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Review

Electrocoagulation technique for removing Organic and Inorganic pollutants (COD) from the various industrial effluents: An overview

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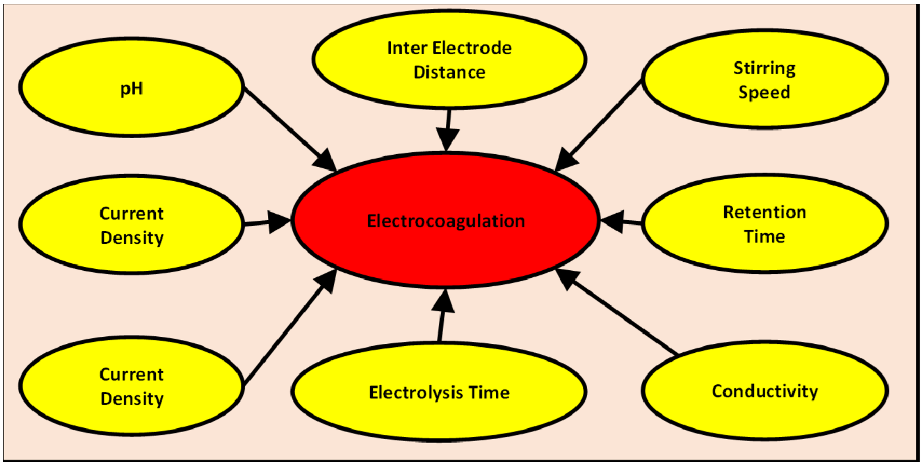
ABSTRACT

The treatment and reuse of industrial wastewater plays a foremost role in succeeding environmental protection and water security. The electrochemical treatment technology has attracted a great deal of attention because of its compact, high particulate removal, free from chemicals, automation, and minimum sludge generation. The objective of the study is to review the existing literature on COD (Chemical oxygen demand) removal from various industrial effluents using electrocoagulation technology, as well as the factors that influence the process. Electricity is passed through electro plates dipped in wastewater during the electrocoagulation process. Metal hydroxide formations occur, which removes pollutants from wastewater via the sedimentation and flotation mechanisms. After a thorough review of various literatures, a detailed discussion on the process influencing parameters such as pH, Current Density, Electrolysis Time, Conductivity, Stirring Speed, and Retention Time has been done which gives useful information on future scope of research in this area.

Keywords: COD removal, Electrocoagulation Process, Industrial wastewater Treatment, Process Influencing factors, Removal Efficiency

Graphical Abstract



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1. Introduction

Water is one of nature's abundant resources and is necessary for animal and plant life. Water pollution is increasing as a result of industrialization and urbanization. The natural water body's pollution is caused by some factors such as rapid industrialization and rinsing water demand for energy protection. The global production and use of chemical compounds that end up in the environment has skyrocketed, and many of these compounds are biologically non-degradable [1, 2]. Many industrial processes generate wastewater that contains toxic organic compounds that are not amenable to direct biological treatment. As a result, the primary concern is to treat wastewater prior to discharge into the environment [3]. The major industries that generate wastewater include pulp and paper, sugar, textile, food processing, tannery, petrochemical, and distillery etc., These industries' effluents have high COD, color, high organic matter, biological oxygen demand, suspended solids, turbidity, extreme pH, and salinity. High COD levels in wastewater discharge cause aquatic animal deaths and odour problems, reducing the aesthetics of the aquatic ecosystem [4].

The EC treatment has been commercial, and it shows a better benefit compare to the current treatment process in terms of equipment simplicity, portable, clear and colorless, and odorless of the treated wastewater [5]. Electrocoagulation is a process that creates metallic hydroxide flocs in wastewater by electro dissolving soluble anodes, which are typically made of iron or aluminium. Due to increased environmental restrictions on effluent wastewater, there has recently been renewed interest in the use of electrocoagulation [6]. The purpose of this review is, to deliberate COD removal efficiencies from various industrial effluents, as well as the significant facts of process influencing parameters such as pH, Current Density, Electrolysis Time, Conductivity, Stirring Speed, and Retention Time. The table below contains a list of review articles related to electrocoagulation treatment techniques, along with their purpose of study Table 1.

2. Electrocoagulation Technology

The electrochemical treatment technology has attracted a great deal of attention because of its environmental compatibility, eco-friendly, automation, high efficiency, cost-effectiveness, and versatility [15], [16]. This method is distinguished by simple equipment, simple operation, a shortened reactive retention period, a reduction or absence of chemical addition equipment, and a reduced amount of precipitate or sludge that sediments rapidly. The process has been demonstrated to be an effective and dependable technology that provides an environmentally friendly method for reducing a wide range of pollutants [17]. Electrocoagulation and electrocoagulation/flotation processes are most effective at removing inorganic contaminants and pathogens from water and wastewater treatment projects [18].

Electrochemical technology is a powerful tool for breaking the most resistant organic compounds or pollutants [19]. In EC process, the coagulant is generated from the sacrificial anode. The charged ionic species are removed from the wastewater by allowing reacting oppositely charged ions or metal hydroxides generated within the effluent. The pollutants such as metals, particles, colloidal solids, clay minerals, organic dyes, soluble inorganic species, oil, and grease from the wastewater were removed from high charged polymeric metallic hydroxide species [20]. The floc formation happens during EC process due to the generation of metal ions. The rapid

Table 1. The list of review articles related to electrocoagulation treatment techniques along with their purpose of study

Sr. No	Source of Article	Purpose of Study
1	[7]	The goal of this paper is to look into the factors that influence the efficiency of the EC method and the possibility of increasing elimination efficiency by combining it with other methods.
2	[8]	The purpose of this paper is to provide a general overview of the most relevant electrochemical methods in the treatment of sanitary landfill leachates.
3	[9]	This review attempts to identify specific research gaps in order to develop electrocoagulation as a reliable and cost-effective water treatment technology.
4	[10]	The purpose of this work was to review studies conducted primarily between 2008 and 2011 on the wide and versatile range of feasible EC applications used in the purification of various types of water and wastewater.
5	[11]	The goal of this proposed study is to discuss about different types of water and wastewater that have recently been treated with electrocoagulation-electro flotation (ECF) technology.
6	[12]	The purpose of this study is to examine the potential of electrocoagulation for the treatment of industrial effluents, specifically the removal of dyes from textile effluent.
7	[13]	The primary goal of this review is to present bench and field scale research studies for EC and ECF technology used to remove various pollutants from water and waste-water treatment plants.
8	[14]	The electrocoagulation-ultrasonication process was summarized in this study, along with the influence of important operational parameters on pollutant removal, as well as the drawbacks and advantages of this technique in the removal of various industrial pollutants.
9	Proposed Research	The purpose of this review is, to discuss the COD removal efficiencies from various industrial effluents and deliberate the important facts of process influencing parameters.

