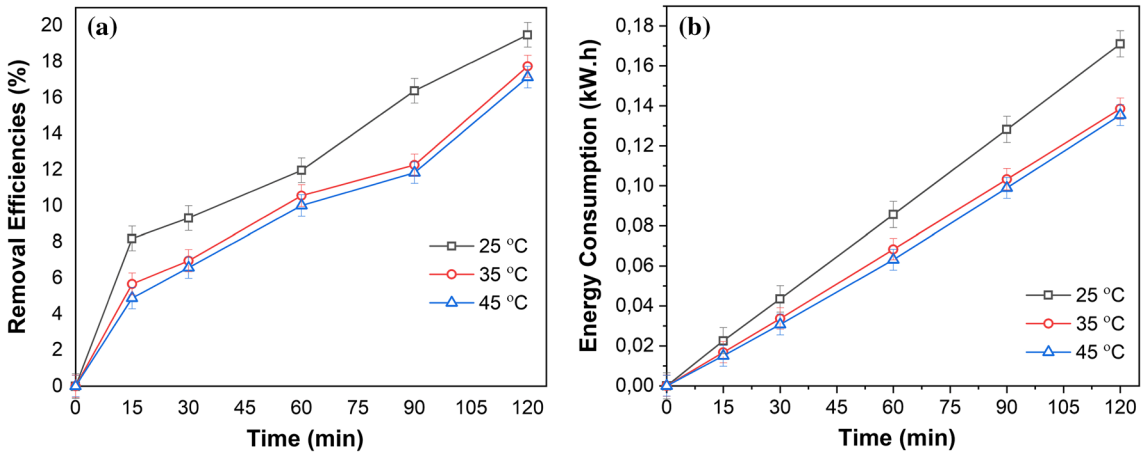


Fig. 3 TOC removal and energy consumption at different temperatures and operational times (pH 5.0, 3.0 Amper, 120 min, and 3.0 g/L of NaCl)

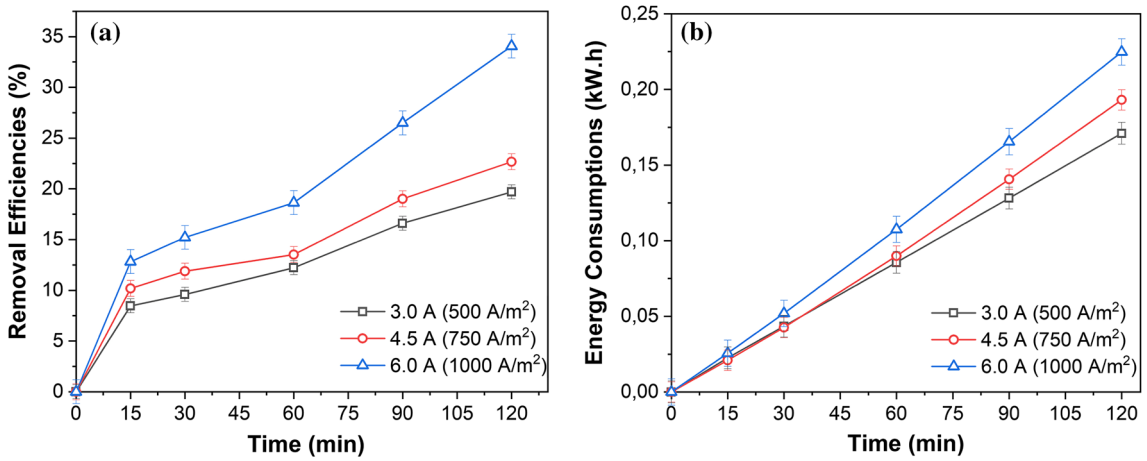


Fig. 4 TOC removal and energy consumption at different currents (25 °C, pH 5.0, 120 min, and 3.0 g/L of NaCl)

0.17102, 0.19308, and 0.22475 kWh for 3.0, 4.5, and 6.0 A, respectively. The increase in energy consumption with current was determined to be nonlinear.

The effect of time

The analysis of the effect of time on TOC removal efficiency revealed a positive relationship between time and TOC removal, with increased time leading to increased TOC removal. This trend was observed throughout the other experiments conducted in this study. Therefore, it was decided to experiment with 6.0 A (1000 A/m^2), 3.0 g/L NaCl, and an initial pH of 5.0 for 600 min. The results were indicated in Fig. 5.

