How to Estimate the Best Treatment Conditions for Sunflower Oil Wastewater Using Advanced Electrooxidation Process

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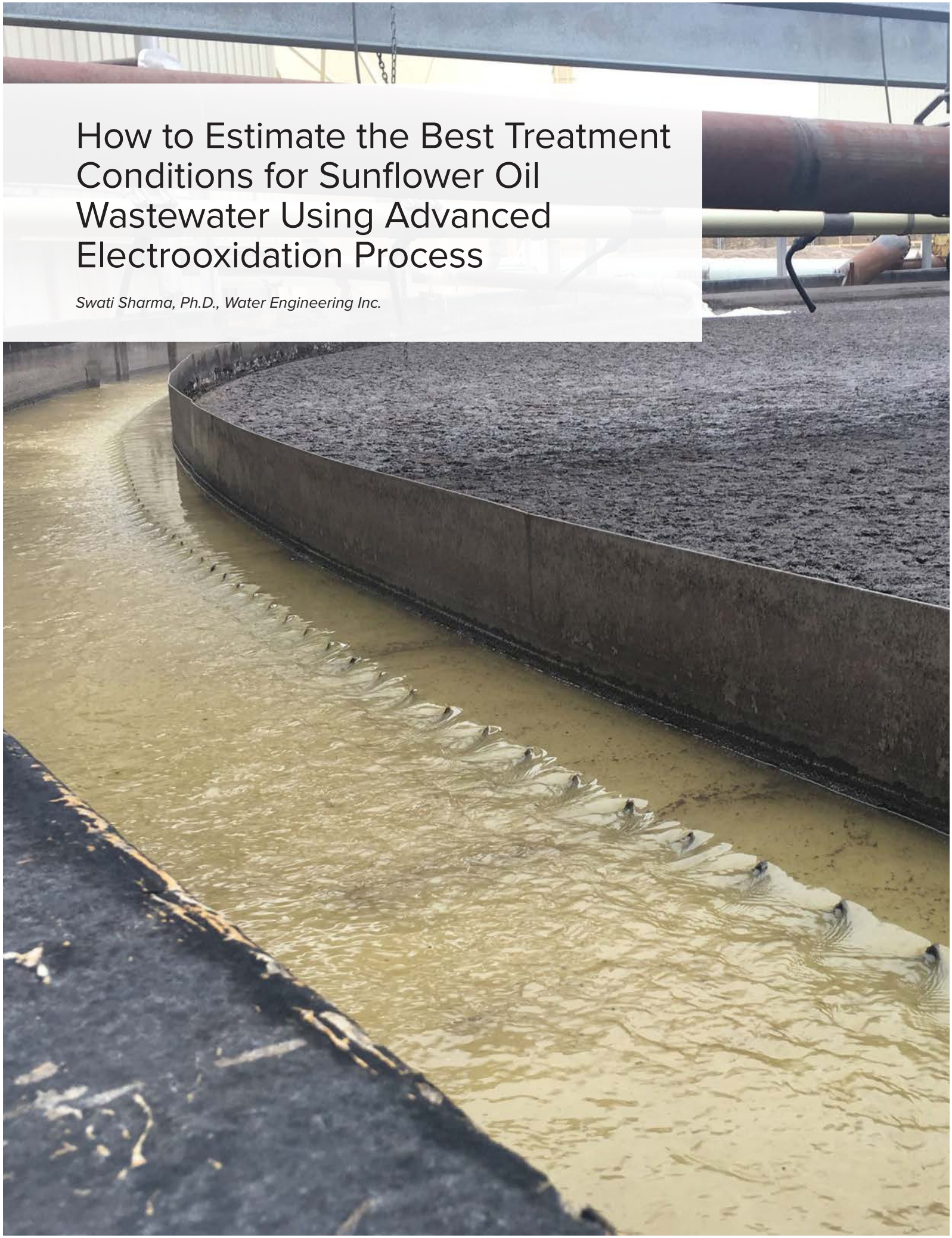


Sunflower oil refinery wastewater produces large quantities of fatty-acid-rich wastewater with a high concentration of organic pollutants (1). Sunflower oil wastewater is typically treated by dissolved air flotation (DAF) and chemical coagulation followed by anaerobic digestion (2–4). Over time, the efficiency of the DAF system is reduced due to a high influx of oily/fatty contents coming in at a large loading rate. As a result, the wastewater is either diverted from DAF to storage ponds or redirected to the anaerobic lagoons, thereby resulting in increased organic loads. These processes take up huge acres of land and potentially contribute to environmental issues (5, 6).