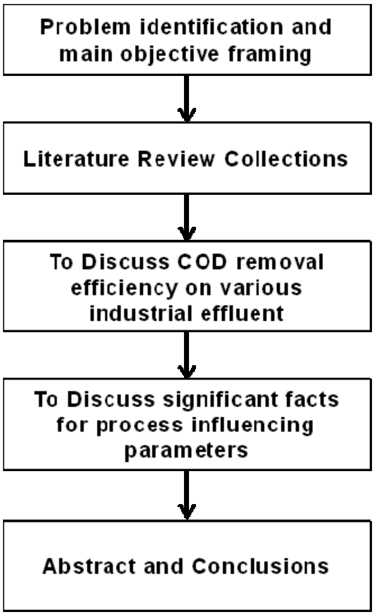

Fig. 1. Research methodology

adsorption and trapping of colloidal particles are occurring because of the flocs having a greater surface area. The major influencing parameter involved in the EC process were pH, CD, ET, conductivity, nature of electrode material, and ID [21]. The research methodology for this literature review was shown in Fig. 1.

2.1. Basic Mechanism of Electrocoagulation Process

The basic principle of EC is producing an insitu coagulant by using Al and Fe electrodes instead of Al and Fe salts. The most advantages of the EC process over chemical coagulation are the partial absorption, electro floatation, and electro-oxidation process are occurs simultaneously during electrolytic reactions [22]. For considering a pair of Al electrodes, the Al^{3+} and hydroxyl radical ions in the wastewater can react to form various mononuclear species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$ and polynuclear species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$. This species are transformed into aluminum hydroxide $Al(OH)_3$ and it having a larger specific area. The oxidation and reduction mechanism of the Fe electrode is shown in Eq. (1) to (8). The sedimentation and hydrogen flotation process to remove the aluminum hydroxide species in the solution [23,24].

First Mechanism

Anode $$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2\ e^- \tag{1}$$

$$Fe^{2+}_{(aq)} + 2(OH)^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \tag{2}$$

Cathode $$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2\ OH^-_{(aq)} \tag{3}$$

Total $$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2\,(s)} + H_{2\,(g)} \tag{4}$$

Second Mechanism

Anode $$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^- \tag{5}$$

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2\,(g)} \rightarrow 4Fe(OH)_{2(s)} + 8\,H^+_{(aq)} \tag{6}$$

Cathode $$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2\,(g)} \tag{7}$$

Total $$4Fe_{(s)} + 10H_2O_{(l)} + O_{2\,(g)} \rightarrow 4Fe(OH)_{2(s)} + 4H_{2\,(g)} \tag{8}$$

The $Fe(OH)_{n(s)}$ are present as gelatinous suspension form in the aqueous medium, which can remove the pollutant in the wastewater by coagulation aided with complexation or electrostatic adsorption. To chemically bind hydrous ions, the pollutants act as a ligand in surface complexation mode and its reactions are given in Eq. (9). The $Fe(OH)^{4-}$ and $Fe(OH)^{6-}$ ions are may present in alkaline and acidic conditions. Hence, the EC for both cationic and anionic species is possible under Fe sacrificial electrodes [25].

$$L - H_{(aq)}\ (OH)OFe_{(s)} \rightarrow L - OFe_{(s)} + H_2O_{(l)} \tag{9}$$

The EC reactions from Al electrodes are given in Eq. (10) to Eq. (12). The generation of hydroxide species polymerizes Al cations into $Al_n(OH)_{3n}$ that can absorb or entrap the pollutant [26].

Anode $$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \tag{10}$$

Cathode $$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)}\uparrow + 2OH^-_{(aq)} \tag{11}$$

In solution between electrodes:
$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)}\downarrow \tag{12}$$

The general reactions of the EC process are given in Eq. (13) and Eq. (14). The selection of electrode material depends on the various parameters such as cost-effectiveness, material availability, oxidation potential, toxicity, and properties of the pollutant [27,28]. The mechanism of EC process was shown in Fig. 2.

Anode $$M^{n+}_{(aq)} + nH_2O_{(l)} \rightarrow M(OH)_{n(s)} + nH^+ \tag{13}$$

Cathode $$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)}\uparrow + 2OH^-_{(aq)} \tag{14}$$

3. Discussion of COD Removal Efficiency From Various Industrial Effluent

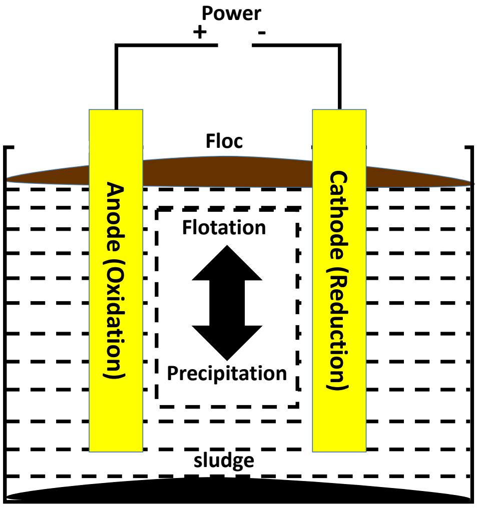

Fig. 2. The mechanism EC process

3.1. Petroleum and Yogurt Industry Effluent

The effluent from the petroleum industries contains aromatic and aliphatic petroleum hydrocarbons. During EC process, 42% to 63% of COD removal efficiency was observed under various operating conditions. According to this article, as temperature rises, so does the solubility of aluminium sulphates [29,30]. Using Fe electrodes under optimal circumstances such as CD-30 mA/cm^2, ET-90 minutes, and 0.75 g/L polyelectrolyte resulted in the highest removal efficiency (84 percent). The experimental analysis demonstrates that raising a CD - 20 to 30 mA/cm^2 enhances COD removal efficiency, however increasing the sodium carbonated concentration decreases removal efficiency. The sludge turned brown due to the development of iron oxide [31].