It was observed that the amount of TOC decreased to 159.10 mg/L at the end of 600 min,which was estimated to be 97.2% removal efficiency. After 600 min, the energy

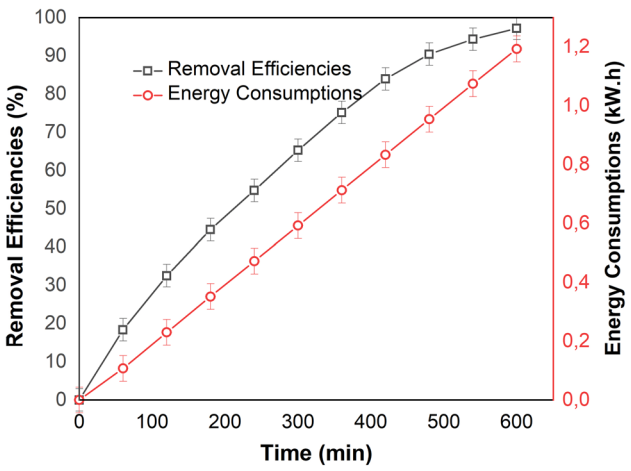


Fig. 5 The effect of time on removal efficiency and energy consumption (25 °C, pH 5.0, 6.0 Amper, and 3.0 g/L of NaCl)

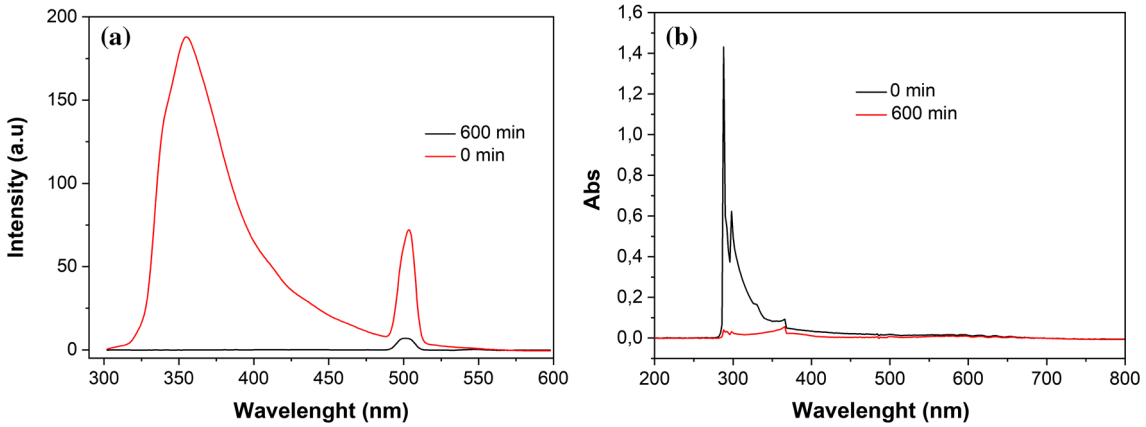


Fig. 6 Fluorescence and UV–Vis spectra of wastewater (25 °C, pH 5.0, 6.0 Amper, and 3.0 g/L of NaCl)

consumption was calculated at 1.193 kWh. The number of electrons transferred in EO systems increased with current and time, consequentiallyincreasing treatment efficiency.

Characterization

Fluorescence spectrophotometer and UV/VIS measurements were carried out in ten times diluted wastewater. As a result of both measurements, a significant decrease in the axis of y during the treatment process was observed (Fig. 6).

The fluorescence spectrum of pure PVA showed fluorescence peaks at 370 nm and 500 nm at room temperature (Fig. 6a). According to the PVA fluorescence data in the literature, it is possible to observe a weak sudden fluorescence peak in the range of 400–510 nm (Mieloszyk et al. 1987; El-Bashir et al. 2017). As shown in Fig. 6a, the peaks thought to belong to the existing PVA after 600 min of EO disappeared, and this supported the characterization results. The UV–Vis results are supported by other characterization data showing that PVA in Embroidery wastewater degrades after the EO process. The absorbance of pure PVA in UV–Vis is between 200 and 400 nm. The maximum absorbance has been observed in the UV region, and a significant absorbance in the Vis region (Gates 1934; Raut and Murhekar 2014; Tan et al. 2016).