Currently, electrochemical processes are being studied to find an alternative solution to these traditional treatment methods. These processes are an advanced technology that achieve a chemical reaction through generation of electricity. Electrochemical processes help minimize the use of chemicals, thereby preventing formation of byproducts.

Of the various types of electrochemical processes, the most common is electrocoagulation (EC), which is found to be effective in removing small colloidal and suspended particles. On the other hand, advanced oxidation processes (AOPs), such as electro-oxidation (EO), electrofenton (EF), electroperoxidation (EP), and electrochemical peroxidation (ECP), have been effective in removing small organic compounds via oxidation. EC, when coupled with EO, has achieved better treatment of carwash, petroleum, tobacco, and olive oil processed wastewater.

This study is focused on investigating the efficiency of EC+EO and ECP methods through optimum parameter conditions for maximum removal efficiency of total organic carbon (TOC), chemical oxygen demand (COD), dissolved organic carbon (DOC), and soluble COD (sCOD) in sunflower oil refinery wastewater.

Materials and Methods

The raw wastewater samples were collected from a local oil refinery in Fargo, North Dakota. The raw influent was analyzed for TOC, COD, DOC, and sCOD right after collection, and the wastewater was stored at 4 °C. The samples were discarded every three days and collected afresh. The unfiltered samples were analyzed for TOC and COD. The samples were then filtered through 1.2 -micron (µm) glass microfiber filter paper followed by 0.45-µm pore size filter paper to determine initial parameters in the sample. The pollutants passing through the 0.45-µm filter were considered to be soluble components.

About 50 milliliter (mL) of raw sample was filtered and used to determine initial concentrations of sCOD and DOC. The sCOD was analyzed using Hach testing kits TNT 821 and 822 (COD 0-150 milligrams per liter [mg/L] and 2-1500 mg/L, respectively). The DOC was analyzed using a Shimadzu TOC-L analyzer. The EC+EO and ECF processes were carried out simultaneously. The combined EC+EO process was performed in two phases:

- **Phase 1:** EC using aluminum electrodes as anode and cathode.
- **Phase 2:** EO process using boron doped diamond (BDD) electrode as anode and stainless steel as cathode.

On the other hand, the ECF process was carried out using iron electrodes. Hydrogen peroxide (H2O2) was added externally at a dosage of 3 mL per 250 mL of sample (7, 8). The conductivity and pH were adjusted using sodium chloride (NaCl) and acid/base, respectively. The samples were collected from the reactors at regular intervals and analyzed for organic concentration.

Statistical Analysis

Box Behnken Design (BBD) was considered as the expermental design for evaluating the operating conditions at optimum conditions. The statistical analysis and modeling was performed using Design-Expert® software where the independent variables under consideration are pH/H_2O_2 dosage, current density, and time. Three different levels were selected for each variable based on preliminary experimental study.

Results and Discussion

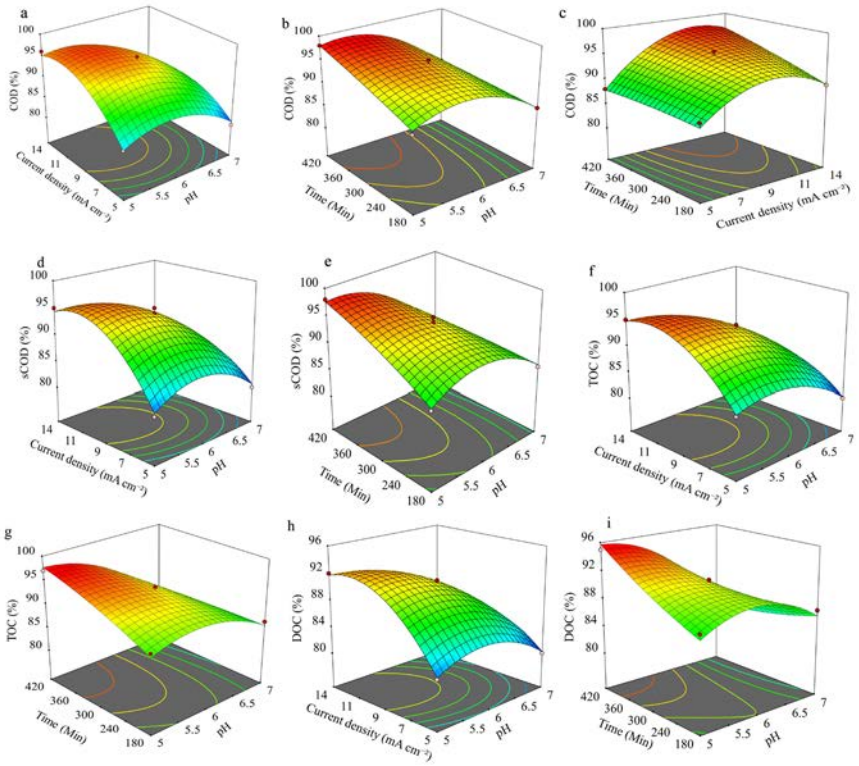
TOC, COD, sCOD and DOC Removal in EC+EO Process