3.2. Ayurveda Pharmaceutical Effluent

The Al and SS electrodes were removed 78% and 68% of COD from Ayurveda pharmaceutical wastewater. The operating parameters such as pH, CD, ET, and salt concentration are optimized by performing response surface methodology (RSM) modeling. The experimental results show that the removal of COD from SS was greater than the Al electrodes (COD (%): Al<SS). The CRE and treatment cost from SS was less than the Al electrodes (Color (%) and Treatment cost ($): Al>SS). The desirability function approach for the multi-response optimization was used to optimize the number of responses namely, maximum color, COD removal, and minimum energy consumption. The optimum operating condition for the Al electrode was pH-6.0, CD-99.89 A/m^2, and electrolyte concentration-1.5 g/l. simultaneously; SS electrode was pH-7.5, CD-125.8 A/m^2, and electrolyte concentration-1.25 g/l. The contact time of a both the electrodes were same which was 120 minutes. The SS removes higher COD compared to the Al electrode [32–35].

3.3. Chicken Processing and Skim serum Effluent

In the chicken processing wastewater, the Fe electrodes with two different arrangements with horizontal and vertical manner were used. The horizontal and vertical electrode arrangements remove 88.5% and 96.2% of COD under 16 minutes of ET and CD-4 mA/cm^2. The electrode and power consumption from horizontally assisted electrodes were greater than the vertically assisted electrodes [17] [36–38]. In batch mode operation by using aluminium as anode and graphite as cathode, the COD removal efficiency was found to be 70% with the operating time of 45 minutes. The electrochemical treatment removes colloidal particles. The threshold current may perhaps vary depending on the actual properties of the electrode material. Subsequently, the Carbon released from the electrode surface can also add up to the carbon content of the treated solution [39].

3.4. Almond and Vegetable Oil refinery Effluent

From the experimental study of Almond industry wastewater in lab-scale batch mode operation; the optimized parameters such as Ti/RuO$_2$ as the anode, pH-9, CD-50 mA/cm^2, and chlorine content – 2000 mg/l were considered and the COD removal efficiency of 75% was observed. The pilot-scale study was carried out based on lab-scale experiment study results. From the experimental study, the author was proved as the electro-oxidation technique was suitable for the treatment of wastewater [40–43]. The EC process removes 98.90% of COD from vegetable oil refinery effluent. The effect of current density shows, rate of bubble generation increases and the bubble size decreases with increasing current density; both of these trends were beneficial in terms of high pollutant removal efficiency by H_2 flotation [44,45].

3.5. Bio-digester and Cheese whey Wastewater Effluent

The Cu electrode pairs remove 80% COD from grain-based bio digester effluent. The optimum operating conditions were pH-3.5 and CD-89.3 A/m^2. The electrode and power consumptions were 3.667 mg/l and 11.42 Wh/l. The treated effluent containing 3.521 mg/dm^3 of Cu which was below the central pollution control board maximum discharge limits of 4 mg/l. The effective settling rate was found between pH-6.5 to pH-8 due to the formation of heavy flocks which settle down at this range of pH. The settling rate of pH was in the order of pH-3.5> pH-5> pH-6.5> pH-8 [46,47]. In cheese whey wastewater the three-factor (pH, CD, and ET) and five-level CCD statistical analysis were performed with eighteen numbers of experimental studies. The 66.64% of COD were removed under optimum conditions with pH-7.36, CD-5.90 mA/cm^2, and ET-30.94 minutes. The residual COD was still high due to less significant removals of glycerol and methanol, which were the two main compositions of organic matter other than oil and grease in the wastewater. In oil and grease wastewater, the permeate flux and water recovery rate were captured from membrane fouling studies were 22 L (m^2 h) and 87.83%. The experimental results represent, an EC pretreatment was improved a reverse osmosis performance where the permeate flux and product water quality under refined conditions [48,49].

3.6. Pulp and Paper Industry Effluent

The Fe electrodes were employed to treat effluent from pulp and paper industries wastewater. The continuous mode EC process removes 82% of COD under optimum conditions such as pH-7.5, ET-30 minutes, CD-60 A/m^2, and recycle flow was 0.2 l/min. The circulation flow varied between 2.0 to 8 L/minutes. The 60% to 82% of COD removal occurs where the circulation flow rate 2.0 to 5.2 L/minutes. Further increasing the flow rate above 5.2 L/minutes, the removal efficiency was decreased due to the minimum amount of coagulant attached to pollutants at a higher flow rate. The anodic dissolution of Fe increases at a high current results, the greater amount of precipitate which removes pollutants [50].

3.7. Dye and Tannery Effluent

The synthetically prepared dye solution was treated with continuous-flow electrocoagulation reactors using Al electrodes. The 92.60% and 90.93% of color and COD removal was occurs where the CD is 135 A/m^2. The Tukeys test for statistical analysis was performed in first and second reactors considering to response factor COD. The electrode weight loss and COD concentration was correlated with the first and second reactor. Pearson correlation analysis revealed a significant and positive correlation between COD removal and electrode weight loss ($r = 0.98$, $P < 0.001$) indicating as removal of COD concentration increases electrode weight loss increases. The electrode consumption from the first reactor was greater than the second reactor while increasing the CD. The effective CD from this study was 135 A/m^2 [18, 51]. The tannery industrial effluent was treated with EC technique with Fe electrodes under batch mode operation. Two factorial statistical design was performed to optimize the independent variables such as pH, CD, ET, and ID distance. The higher COD removal 55.7% occurred at pH-7. The EC technology was cost-effective to remove the pollutants from tannery industry wastewater compared to conventional treatment methods [52].