Structural analysis of the Embroidery process raw and treated wastewater was performed with the FT-IR spectrum. It was carried out on solid samples obtained by the evaporation of 5 mL aqueous solutions taken from these samples in Petri dishes. FT-IR spectra are given in Fig. 7. The company that produces this wastewater stated that water-soluble interlining is used in embroidery production. The raw material for the interlining is PVA. So, it was determined that PVA made up a large proportion of the pollutants in the wastewater generated. A number of publications have demonstrated that the FT-IR spectrum of the Embroidery process wastewater (0 min) is the same as the pure PVA spectrum (Zhang and Yu 2004; Jipa et al. 2012; Ye et al. 2017). Absorption peaks of wastewater were found at-OH stretching at − 3290 cm^{-1} and low-intensity asymmetric stretching of $–CH_2$ peaks at 2935 cm^{-1} (Zhang and Yu 2004; Liu et al. 2010; Jipa et al. 2012). These two peaks were not seen in the FT-IR spectrum of treated wastewater. This indicates that –H is separated from the –OH group attached to the –CH group in the structure. The bending peak of the 1082 cm^{-1} –OH group is in the form of a large peak that becomes a severe peak at 1091 cm^{-1} after EO known as the –CO stretching peak (Chen et al. 2001; Ye et al. 2017). After the process, the $–CH_2$ peak at 918 cm^{-1} and the C–C tension peak at 830 cm^{-1} disappeared and gave the peak of 1,2 disubstituted –C–H bending structure at 880 cm^{-1}. When we consider both spectra, it was predicted that the high amount of PVA in the embroidery process wastewater is degraded and the possible halogens (peaks at 655–615 cm^{-1}) are attached to the structure where the polymer structure deteriorated. The mechanism of oxidation has been confirmed by many scholars, mainly the free radical oxidation process (Song et al. 2021). The FTIR results of this study also support this conclusion. The mechanism of oxidation was mainly affected and controlled by $HO^{\cdot}$ (Eq. 2) and ClO^{-} (Eq. 8). The PVA in the wastewater was almost completely removed. The infrared characteristic peak of PVA disappeared, showing that $HO^{\cdot}$ and ClO^{-} can break long-chain PVA molecules into short-chain small molecules.

The FT-IR spectrums shown were obtained after evaporation of water and other volatile components at 80 °C. As shown in Fig. 7, after 600 min of EO, the peak at 1100 (1/cm) in the spectrum became sharp, and two additional peaks at 610 and 1400 were observed.

Wastewater consists of pollutants with a wide range of molecular weights, depending on the process by which they are produced and the raw materials used. Monitoring the

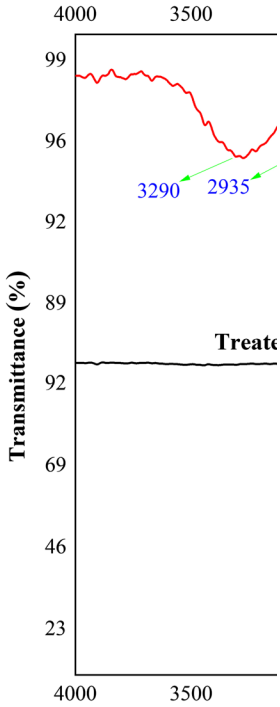


Fig. 7 FT-IR spectrum of the raw and treated wastewater

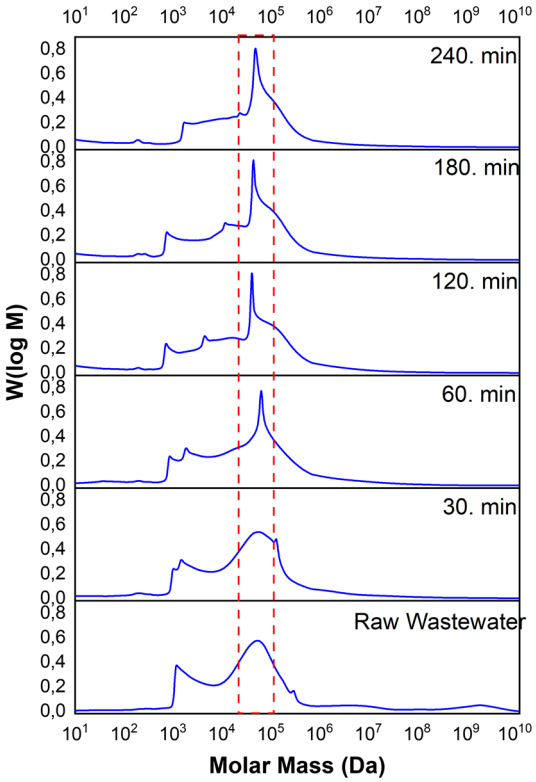


Fig. 8 Molar distribution of wastewater during EO at the optimum treatment conditions

molecular weight distributions of these pollutants provides important information about the treatment mechanism. Polyvinyl alcohol (PVA) is a synthetic polymer derived from the hydrolysis of polyvinyl acetate. It is widely recognized that PVA is a water-soluble polymer with a high molecular weight.

