Activated carbon assisted electrocoagulation process for treating biotreated palm oil mill effluent

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Abstract. Electrocoagulation (EC) is a sustainable wastewater treatment alternative that is widely studied because of its environmentally friendly nature, versatility, and simplicity in setup and operation. However, EC alone cannot treat wastewater up to reusable standards and requires integration with other processes, mostly by adding highly hazardous oxidants. This work aims to investigate the combination of powdered activated carbon (AC) with biotreated palm oil mill effluent (BPOME) as wastewater sample, in the EC reactor, and to optimize its concentration for maximum pollutant removal efficiency. Ranging from 0.5–1.5 wt. % concentration of AC mixed with EC reactor, EC was carried out with its critical parameters set to a current of 1.75 A (i.e., 160 mA/cm² current density) and initial pH 6 and 10 mm interelectrode distance with aluminum electrodes. The EC treated wastewater was sampled from 5 minutes to 60 minutes and the parameters monitored were total suspended solids (TSS), turbidity, color and chemical oxygen demand (COD). Turbidity, TSS and color were removed nearly to completion within 5 to 15 minutes of EC, whereas maximum COD removal was determined to be 84.6 % with 1 wt. % powdered AC combined with EC, which is an increase of about 14.6% compared to EC with no AC addition. The optimum concentration of AC for maximum removal efficiency on BPOME was 1 wt. % (2 g per 200 ml). Addition of AC in EC resulted in a faster pollutant removal rate, with enhanced process efficiency.

1. Introduction
It is crucial to develop an alternative treatment system to sustainably treat industrial effluents without requiring or producing hazardous chemicals, to lead towards a circular economy with environmental sustainability. Therefore, electrocoagulation (EC) is a topic of exhaustive study due to its simple and inexpensive operation and maintenance, eco-friendly nature, and the ability to treat a wide range of pollutants in various types of wastewater [1]. EC is performed by passing current in the target wastewater through metal electrodes, typically aluminum or iron electrodes. Consequently, metal hydroxides form in the EC reactor that destabilize the pollutants which come together as flocs, which are easily separated from the wastewater. However, EC alone cannot treat heavily polluted industrial wastewater, up to reusable standards. There is a need for an integration of a sustainable process to enhance EC. EC is often employed as a pre-treatment process for membrane based purification systems as the huge amount of pollutants removed by EC significantly contributes to membrane fouling mitigation [2]. The addition of hazardous oxidants to the wastewater, such as hydrogen peroxide through advanced oxidation processes, is widely explored to achieve a desirable outcome [3–5]. But it is not environmentally friendly and is a chemical intensive process, requiring toxic oxidants. An interesting approach is to add eco-friendly adsorbents, such as activated carbon (AC) and to investigate the synergistic effect of EC with AC...
adsorption to effectively treat severely contaminated industrial effluents. Sher et al. (2021) achieved promising results by coupling powdered AC with EC for general wastewater treatment [6]. This study explores the addition of commercially available powdered AC to combine with EC to treat heavily polluted biotreated palm oil mill effluent (BPOME). BPOME is the final form of the effluent after biological treatment, ready for environmental discharge from the palm oil industries. The characterization of BPOME is presented in Table 1.

Table 1. Characterization of BPOME.

| Parameter                        | Average value |
|----------------------------------|---------------|
| Chemical Oxygen Demand (COD), (mg/L) | 1981          |
| Total Suspended Solids (TSS), (mg/L) | 192           |
| Color, (PtCo)                    | 2882          |
| Salinity, (ppt)                  | 8.2           |
| Total Dissolved Solids (TDS), (g/L) | 7.91          |
| Conductivity, (mS/cm)            | 14.1          |
| pH                               | 7.9           |
| Turbidity, (NTU)                 | 332           |

2. Methodology

A 250 ml beaker was used as the EC reactor. Aluminum electrodes with dimensions 1.55 mm x 20 mm x 100 mm and HACH COD vials High Range (HR) were purchased from Jecre Trading, Malaysia. Alligator clips and direct current (D.C) supply unit, Twintex (TP-2303K, Taiwan) were used to pass current through the electrodes to form the electrochemical cell. Figure 1 shows the schematic diagram of the EC setup.

