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Preventing of Cathode Passivation/Deposition in Electrochemical Treatment Methods – A Case Study on Winery Wastewater with Electrocoagulation

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Additional information is available at the end of the chapter

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1. Introduction

Electrochemical methods and processes have been applied for many years in environmental applications such as water/wastewater treatment, recovery of metals, electroplating and qualitative/quantitative analysis in various aqueous media. Among these processes, electrocoagulation (EC) has gained many interest due to providing simple, reliable and cost effective operation for the treatment of wastewaters without and need for additional chemicals, and thus the secondary pollution. EC is declared an environment-friendly technique since the 'electron' is the main reagent and does not require addition of the reagents/chemicals. This will minimize the sludge generation to a great extent and eventually eliminate some of the harmful chemicals used as coagulants in the conventional effluent treatment methods. EC process can effectively destabilize small colloidal particles and generates lower quantity of sludge compared to other processes [1]. This technique uses a direct current (DC) source between metal electrodes immersed in polluted water [2]. In this method, soluble metal electrodes (such as iron and aluminium mostly) form metal hydroxides when subjected to a suitable current. The metal hydroxides act as coagulants and lead to the removal of various contaminants [3]. The pros and cons of the EC are tabulated in Table 1

EC is an efficient technique since adsorption of hydroxide on mineral surfaces are a 100 times greater on 'in situ' rather than on preprecipitated hydroxides when metal hydroxides are used as coagulant [3]. Besides, the 'electron' is the main reagent and does not require addition of the reagents/chemicals, which will minimize the sludge generation to a great extent and eventually eliminate some of the harmful chemicals used as coagulants in the conventional

effluent treatment methods. EC process can effectively destabilize small colloidal particles and generates lower quantity of sludge compared to other processes [1]. EC has been successfully applied to the treatment of a lot of wastewaters including either organic or inorganic pollutants as well as drinking waters due to its benefits: environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness. Additionally, electrochemical based systems allow controlled and rapid reactions, smaller systems become viable and, instead of using chemicals and micro-organisms, the systems employ only electrons to facilitate water treatment [3, 5]. However, the main drawback of conventional EC (DC-EC) is inevitable formation of an impermeable oxide film on the cathode, which results in lower removal performance of pollutants and higher operating costs (due to higher energy consumption) [3, 6].

In the EC process, an electric field is applied to the medium for a short time, and the treated dispersion transferred to an integrated clarifier system where the water-contaminant mixture separates into a floating layer, a mineral-rich sediment, and clear water. The aggregated mass settles down due to gravitational force. The clear water can be extracted by conventional methods [4]. Generally, DC power supply is traditionally employed to generate an electric field and ion transportation between the immersed sacrificial electrodes in the EC reactor. However, the major threat of the EC process using DC is that an impermeable oxide film may be formed on the cathode during the electrolysis. This leads a “*cathode passivation*”, which decreases the ionic transfer between the anode and cathode directly, hindering the metal dissolution and indirectly preventing metal hydroxide formation. Electrolytic dissolution of anode and electrolytic deposition of cathode in the EC cell employing DC power supply are schematically shown in Fig. 1. The DC-EC technology is inherent with the formation of an impermeable oxide layer on the cathode as well as deterioration of the anode due to oxidation. These limitations of the DC-EC process have been minimized to some extent by the addition of parallel plate sacrificial electrodes in the cell configuration. However, many have preferred the use of alternating current (AC) power supply in EC process [4, 7]. According to the reference [4], the AC cyclic energization is believed to retard the normal mechanisms of electrode attack that are experienced in DC-EC system, and thus, ensure reasonable electrode life. In addition to that, since the AC electric fields in an AC-EC separator do not cause electrophoretic transport of the charged particles due to the frequent change of polarity, it can induce dipole–dipole interactions in a system containing nonspherical charged species. As a result, the AC electric fields may also disrupt the stability of balanced dipolar structures existing in such a system. This is, however, not possible in a DC-EC separator using DC electric fields.