3.8. Automobile Wash Effluent

The Automobile wash water effluent was treated with different combinations of electrodes such as Al, Fe, SS and Cu. The variable and response parameters for the optimization were ID (10 cm, 5 cm and 2.5 cm), CD (5 A/m^2 to 30 A/m^2), ET (10 to 60 minutes), pH (4 to 10) and COD, turbidity, oil and grease. The Cu (anode) and Al (cathode) electrode combinations were remove 95.1% of COD when the ID, CD, ET and pH was 5 cm, 25 A/m^2, 40 minutes and 6. The ID was reduced 10 cm to 5 cm removal efficiency was decreased. Simultaneously, from 5 cm to 2.5 cm removal efficiency was increased due to the poor circulation of electrons between the electrodes. The pollutant removal efficiency increases as CD raises to 25 A/m^2, Further increasing CD, the pollutant removal efficiency and the rate of oxidation reaction decreased that supports the phenomena of corrosion and forms the oxide layer on the active surface of the Cu electrode. The cost of treatment at natural pH was INR. 386.01/m^3 [53,54].

3.9. Printing Ink Effluent

The Zn and Ti electrodes were anodes and SS was cathode in all the experiments for treating the real printing ink wastewater. The COD removal efficiency recorded by employing Zn and Ti electrodes was 28% and 36% in 10 minutes of ET and 50% and 47 % of removal in 90 minutes of operation. Here, the CD of Zn and Ti electrode were 20 and 15 mA/cm^2 respectively. The rate of removal efficiency for the COD was reduced because of the phenomenon of desorption. The Zn molecular weight was greater than Ti, which leads to the production of heavier coagulant complexes that can precipitate more effectively. The maximum removal efficiency was achieved in 4 cm ID. However, by decreasing the ID, the removal efficiency was decreased because it reduces the electrical energy for ion motion. The energy consumption for Zn and Ti electrodes was 1.9 kW h/m^3 and 1.7 kW h/m^3 where the CD is 15 mA/cm^2. The energy and mass consumption for the Zn electrode was greater than the Ti electrodes [55,56].

3.10. Dairy and Municipal Sewage Effluent

The dairy industrial effluent was treated with pair of Fe electrodes. The maximum COD removal efficiency of 98% was achieved under certain operating conditions such as CD-0.6 mA/cm^2, ET-60 minutes, and sodium chloride concentration 0.3 g/L. The effects of pH of wastewater on EC are reflected by the solubility of metal hydroxides due to high conductivity. The power and electrode consumption under the optimum conditions were 0.003 kWh/kg COD and 0.0204 g electrode/kg COD. The $Fe(OH)_{n(s)}$ complexes formed remain in the aqueous stream as a gelatinous suspension. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization. The estimated regression for Langmuir, Freundlich and Temkin isotherm were 0.81, 0.99 and 0.95. The significant regression was from the Freundlich isotherm ($r^2=0.99$) model [57,58]. The municipal wastewater was treated with EC technique concerning various pollutants such as COD, turbidity, and TDS by using Al electrodes. The electricity obtained from Solar panel was utilized. The final pH was in the range of 7.4 to 8.5. The re-treatment was not a necessity because Al act as a pH neutralizer [59]. The zeta potential was used to identify the optimum conditions of CD and ET. The optimum CD and ET were 40 A/m^2 and 20 minutes. At this stage, energy consumption and zeta potentials were 2.27 kWh/m^3 and -0.92 mV [60].

3.11. Potato Chips and Rose processing Effluent

In wastewater obtained from potato chips manufacturing effluent Al and Fe electrodes were used for the treatment. The Al electrodes performance was greater than the Fe electrodes. The drawback of the Fe electrode was easily corrodible in open connections and the appearance of colored supernatant in the treated effluent. The energy consumption was increased with increasing applied voltage. The variation of electrode consumption was determined from actual and theoretical consumption. The advantage of the process was the formation of dried sludge and minimum retention time. The power consumption under optimum conditions was 4 kWh/m^3 [61]. The pH value of treated effluent was higher than the untreated effluent due to the evolution of hydrogen production. The optimum operating conditions identified from the rose processing effluent were CD-0.5A, voltage-15 V and ET-20 minutes, the energy consumption was 6.25 kW/m^3 [62].

3.12. Corrugated board Packaging Effluent

The Fe and Al electrodes were employed to treat corrugated board packaging plant printing ink wastewater. The dependent parameters were COD and CRE and also the independent parameters were

COD concentration, electrode type, CD. The pH of treated wastewater was slightly greater than the untreated wastewater due to Lewis acidity of both electrode ions, which counterbalance the constant formation of OH- ions at the cathode. The maximum COD removal efficiency was achieved under short period of ET in lower concentration which indicates the insufficient formation of coagulant species that are required to sediment the large particles. However, the molecular weight of the Fe electrode was greater than the Al electrode. The sludge volume index (SVI) was dependent on the applied CD. The SVI was 150 mL/g under operating conditions were pH-7, CD-20 mA/cm^2 and pair of Al electrode. A toxic potential of printing wastewater was decreased after treatment which was confirm from the Thamnocephalus platyurus toxicity test. The treatment cost from the Al electrode (0.32-2.50€) was greater than the Fe electrode (0.27-1.90€) [63,64].

3.13. Olive Processing Effluent

The table olive processing effluent was studied with pilot and lab-scale experimental setup considering to removal of COD and Color. The sedimentation rate of Al electrodes was greater than the Fe electrodes. As the number of flocs rises, a potential to adsorb organic pollutants in the wastewater also rises. In pilot-scale operation, Al electrode pollutant removal efficiency was greater than Fe electrode. The 42.5% of COD removal was obtained from Al electrode. Here, the optimum conditions were CD-5.65 mA/cm^2 and ET-50 minutes. The Fe and Al metal concentration with respective electrode treatment were 0.3 mg/l and 0.8 mg/l. In lab-scale experimental study, Al and Fe energy consumption was 1.41–7.5 kWh m^3 and 2.4–38.0 kWh m^3. Here, Al energy consumption was less than the Fe energy consumption. In both study, the metal dissolution of Al was less than the Fe electrode. The Al electrode was effectively treated the table olive mill wastewater over the Fe electrode [65, 66].