BPOME was collected from the final discharge pond released at 23 tons per hour capacity-based discharge, in Negeri Sembilan based palm oil mill, Malaysia. The collected effluent was stored at 4°C temperature, to prevent degradation due to biological activity.

Commercially available powdered AC was added to the EC reactor and EC process was run with the parameters, current density 160 mA/cm² (1.75 A), initial pH 6 and 10 mm of interelectrode distance. The parameters namely COD, turbidity, TSS and color were monitored from 5 to 60 minutes of EC operation. To control the initial pH of the samples, 5% HCl and 0.1M NaOH solutions and pH meter (Mettler Toledo, MP220 model, USA) were used. With 250-300 rpm stirring speed, and 1 g of AC, the EC-AC coupled process was carried out like the work of [8]. To optimize the AC dosage for optimum EC performance and COD removal, the EC coupled adsorption process was run with AC ranging from 1 g to 3 g (0.5 wt % to 1.5 wt %), as shown in Table 2.
Table 2. Wt.% of powdered AC and its equivalent mass per working volume.

| AC (wt %) | AC mass (g) per 200 ml sample |
|-----------|------------------------------|
| 0.5       | 1.0                          |
| 1.0       | 2.0                          |
| 1.5       | 3.0                          |

The resulting removal efficiency ($R_e$) values were calculated with the following Equation (1).

$$R_e (%) = \frac{X_i - X_f}{X_i} \times 100$$

where, $X_i$ and $X_f$ are the initial and final concentrations of COD, TSS, turbidity and color.

The wastewater samples were measured for COD, color and total suspended solids (TSS) before and after EC using spectrophotometer (HACH DR 5000, USA) according to American Public Health Association (APHA) procedures [9]. Multi-meter (HACH sensION5, USA) was used to measure the total dissolved solids (TDS), conductivity, and salinity of the wastewater samples. Turbidity of the samples were monitored with turbidimeter (HACH 2100P, USA). Filter papers of 0.45 µm pore size were used to separate flocs from the EC treated solution for characterization. X-Ray Diffraction (XRD) was carried on D2 Phaser 2nd Gen, Bruker and operated with 0.25s of time/step. All experiments were carried out in room temperature.

3. Results and discussion

The optimized EC operational parameters, intial pH 6, and current density 160 mA/cm$^2$ (current 1.75 A) from previous work [7], were used for all the experiments from 0 to 60 minutes, and the treated wastewater was monitored for TSS, color, turbidity and mainly COD values. The outcome of this control study (with 0 wt. % AC) is summarized in Figure 2.

![Figure 2](image-url)

**Figure 2.** Removal efficiency of COD, TSS, color and turbidity % without AC in EC of BPOME.

Turbidity and TSS depicted a remarkably similar removal rate compared to the other parameters (color and COD), without addition of any AC. The colloidal destabilization by the aluminum hydroxide-based coagulants generated in situ worked effectively to remove all suspended solids from the BPOME. Besides, the quantity of suspended solids results in the turbidity of the wastewater, therefore, their removal rates depict a negligible difference between them. The same pattern was observed in EC coupled with powdered AC, but with a higher rate of removal, presented in Figure 3.
Figure 3. Turbidity and TSS removal % within 5 minutes of EC (combined with AC at 0.5 wt.% - 1.5 wt.%).