To prevent the main disadvantage of the EC, cathode passivation, AC can be preferred as power supply or anode and cathode can be replaced periodically with each other in DC mode. However, the latter option is not feasible for continuous operations in practical. The alternating pulse current (APC) method was proposed with experimental results in detail for the first time by Mao et al. [8] by using AC power. However, the rectangular wave produced by “a time relay from already existing DC power supply” was declared by Eyvaz et al. [9] for the first time in EC applications.

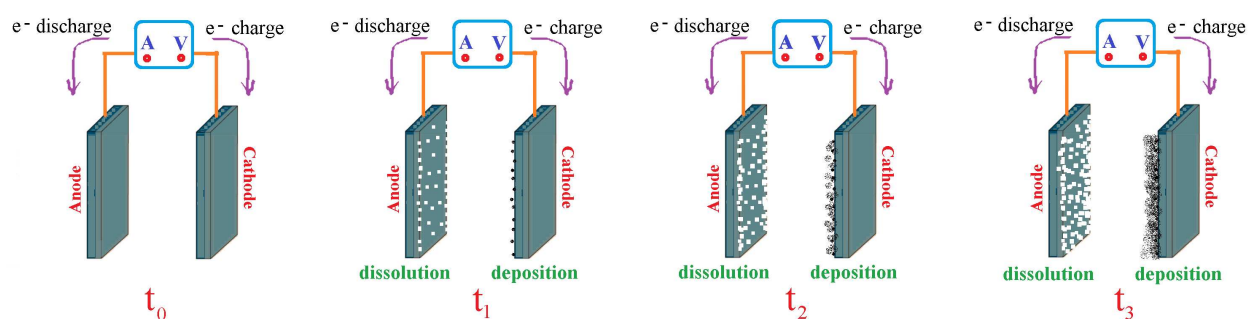


Figure 1. Schematic representation of electrode surface change during the EC treatment using DC supply (t_0 – t_3 are treatment times of continuous process in order).

Mao et al. [8] proposed a novel current feed style in electrocoagulation aiming at preventing the cathode passivation by using AC in synthetic oily wastewater. They investigated the effects of APC on the aluminium electrodes' surfaces by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), not observing passivation of Al, also achieving uniform dissolution of anode and cathode. Similar to APC, periodic reversal current feed was obtained by a simple time relay device integrated with a DC power supply by Eyvaz et al. [9]. They used this system to prevent electrode passivation of aluminium electrodes in EC of textile dye solutions. Their results indicated that APC was found superior to DC and higher removal efficiencies in shorter operation times and longer fill-and-draw periods could be gained by APC. Removal efficiencies increased in APC system after optimum operation time belongs to DC system as well. In another research containing the comparison of AC and DC, Vasudevan et al. [10] reported that under the identical experimental conditions, similar cadmium removal efficiencies (97.5% and 96.2%) were achieved. However, the benefits of reducing energy consumption were two fold with AC (0.665 and 1.236 kWh/m³ for AC and DC, respectively).

According to the research of Keshmirizadeh et al. [11], equal removal efficiencies were obtained in direct current and alternating pulse current. In the APC mode, the water recovery was very significant, measuring as high as 0.92 m³/m³ wastewater. For DC mode, the water recovery was less than 0.5 m³/m³ of wastewater. The APC mode was found to be more efficient than the DC mode with a lower anode over-voltage, slower anode polarization and passivity, and lower tank voltage. The operating time was 3–25% less when APC mode was used, based on initial Cr(VI) concentration of 50–1000 mg/L, respectively. Because of the reduction in operating time, less energy was consumed, which made the APC mode more cost effective. Application of APC eliminated uneven wear (dissolution) of electrodes; typically, the anode material dissolved and electroreduction products stuck to the cathodes when DC mode was used. When the APC mode was employed, electrocoagulation produced a highly dense or compact sludge at the reactor bottom, resembling dense clay soil layers. It also produced more clear supernatant. The APC mode minimized waste and increased sludge stability.

More recently, periodic electrode reversal method (PREC) in EC was optimized by response surface methodology (RSM) for color removal of synthetic Methyl Orange wastewater by Pi et al. [12]. Color removals of 97 % with PREC and 82 % with conventional EC were gained in

the optimal RSM conditions. It is concluded that EC with PREC can effectively retard cathodic passivation by resulted in lower energy and electrode material consumptions.