3.14. Egg Processing Effluent

The turbidity, COD, and BOD were removed from the egg processing industry effluent by employing pair of Al electrodes. The pollutant removal efficiencies were high up to 3 cm ID. The removal efficiency was decreased above 3 cm ID due to less interaction of ions with hydroxide polymers. The maximum pollutant removal efficiency was obtained at 200 rpm stirring speed. This confirms the fact that the removal efficiency is diffusion controlled, and the increase in stirring speed leads to an increase in the intensity of turbulence and reduces the diffusion layer thickness at the electrode surface, and improves the mixing conditions in the electrolyte bulk. The independent parameters were optimized by using BBD design. The optimized variable parameters were CD-20 mA/cm^2, initial pH-6, electrolyte concentration-1.5 g/l and ET-30 minutes. At this stage, 89% of COD removal was recorded [67,68].

3.15. Metal Cutting and Paper Recycling Effluent

The independent variables for the optimization were pH, CD, and ET. Consecutively, the dependent variables were COD and TOC from metal-cutting wastewater. The treatment cost for Al (0.371 €/m^3) electrode was less than the Fe electrodes (0.337 €/m^3) and also COD removal efficiency of the Al (COD: 93%) electrode was greater than the Fe (COD: 93.5%) electrode. The P-value <0.01 and Prob>F value was less than 0.05 observed. Which indicates the model was significant. The greater R^2 values were observed in both Al (R^2-0.927 for COD) and Fe electrodes (R^2-0.904 for COD). The actual COD, TOC, and turbidity removal efficiencies at optimized conditions are found to be 93.0%, 83.0%, and 99.8% for Fe electrode and 93.5%, 85.2%, and 99.9% for Al electrode [69]. The COD, TSS, color and ammonia removal efficiencies were practiced by EC techniques from paper recycling wastewater. The flocs of $Al(OH)_3(s)$ have large surface areas, which are useful for a rapid adsorption of soluble organic compounds and also for trapping of colloidal particles. The electrodes remove 79.5% of COD under optimum conditions such as pH-7, operating time-60 minutes and voltage-10 V. The reactor specific energy consumption was 11.5 kWh/m^3 [70–72].

3.16. Paint Manufacturing Effluent

The Al and Fe electrodes were practiced to treat paint manufacturing industry wastewater. The Fe electrode consumption was 2.67 times greater than the Al electrode consumption. Here, the pH was 6.65. The operating cost for the Fe electrode was 2.4 times expensive than the Al electrode under optimum conditions. The sludge generation rate was high in both electrodes due to the elevated dissolution rate of the anode. The Fe and Al electrodes remove 93% and 94% of COD under optimum conditions such as CD-35 A/m^2 and ET- 15 minutes. The CD is also an important parameter for controlling the reaction rate in most EC processes. It is well known that the amount of CD determines the coagulant dosage, and size of the bubble production, and hence affects the growth of flocs and bubble production. The Al electrode performance was greater for an operating cost and pollutant removal efficiency [73–76].

3.17. Grey Wastewater and Morrocan Olive Mill Effluent

The SS electrodes were employed to treat grey wastewater by using batch mode EC technique. The BBD was carried out to optimize dependent and independent variables. The greater R^2, adjusted R^2 and predicted R^2 values were recorded from quadratic model. Here, the COD was response variable. The optimum parameters were obtained for considering Derringer's desired function. The optimum variables were pH-7, CD-20 mA/cm^2, ID-5 cm and ET-20 min. The COD removal under optimum was 95.40%. The lower removal efficiencies was noticed pH beyond a six due to the formation of monomeric $M(OH)_4$ species [77, 78]. The Al electrodes practiced to the Morrocan olive mill effluent. The specific energy, electrode consumption and cost of treatment was 2.63 kWh/kg COD removed, 0.085 kg Al/kg COD and 0.27 €/kg COD removed. The five time diluted wastewater containing 20000 mg/l of COD. The 70% and above COD was removed under the optimum conditions such as ET-15 minutes, 2 g/l of NaCl and CD-250 A/m^2. Adding NaCl to the wastewater is probably a better choice for increasing the performance of the EC technique [79,80].

3.18. Medical Waste sterilization and Distillery Industry Bio-digester Effluent

The COD and phosphate was removed from the medical waste sterilization plant effluent. The total and soluble COD presents in the effluent were 2517.95 mg/l and 1821.03 mg/l. Taguchi experimental statistical analysis was carried out to optimize the independent variables such as pH, CD, concentration and ET considering to response variable such as total phosphate and COD. Taguchi experimental design method has proved to be beneficial since it not only reduces the number of experiments but also specifies controllable and uncontrollable factors. The 52.04% of COD removal efficiency was achieved under optimum conditions such as pH-5, CD-3.5 mA/cm^2, one fourth of concentration (1/4 C_0) and ET-40 minutes [81, 82]. The Al electrode was employed to treat the distillery industry bio digester effluent. The CCD was performed to optimize the dependent and independent variables. The dependent variables were CD, pH, ID and ET. The independent variable was COD removal efficiency. The significant R^2 (coefficient of determination), adjusted R^2, predicted R^2 and p values were obtained from this model. The 52.2% of COD was removed under optimum conditions such as

Table 2. The Assessment of COD removal efficiency for various industrial effluents