In the EC process, the coagulation time decreased with an increase in current density. Using Al electrodes resulted in high removal of particulate organic concentration within a short time, ranging between 90% and 93% at all current densities under study. It was observed from this current study as well as previous literature that the EC process is efficient in removing particulate organics compared to that of dissolved organic compounds. Thus, the EO process was combined with

the EC process for further removal of dissolved organic pollutants. Performing EO after EC for 7 hours (h) achieved removal of an additional 80% of the remaining EC effluent organic concentration.

The data for the EC+EO were fitted to quadratic models, and the model significance was tested using ANOVA (Table A). The best treatment condition yield through response surface plotting shows that the optimal treatment efficiency in Phase 1 of the EC+EO process was at current density of 5.69 milliamps per square centimeter (mA/cm^2) when operated for 18 minutes (min) at a pH of 6.07. In these operating conditions, the removal achieved for TOC and COD was 90% and 73.7%, respectively. For the EO process, the maximum removal of organic concentration was achieved at a pH of 5.27 and current density of 11.56 mA/cm^2 at the end of 400 min. The combined EC+EO process removed 95% of the raw influent organic concentration. From the response surface plotting presented in Figure 1, it can be inferred that the current density did not have significant impact on EC process; however, when EC+EO were combined, the effect of current density played an important role in achieving desired removal efficiency.

Figure 1: Interaction effects of current density, pH, and time in the EC+EO process.



TOC, COD, sCOD, and DOC Removal in the ECP Process:

The variables considered for the ECP process were H_2O_2 dosage, current density, and time. The only difference in the selection of variables between EC+EO and ECP is choosing H_2O_2 dosage over pH. This is due to the fact that Fenton's Reaction is optimum at pH 2.8. Below or above this pH, Fenton's Reaction produces undesirable intermediate reaction inhibitory complexes. Thus, the pH in this process was kept constant at 2.8. On the other hand, the H_2O_2 dosage is critical in the formation of hydroxyl ions, which is the key redox exchange ion for the advanced oxidation process. At optimum operating conditions, which are achieved at an H_2O_2 dosage of 14.2 mL/L and a current density of 7.56 mA/cm^2 for 278 min.

The overall removal efficiency achieved using this process ranged between 81% and 85% of organic pollutants. The statistical significance was analyzed using BBD, and the model adequacy was tested using ANOVA, as presented in Table A. Figure 2 shows the interaction effects of time, current density, and H_2O_2 dosage in the ECP process. It is

observed that H_2O_2 dosage and time had a positive effect on the removal process. The results showed that an increase in current density decreases the time required to remove the organics. However, the percentage removal remains consistent at all current densities applied. The ECP process also yielded comparable results, and the removal was comparatively lower than that of EC+EO process. A previous study conducted by Sharma and Simsek (9) that investigated the effect of current density and time in the canola oil refinery wastewater using EC+EO and ECP processes achieved similar conclusions. It was observed that an increase in applied current density significantly decreases the time of operation maintaining a consistent removal.

Figure 2: Interaction effects of current density, H_2O_2 dosage, and time in the ECP process.