Table 3. Characterization of EC treated BPOME with 0.5 wt. % AC.

| Parameters/EC time (minutes) | 0    | 5    | 10   | 15   | 30   | 45   | 60   |
|-----------------------------|------|------|------|------|------|------|------|
| COD (mg/L)                  | 1981 | 588  | 596  | 592  | 493  | 467  | 560  |
| TSS (mg/L)                  | 192  | 1    | 0    | 0    | 0    | 0    | 0    |
| Color (mg/L)                | 2882 | 112  | 78   | 52   | 11   | 6    | 0    |
| Turbidity (NTU)             | 332  | 0.89 | 0.4  | 0.5  | 0.45 | 0.78 | 0.47 |

Table 4. Characterization of EC treated BPOME with 1.0 wt. % AC.

| Parameters/EC time (minutes) | 0    | 5    | 10   | 15   | 30   | 45   | 60   |
|-----------------------------|------|------|------|------|------|------|------|
| COD (mg/L)                  | 1981 | 435  | 306  | 316  | 452  | 436  | 490  |
| TSS (mg/L)                  | 192  | 0    | 0    | 0    | 0    | 0    | 0    |
| Color (mg/L)                | 2882 | 16   | 16   | 14   | 7    | 0    | 1    |
| Turbidity (NTU)             | 332  | 0.95 | 0.7  | 0.6  | 0.5  | 0.9  | 0.1  |

Table 5. Characterization of EC treated BPOME with 1.5 wt. % AC.

| Parameters/EC time (minutes) | 0    | 5    | 10   | 15   | 30   | 45   | 60   |
|-----------------------------|------|------|------|------|------|------|------|
| COD (mg/L)                  | 1981 | 351  | 504  | 492  | 448  | 457  | 459  |
| TSS (mg/L)                  | 192  | 0    | 1    | 0    | 0    | 0    | 0    |
| Color (mg/L)                | 2882 | 26   | 30   | 5.5  | 19   | 5    | 0    |
| Turbidity (NTU)             | 332  | 1.9  | 0.5  | 0.4  | 2.0  | 1.2  | 0.4  |
Figure 4. Bar graph representation of EC treatment efficiency (combined with AC) on BPOME in terms of color removal % vs time, with current density 160 mA/cm² and pH 6.

A significant reduction in color, as shown in Figure 4, was observed within 5 minutes of EC (coupled with AC) through a visible inspection, which was verified with chemical analyses. Tables 3-5 depict the sampling results in terms of COD, TSS, color and turbidity removal of the EC-AC treated BPOME from 5 to 60 minutes of treatment. It is evident from the data, that within 5 minutes of EC operation with addition of powdered AC, over 95% of turbidity, TSS and color were removed. This outcome is impressive as the process does not require harmful oxidants to break down the organic pollutants in the sample effluent. In maximum 15 minutes, all TSS and turbidity were removed from BPOME with EC alone with 0% AC (control). Using EC (set parameters: current density-160 mA/cm², initial pH-6) on BPOME without the addition of powdered AC, resulted in a maximum of 70% removal of COD in 60 minutes of EC (Figure 2). In the range of 0 to 60 minutes, maximum color removal of 99% was achieved at about 45 minutes of EC, and maximum COD removal was 70% in 60 minutes. However, with AC addition, the fastest removal % noted was of TSS from BPOME for all concentrations of powdered AC added, followed by turbidity, color and COD. The combined action of the adsorption of colloids by both AC along with the metal coagulants generated in the EC reactor, greatly enhanced the efficiency of the EC process, that contributed to a much higher pollutant removal rate. This conclusion also corresponds to the study reported by [8], where addition of granular AC in EC process, remarkably reduced the time required for humic acid removal from paper industry based wastewater.

No substantial difference in terms of TSS and turbidity removal rate was noted with AC addition in EC (Figure 3). The metal hydroxides generated by EC in situ was enough to completely destabilize the suspended solids and subsequently, turbidity. However, faster color and COD removal was observed with AC addition, relatively. The powdered AC addition enabled the breakdown of pigmented compounds (mainly phenols), present in the BPOME. Figure 4 shows that most of the color (>99%) is removed with 1 and 1.5 wt. % AC addition to EC, within the first 5 minutes of the process.

The primary parameter chosen to determine the best removal efficiency in this study is COD, as it denotes the total amount of oxygen required to degrade all the organic pollutants in the wastewater. Therefore, COD gives an estimation of the level of organic pollution of wastewater [10]. Besides, the COD values depicted a distinct difference while observing the EC efficiency with and without AC. With COD removal %, as the main criteria for measuring the EC effectiveness, the values are compared and visualized in Figure 5.
Figure 5. COD removal % with and without AC coupled with EC.