Source	Source / Reference	Electrode	Current Density	pH	Electrolysis Time (minutes)	Initial COD(mg/l)	Removal Efficiency(%)
Petroleum refinery	[89]	Al-Al	13	8	60	4050	42.0
Yogurt industry	[31]	Fe-Fe	30	4.53	90	6500	84
Ayurveda pharmaceuticals Wastewater	[33]	Al-Al	9.98	6.0	120	4200	63.23
		SS-SS	12.58	7.5	120	4200	85.65
Chicken Processing Plant	[17]	Fe-Fe	4	8.2	12	1140	88.5
			4	7.9	16	1142	96.2
Almond industry	[43]	DSA-Cl$_2$ (Ti/RuO$_2$) - SS	50	9	15	2000	75
Photo- voltaic wafer manufacture plant	[90]	Fe-Fe	12.5	6	300	700	75
Vegetable oil refinery	[44]	Al-Al	35	7	90	15000	98.90
Rice grain based distillery effluent	[46]	Cu- Cu	8.93	3.5	120	11500	80
Produced water from oil field	[48]	Fe-Graphite	5.90	7.36	30.94	280	66.64
Paper Industries	[50]	Fe-Fe	6.0	7.5	30	2950	82
Tannery effluent	[52]	Fe-Fe	68	7	45	12225	55.7
Textile wastewater	[18]	Al-Al	16.5	5 to 7	--	514	92.60
Automobile wash water effluent	[53]	Cu-Al	2.50	6	40	--	95.1
Real printing wastewater	[56]	Zn-SS	15	6.8	90	6950	41
		Ti-SS	15	6.8	90	6950	47
Municipal wastewater	[60]	Al-Al	4.8	--	20	--	92.01
Dairy wastewater	[57]	Fe-Fe	0.6	7	1	18300	98.0
Treatment of landfill leachate	[91]	Fe-Fe	23.80	7.73	60	7230	45.1
Potato chips manufacturing wastewater	[61]	Al-Al	20	4	30	2200 to 2800	60
Rose processing wastewater	[62]	Fe-Fe	0.80	6.4 to 7.1	20	9500	79.8
Printing ink wastewater	[63]	Al-Al	41.67	6.8-7.0	15	5000	76.78
Table olive processing wastewaters	[65]	Al-Al	166.7	5.5 - 6.0	90	3000	50
		Al-Al	5.65	--	50	1000	42.5
Egg processing effluent	[67]	Al-Al	20	6	30	3200 to 4300	89
Diesel removal from oily wastewater	[29]	Al-Al	3.125	7	40	--	99.1
Metal Cutting Wastewaters	[69]	Al-Al	6.267	5.01	24.39	17312	93.5
Paint manufacturing wastewater	[73]	Al-Al	3.50	6.95	15	19700	94
Paper-recycling wastewater	[72]	Fe-Al	--	7	60	900	79.5
Grey wastewater	[77]	SS-SS	20	7	20	646	94.75
Moroccan olive mill wastewater	[79]	Al-Al	25.0	4.2	15	20000	>70
Medical waste sterilization plant	[81]	Al-Al	3.5	5	40	--	52
Treatment of Bio digester Effluent	[83]	Al-Al	12	6	150	15600	52.23
Bulk Drug Industry	[87]	Al-Al	8	6.8	25	34000	23.53
Pharmaceutical Wastewater	[84]	C-SS	7.606	6.56	86.89	34400	30.89

pH-6, CD-120A/m^2, ID-1 cm and ET-150 minutes. If the pH_0 was less than 6, a protons in the solution get reduced to H_2, and thus, the proportion of hydroxide ion produced is less and consequently there is less removal efficiency [74,83].

3.19. Pharmaceutical and Drug Industry Effluent

The Al electrode was practiced to treat high-strength pharmaceutical effluent. The CCD was used to optimize the optimum independent and dependent variables. The dependent variables were pH, CD and ET and also independent variable was COD removal efficiency. The main advantage of using this design was the lower number of runs; it was reported be much more efficient than the other available designs, such as CCD and three-level factorial designs. The significant R^2, adjusted R^2 and predicted R^2 were obtained from the ANNOVA results. The 30.89% of COD removal efficiency was achieved under optimum conditions such as pH-6.56, CD-76.06 A/m^2 and CT-86.89 minutes [84–86]. The average COD recorded from the bulk drug industry effluent was 34000 mg/l. The Al and C electrode were employed to treat the wastewater. The C and Al electrode removes 34% of COD in 120 minutes of ET and 23.53% of COD in 25 minutes ET. The COD removal efficiency for C electrode was greater than the Al electrode. In view of high concentration of chlorides, both direct and chlorine assisted indirect oxidation routes are possible in case of electro oxidation [87,88]. The Assessment of COD removal efficiency for various industrial effluents was given in Table 2.

4. Effect of influence parameters for electrocoagulation techniques

4.1. Influence of pH

The pH of the wastewater is performing a significant role in the EC techniques. The reduction of COD was accomplished by precipitation and coagulation through metal hydroxide generated from the process. The lower and upper pH did not provide enthusiastic removal efficiency. However, The pH-8 was found to be active removal efficiency [89]. The minimum solubility of metallic species was observed at pH 6-7. If pH less than 4, $Al(H_2O)_6^{3+}$ was predominant due to hydrolysis of Al^{3+} ions in an aqueous solution. Moreover, pH between 5 to 6, the $Al(OH)^{2+}$ and $Al(OH)_2^+$ was predominant; pH>9, the $Al(OH)_4^-$ was predominant [44]. The $Al(OH)_3$ having a large surface area helpful to trap the colloidal particles and adsorb the soluble compounds, results, the peak removal efficiency was happen [72, 92]. The different metals were influenced in the EC process. The final wastewater pH was depended on an initial pH and type of electrode material. For example, the pH level for the treated wastewater by using Zn electrode was greater than the Ti electrode because of dissociation level at water molecule was higher in the Zn comparing to Ti [56] and also, the Fe electrode, the final pH was always greater than the initial pH. The wastewater having over-saturated carbon dioxide which causes increase pH due to evaluation hydrogen gas bubbles [62]. The EC process was controlling the high-level pH change in the treated wastewater because of production and consumption of hydroxyl radicals [93]. The influence of pH for removing pollutant from wastewater was given in Table 3.

4.2. Influence of Current Density

The current density was an important tool for determining the amount of metal ion generation, coagulant dosage, and bubble formation rate in the EC process. The peak pollutant removal were obtained by increasing by increasing the current density due to generation of hydroxide flocs [31] and also, the pollutant removal rate was boosted up by rising CD at certain level due to large amount of bubble generation was happen [89]. The production of higher copper hydroxides was provided greater COD removal efficiency due to precipitation and sweep coagulation. The formation of the Cu^{2+} ion was increased by increasing the CD because of the theoretical amount of metal ion supplied from the unit surface area was directly proportional to the CD [46]. The ferrous ion formation from the electrode was affected by applied current. The Fe metal hydroxides destabilize colloidal particles, and it settled down by the mechanism of precipitation. The CD was main factor to determine amount of coagulation production from an anode and it was directly proportional to total electrical charge passing

Table 3. The influence of pH for removing pollutant from wastewater

Sr.NO	Industry	Remarks
1	Oil and Crease Contaminated Wastewater	In acidic pH, the copper hydroxide ions were positively charged and predominant. Hence, the Cu^{2+} ion generation increases the COD removal efficiency, and then the solution reaches alkaline pH due to excess formation of copper insoluble species [53].
2	Potato chips manufacturing	In the potato chips manufacturing wastewater, the initial pH was varied between 2 to 8 and the final pH was reached as 3.8 to 8.6 because of hydroxyl ions accumulate in the wastewater [61].
3	Petroleum refinery	The solid aluminium hydroxide is also thought to help reduce COD by coagulating and co-precipitating with organic compounds in wastewater. Both extremely low and extremely high pH values do not favour precipitation, and the most favourable condition would be somewhere in the middle, which was discovered to be 8 [89].
4	Paper-recycling wastewater	CO_2 is oversaturated in wastewater at low pH and can be released during H_2 evolution, resulting in an increase in pH. The final pH does not change much in alkaline medium (pH> 8), and a slight drop was obtained. Because of the balance between the production and consumption of OH ions, the EC can act as a pH buffer [72].