Although many researches on treatment of synthetic or real industrial wastewaters with EC are available, very few researches have been carried out on the economical applicability of AC electrocoagulation. Therefore, in this chapter, the effects of power supply type (DC or AC) on EC performance were investigated both technically and economically. An adjustable time relay plugged into the DC power supply was employed to obtain APC to avoid additional AC power supply cost. Winery wastewater was selected as the model electrolyte solution due to its high strength pollutant capacity and APC, an (almost) new method, was applied to the winery wastewaters for the first time with this study.

2. Brief description of electrocoagulation

EC is a complicated process involving many chemicals and physical phenomena that use consumable electrodes to supply ions into the wastewater stream. In an EC process the coagulating ions are produced 'in situ' and it involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the 'sacrificial electrode', (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs. The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions have been described in broad steps and may be summarized as: (1) Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode, (2) Charge neutralization of the ionic species present in wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic interparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process. (3) Floc formation; the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium. The solid oxides, hydroxides and oxyhydroxides provide active surfaces for the adsorption of the polluting species. EC has been successfully employed in removing metals, suspended particles, clay minerals, organic dyes, and oil & grease from a variety of industrial effluents [3]. A brief literature review of EC efficiency on the treatment of different waters/wastewaters is presented in Table 2.

In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminium, which causes two separate reactions: (1) Fe/Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyze to polymeric iron or aluminium hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions and precipitation or physical and chemical attachment to colloidal materials being generated by the electrode erosion. They

are then removed by electro-flotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated in situ. (2) Water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and, through natural buoyancy, float the flocculated pollutants to the surface [3]. The most important reactions are summarised in Fig. 2.

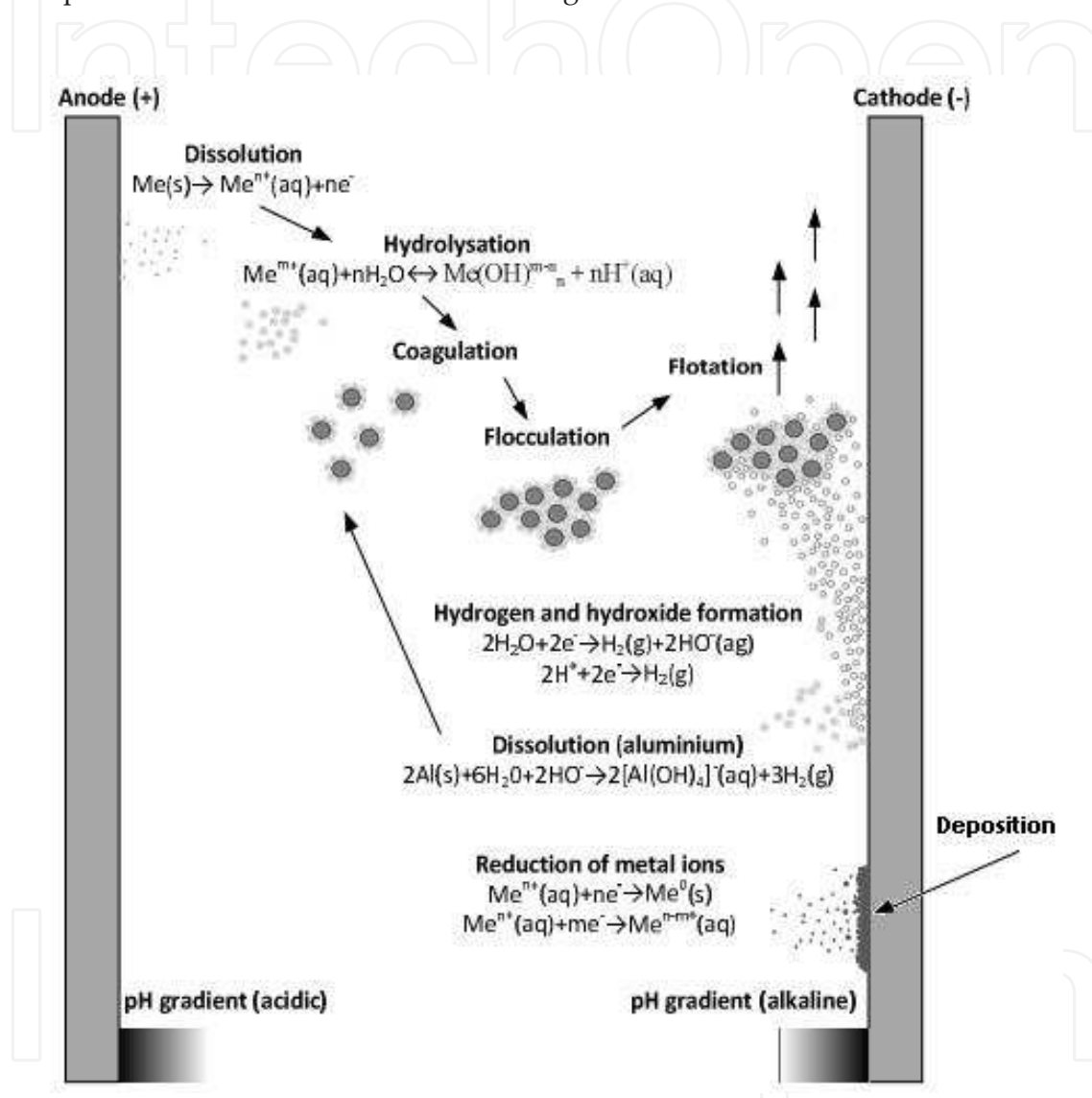
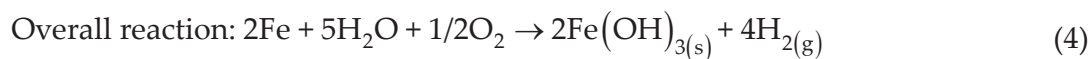
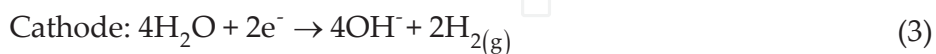
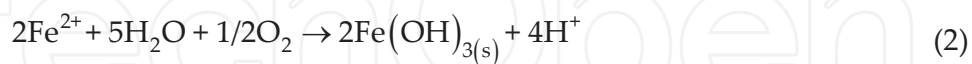