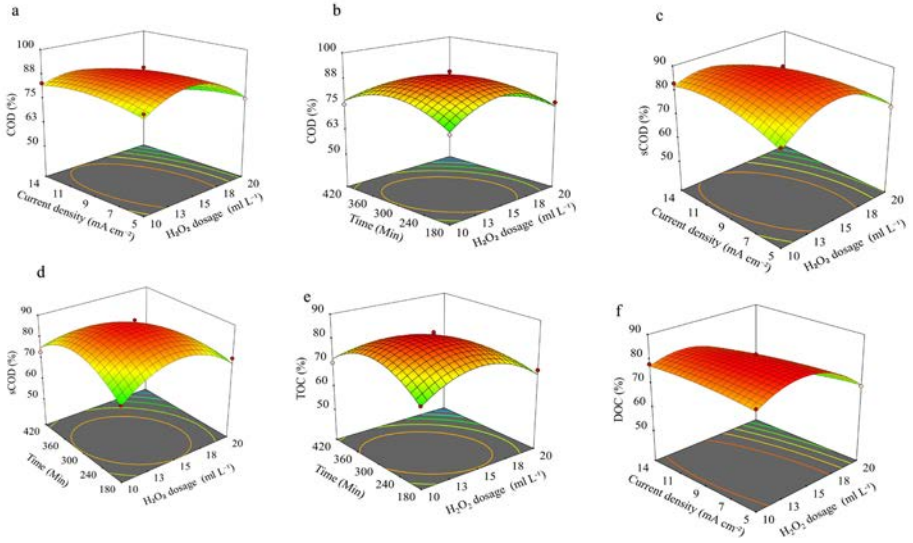


Table A: ANOVA Results for the Quadratic Models for Sunflower Oil Wastewater

Response (Y, %)	*Source*	*EC+EO*					*ECP*				
		SS	*DF*	*MS*	*F-value*	*p-value*	*SS*	*DF*	*MS*	*F-value*	*p-value*
COD	Model	376.50	8	47.06	53.98	<0.0001	1229.77	8	153.72	29.59	0.0003
	Residual	5.23	6	0.8718			31.17	6	5.19		
	Lack of Fit	4.56	4	1.14	3.42	0.2387	28.50	4	7.13	5.34	0.1638
	Pure Error	0.6667	2	0.3333			2.67	2	1.33		
	Total	381.73	14				1260.93	14			
		R^2=0.9863		Adj R^2=0.9680 C.V%=1.03			R^2=0.9753		Adj R^2=0.9423 C.V.%=2.93		
sCOD	Model	427.01	7	61.00	34.64	<0.0001	1424.57	8	178.07	39.33	0.0001
	Residual	12.33	7	1.76			27.17	6	4.53		
	Lack of Fit	10.33	5	2.07	2.07	0.3576	24.50	4	6.13	4.59	0.1867
	Pure Error	2.00	2	1.0000			2.67	2	1.33		
	Total	439.33	14				1451.73	14			
		R^2=0.9719		Adj R^2=0.9439 C.V.%=1.50			R^2=0.9813		Adj R^2=0.9563 C.V.%=2.82		
TOC	Model	375.50	7	53.64	36.70	<0.0001	1074.00	7	153.43	31.84	<0.0001
	Residual	10.23	7	1.46			33.73	7	4.82		
	Lack of Fit	9.56	5	1.91	5.74	0.1550	31.73	5	6.35	6.35	0.1417
	Pure Error	0.6667	2	0.3333			2.00	2	1.0000		
	Total	385.73	14				1107.73	14			
		R^2=0.9735		Adj R^2= 0.947 C.V.%=1.36			R^2=0.9695		Adj R^2=0.9391 C.V.%=3.03		
DOC	Model	289.93	7	41.42	41.42	<0.0001	997.16	8	124.64	40.55	0.0001
	Residual	7.00	7	1.000			18.44	6	3.07		
	Lack of Fit	6.33	5	1.27	3.80	0.2214	15.78	4	3.94	2.96	0.2683
	Pure Error	0.6667	2	0.3333			2.67	2	1.33		
	Total	296.93	14				1015.60	14			
		R^2=0.9764		Adj R^2=0.9529 C.V.%=1.15			R^2=0.9818		Adj R^2=0.9576 C.V.%=2.45		

Conclusion

The sunflower oil wastewater was treated using two different electrochemical processes: combined EC+EO and ECP. The study showed that combining EC and EO resulted in higher organic removal. The removal efficiency had a significant dependence on current density, pH, and time. The performance of ECP was maximum at optimized operation conditions, and H_2O_2 dosage impacted the organic removal concentration.

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