Table 4. The influence of Current Density for removing pollutant from wastewater

Sr.No	Industry	Remarks
1	Rice grain based distillery effluent	The removal of colour and COD increases with increasing current density. Because the theoretical amount of ion supplied per unit surface area by the current density is directly proportional to CD, the number of Cu^{2+} ions increases as current density increases [46].
2	Grey wastewater	The COD removal efficiency was increased CD up to 20 mA/cm^2. After increasing the CD, the removal efficiency was observed to be stable. Coagulant production on the anode and cathode increases as current density increases. [77].
3	Paper-recycling wastewater	The pollutant removal efficiency was decreased by the mechanism of destabilization. Some were: neutralization of charge, compression of the double layer, and floccreation [56].

through the system [48, 50]. The corrosion and oxide layer formation on anode surface was happen by increasing CD after certain interval. it was affected by the pollutant removal efficiency due to passivation effect [53]. The sludge production was increased by increasing the CD because of coagulant and metal hydroxide formation is directly proportional to CD. For considering this stats, the sludge production rate was more in Al and Fe electrodes due to elevated dissolution rate of the anode [29]. The COD removal efficiency dependant on the charge supplied to the unit volume of solution [94]. The influence of Current Density for removing pollutant from wastewater was given in Table 4.

4.3. Effect of Electrolysis Time

ET is the most important parameter in the EC process. The higher operating time consumes maximum energy consumption and operating cost. Hence, the optimization of ET is a necessity for cost-effective economical treatment [95]. During the electrolysis operation, the anodic reactions occurred in the positive electrode and cathodic reactions occurred in the negative electrode. The production of metal ions was determined by an ET. The released ions were neutralized the charged particles and the pollutant removal was occurred by the principle of coagulation [96,97]. According to the Faradays law, the coagulant generation was increased concerning to operational time. With increasing ET, the passivation of the electrode surface increased, resulting in the formation of an impermeable layer on the anode surface. It had an effect on the efficiency of pollutant removal [31, 33].

The COD removal efficiency depended on the concentration of metal ions released from the electrode and operation time [17]. The production of metal ions or hydroxyl radicals was increased by increasing the reaction time and it makes hydro complexes to removes the pollutants in wastewater [63]. The hydroxide flocs and metal ion concentration were increased with increasing the ET and it accelerates the bubble generation rate. The enlargement of flocs occurred during the EC process as a result of charge neutralisation. The flocs broke due to the sheer effect of the stirrer and the formation of unstable flocs [98, 99]. The influence of Electrolysis Time for removing pollutant from wastewater was given in Table 5.

4.4. Influence of Conductivity

The sodium chloride was effective electrolyte material comparing other electrolytes. The electrochemical cell resistance was increased by the presence of chloride ions due to the formation of the insulating layer on the electrode surface [100]. The role of electrolytes was to increase the conductivity of the solution and reduce the cell voltage due to the reduction of ohmic resistance of the wastewater [93]. The hypochlorite ions were produced by adding sodium chloride to the EC system and the pollutant removal was observed because hypochlorite ions act as a strong oxidizing agent. The excess amount of electrolyte minimizes the pollutant removal efficiency [101, 102]. The disadvantage of NaCl electrolyte was producing toxic chloro-or-

Table 5. The influence of Electrolysis Time for removing pollutant from wastewater

Sr.NO	Industry	Remarks
1	Oily wastewater	The concentration of metal ions and their hydroxide flocs increases as the electrolysis time increases, and thus the COD and diesel removal efficiencies increase. The efficiency of COD and diesel removal is directly proportional to the concentration of metal ions produced by the electrodes. Because metal ions and their hydroxide flocs covered the electrode surface, the pollutant removal efficiencies were nearly constant after 40 minutes of operation. Furthermore, electrode passivation occurred, and the concentration of metal ions and their hydroxide flocs became constant; as a result, the COD and diesel removal efficiencies did not change significantly [29].
2	COD removal from produced water	The removal efficiencies were studied over a time range of 10 to 50 minutes. The COD removal efficiency was increased with increase operational period up to 30 minutes. After increasing operational time, no more significant removal efficiency was found. Increasing the time to 40 and 50 minutes provided a slight reduction in pollutants, which would not have been possible due to the high energy and electrode consumption [48].
3	Olive mill wastewater	The effect of operational time was studied from 3, 6, 10, 15 and 20 minutes interval. In order to remove pollutant in olive mill wastewater, the optimum operational period fifteen minutes was optimized [79].

ganic compounds during the EC process [103]. The chloride ion has reduced the passivity of the electrode surface due to this catalytic action. The chloride ions reduce the passivation effect and increase the current efficiency [95]. The additional coagulant was generated by adding electrolytes because it increases the CD of the solution [98]. The influence of conductivity for removing pollutant from wastewater was given in Table 6.

4.5. Influence of Inter-electrode Distance

The applied current rate was dependant on the space between the electrodes. The current consumption was high in increasing an ID due to variation of electrode resistance [97]. The pollutant removal efficiency was low at greater ID because the rate of Al oxidation and kinetics of charge transfer was low and also resistance to mass transfer was high [100]. The short circuits were occurred by providing a small gap between anode and cathode. The production of oxidizing iron was reduced by increasing the ID because the power consumption was directly proportional to the cell voltage [93, 104]. The ohmic resistance affect the pollutant removal efficiency and rate of electrode energy consumption. The growth of passive anode film and resistance was increased with increasing ID. The flocs degradation was occurred by providing a short ID because of high electrostatic attraction [105]. The pollutant removal efficiency was decreased further increasing the ID because of movement of ions in the solution was decreased. The voltage drop was occurred by an increasing distance between electrodes [106, 107].