Powdered AC concentration of 1 wt. % (2g in 200 ml) is the optimum concentration for addition to EC process for best treatment efficiency in terms of overall COD removal (84.6%) for BPOME as observed in this study, in 10 minutes (Figure 5). With 0.5 wt. % AC, there were more space for pollutant adsorption from BPOME, while with 1.5 wt. %, in the upper limit, the AC quantity exceeding the desired active sites for the coagulant-colloid adsorption, could partly destabilize some of the flocs that have already formed complexes with the metal hydroxides and AC, due to flotation with H₂ release at the anode, or the constant stirring provided to maintain the homogeneity of the reactor constituents. With 1 wt. % AC added to the EC process yielded relatively the highest removal efficiency in treated BPOME in 10 minutes, the overall outcome of which is summarized in Figure 6. Besides, the visual observation of the color and turbidity removal after EC treatment with 1 wt. % AC, is presented in Figure 7.

Figure 6. Summary of the overall treatment efficiency in terms of COD, TSS, color and turbidity removal % in 10 minutes of EC coupled with 1% AC.
Figure 7. Visual observation of color removal on BPOME from 15 to 60 minutes of EC (left to right) 160 mA/cm\(^2\) pH 6 with 1 wt. % AC addition.

The powdered XRD spectra of AC and the sludge resulting from EC assisted with powdered AC on BPOME are presented in Figure 8. The powdered XRD analysis has been carried out with contact angles varying from 20° to 80° in the 2θ range. The powdered AC depicts two notable strong peaks (2θ) at around 25° and 43°, corresponding to the planes (002) and (101); same pattern of which was also observed by [11,12] for powdered AC. The graph represents the hexagonal structure of the carbon material in its graphic form [13]. It is evident that the resulting sludge from EC is mostly powdered AC due to the similarities in the diffractogram pattern, with a visible shift in the peak intensity. The adsorption of organic pollutants combined with flocs of aluminum salts on the AC surface caused a distortion in its crystalline lattice structure, which is reflected by the variation in the peak intensity. Consequently, new sharp peaks at 28° and 29° were observed in the XRD spectrum of EC sludge, differing from AC’s XRD spectrum. Priya and Sureshkumar (2020) made a similar conclusion suggesting the peak intensity variation resulting from AC adsorption [12]. As a large portion of the AC structure retains after EC, the reusability of the AC after EC process is worth exploring.

Figure 8. XRD spectra of AC before after EC treatment on BPOME (as sludge).

4. Conclusion
EC was investigated with AC addition to investigate its ability to enhance the overall treatment efficiency. Within 10 minutes of EC operation, coupled with 1 wt. % of AC, a transparent effluent with 100% TSS removal, 99% removal of both color and turbidity was observed. The maximum COD removal (84.6%) was achieved at this point with a final value of 306 mg/L. The EC treated wastewater was sampled from 5 minutes to 60 minutes and the parameters monitored were TSS, turbidity, color and
COD, Turbidity, TSS and color were removed nearly to completion within 5 to 15 minutes of EC, whereas maximum COD removal was determined to be 84.6% with 1 wt. % powdered AC combined with EC. Therefore, the optimum concentration of AC for maximum removal efficiency on BPOME was 1 wt. % (2 g per 200 ml). A much faster treatment efficiency was noted after AC addition to EC, compared to no AC. Hence, the addition of AC in EC process shows a promising potential for a faster and more efficient treatment of heavily polluted BPOME.

Acknowledgement

The authors express thanks to Ministry of Education (MOE) Malaysia for granting a Fundamental Research Grant Scheme (FRGS), project no. FRGS-19-194-0803 and International Islamic University Malaysia, Faculty of Engineering, for the financial support under Tuition Fee Waiver (TFW) 2019 scheme for outstanding students awarded to AT, to support this work.

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