In the literature, there is a limited number of studies that investigate the molecular changes occurring in wastewater containing polyvinyl alcohol (PVA) during oxidation processes. Yan et al. (2020) reported that wastewater containing PVA contains high molecular weight components which break down to smaller molecular weight components through oxidation processes. Hamad et al. (2014) reported similar findings for polyvinyl alcohol degradation in aqueous solution by UV/H_2O_2 process.

For this purpose, molecular weight distributions of pollutants in wastewater were performed using the HPSEC technique. In the HPSEC technique, wastewater is filtered through a 0.45 µm filter paper and loaded into the HPLC device. Therefore, this technique monitors dissolved pollutants in wastewater. Figure 8 depicts the molecular weight distribution of PVA-containing wastewater, which is monitored at regular intervals during the EO process.

As seen in Fig. 8, raw wastewater contains substantial amounts of pollutants (10^3–10^{10} Da). The components from 10^9 to 10^{10} were of low density and immediately reverted to smaller molecular weight components within the first 30 min of the purification process, concomitantly decreasing the amount of pollutants with molecular weights between 10^3 and 10^6. These observations suggest that the EO process is not pollutant-selective in terms of molecular weight. As shown in Fig. 8 (red line), there is an accumulation of pollutants with molecular weights of 10^4 to 10^5 as the treatment time increases. This means that some intermediate species resistant to the EO process are formed from high molecular components. However, TOC results finally showed that the EO process successfully decomposes these intermediate species.

Conclusion

In this study, the treatment of real wastewater from the Embroidery industry with BDD (Boron Doped Diamond) was explored, and NaCl was used to increase the conductivity of the wastewater. The optimal pH, temperature, current, electrolyte concentration, and process time were determined throughout the process. The amount of TOC in the wastewater was successfully decreased from 6584.0 to 159.1 mg/L after 10 h at 6.0 A current, 3.0 g/L NaCl and 25 °C and initial wastewater pH of 5.01.

In addition, the removal mechanism of the process was elucidated by using HPSEC, FT-IR, UV–Vis, and Fluorescence Spectroscopy methods. Characterization studies have

shown that the main pollutant in wastewater is PVA, which was almost completely removed. The main removal mechanism in the EO process is based on the $HO^{\cdot}$ produced at the anode. However, the presence of halogens such as chlorine in the wastewater is a factor that increases the treatment efficiency. The results of characterization show that the mechanism of oxidation is controlled by $HO^{\cdot}$ and ClO^{-}. The FTIR results indicate that a high amount of PVA in the wastewater was degraded, and the halogens bounded to the part of the polymer. The disappearance of the characteristic infrared peak of PVA also proves that $HO^{\cdot}$ and ClO^{-} can break long-chain PVA molecules into short-chain molecules. However, HPSEC analysis revealed that EO technology is effective not only in the degradation of long chain PVA molecules, but also in the degradation of short chain PVA molecules. It should also be noted that despite the effectiveness of hydroxyl radical and chlorine, a small amount of pollutant remains intact.

Although boron-doped diamond (BDD) electrodes have been shown to be effective in water purification, their high cost has been cited as a major barrier to their widespread use. Reducing the high manufacturing costs of BDD electrodes remains a great challenge. Furthermore, the utilization of alternative treatment methods for PVA (polyvinyl alcohol) wastewater is also accompanied by exorbitant expenses. Consequently, the electrochemical oxidation (EO) system with a BDD electrode presents a remarkable alternative, particularly in the current circumstances, as it circumvents secondary predicaments such as sludge formation.

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Author contributions

EG: Conceptualization, methodology, data curation, writing—review and editing.: SKB: Conceptualization, investigation, supervision, writing—review and editing.: HH: Conceptualization, investigation, data curation.

Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no confict of interest.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

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