In industry wastewater treatment, Maximum pollutant removal efficiency was observed for both current (AC & DC) with iron and stainless steel electrodes at a distance of 1 cm, and increasing the inter-electrode intervals decreases pollutant removal percentage. This high efficiency is most likely due to electro statistic effects caused by the distance between the electrodes. When this distance increases, the electro statistic effect decreases, the mobility of the produced ions decreases, and there is more time for accumulation and clot formation [97]. At author Hashim et al., to treat the EC for removing fluoride from drinking water, results, a series of batch experiments were performed at different IDs such as 5, 8, and 11 mm using a constant CD of 1 mA/cm^2, a time of 25 minutes, and an initial pH of 6. The removal of residual fluoride increased from about 4% to about 15% when the ID was increased from 5 mm to 11 mm. If increasing the ID, the supplied current and amount of flocculants generation was decreased due to increase in resistance and growth of the passive anodic fil [105].

4.6. Influence of Stirring Speed

The movement of ions increased with increasing the agitation speed. At a certain level, the removal efficiency was affected due to flocs degradation, and adsorbed organic content was desorbed. When increasing the agitation speed, the lighter particles float on the surface of the liquid and it serves precipitation [108]. The higher rotational speed has increased a collision in the wastewater and also affect the thickening of flocs and metal hydroxides [109]. The agitation helped to maintain uniform conditions in the beaker and increase the velocity of the ions. The removal efficiency was increased by increasing the rotational speed because flocs were attached. The pollutant removal efficiency was increased with increasing the agitation speed, After optimum conditions, the efficiency was deceased due to desorption of adsorbed particles [102, 110].

For treating distillery spent wash effluent, the author carried out experiments by varying the agitation speed from 200 to 600 rpm to investigate the effect of agitation speed on the COD removal efficiency. As the agitation speed increases, so does the movement of the generated ions, resulting in greater interaction among the ions. The higher the interaction, the more flocs are formed, which are required to coagulate the organic matter. The optimum agitation speed is 500 rpm, and increasing it from 500 to 600 rpm reduced COD removal efficiency. After optimum, the removal efficiency was decreased due to desorption organic matters [108] and also, for considering textile effluent, As the distance between electrodes increases, COD removal variations are found. The amount of COD increased by 70.66% as the distance increased from 1 to 4 cm. In order to get the maximum COD removal efficiency, the two centimetre inter electrode distance was identified as optimum [110].

4.7. Influence of Retention Time

The time provided to settle down the coagulant species after the electrocoagulation process is generally termed as the retention time. The particles were separated from the wastewater where the velocity of particles was greater than the velocity of wastewater flow. The pollutant removal was occurred by increasing retention time due to an increase in the rate of sedimentation of sludge [102, 111]. The COD removal efficiency was increased with an increase in the retention time. After optimum conditions, the removal efficiency

Table 6. The influence of conductivity for removing pollutant from wastewater

Sr.NO	Industry	Remarks
1	Phosphate Mining Process Water	In the EC process, electrolyte was used to increase effluent conductivity, which reduced the voltage between the electrodes at a constant current density. A NaCl is the most effective supporting electrolyte for EC. At 30 minutes interval, increasing the NaCl dose from 0.5 to 4 g/L increased the removal efficiency from 32.8 to 39.8%. In terms of energy consumption and removal efficiency to prevent rapid electrode dissolution, a NaCl dose of 4 g/L appeared to be optimal [100].
2	Textile dye wastewater	The operating cost of iron and aluminium electrode materials decreases as conductivity increases. Whereas as conductivity increases, COD removal efficiency decreases slightly in the case of aluminium and increases slightly in the case of iron electrode. The percentage of the electrode consumption cost to total cost for aluminium is nearly constant at 76%. By increasing conductivity from 1000 to 4000 S/cm, this ratio increases from 33 to 58% for iron [71].

was decreased due to the desorption of adsorbed dye molecules [110]. To investigate the effect of retention time on dye removal efficiency, experiments were carried out and the solution was allowed to settle for various retention times. The dye removal efficiency increased from 68 to 98% as retention time increased from 30 to 150 minutes. The Dye removal efficiency decreased as retention time increased from 150 to 180 minutes due to desorption of adsorbed dye molecules [102].

5. Conclusions

The electrocoagulation technology has been effectively used for removing COD from various industrial effluents. The COD removal efficiency depends on the concentration of metal ions and the process influencing factors such as pH, Current Density, Electrolysis Time, Conductivity, Stirring Speed, and Retention Time. From the literature review, the important findings are listed below:

- The COD removal efficiency was found to be minimum at higher acidic and basic conditions.
- The current density is the most important factor in determining coagulant generation from an electrode, and it is also directly proportional to the electrical charge passing through the system.
- As electrolysis time increases, production of metal ions and hydroxyl radicals increase thus enhancing COD removal efficiency.
- Excess use of electrolyte reduces the efficiency of pollutant removal.
- Because power consumption is directly proportional to cell voltage, increasing the inter electrode distance reduced metal iron production. which have an impact on pollutant removal efficiency
- Higher stirring speed leads to more collisions in wastewater, thus influencing the thickening of flocs and metal hydroxides during the process.
- Thus, Electrocoagulation techniques efficiently remove COD from a wide range of industrial effluents, benefiting small-scale industries with limited wastewater treatment space.

6. Future outlooks

The electrocoagulation technology for removing COD from various specific industrial effluents can be investigated. Further research can be done in hybrid electrocoagulation system such as sono-electrocoagulation, peroxy-electrocoagulation, photo-electrocoagulation and microwave electrocoagulation technique in order maximize the removal efficiency and lower the expenses. Further research can also be done on various factors that influence the hybrid process as well as optimization and modelling of the factors.

Author Contribution

M.S. (PhD student) conducted all the literature review and wrote the manuscript.

S.R. (Professor) supervised and revised the manuscript.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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