Figure 2. Schematic representation of typical reactions during the EC treatment using DC supply [13].

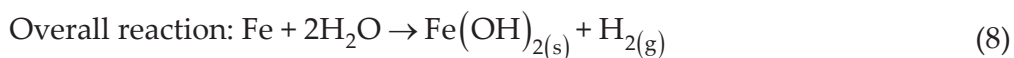
The (EC) process involves generation of coagulants in situ by dissolving sacrificial anodes such as aluminium or iron upon application of a DC. When iron electrode is used as anodes upon oxidation in an electrolytic system, it produces iron hydroxide, $Fe(OH)_n$ where $n=2$ or 3 [14, 15]. The major disadvantage of EC compared to chemical coagulation (usually ferric or aluminium chloride/sulfate) is that high conductivity water is required. This fact is especially relevant for drinking water treatment, as conductivity can not be enhanced by salts due to total

dissolved solids (TDSs) limitations in drinking water [16]. Two mechanisms for the production of metal hydroxide have been proposed when iron electrodes are used [17, 18]:

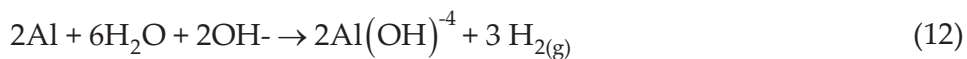
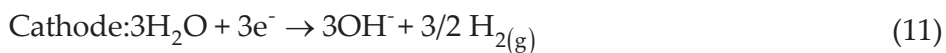
Mechanism I:

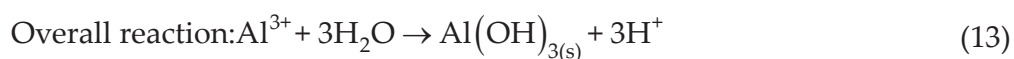


Mechanism II:



When aluminium electrodes in the EC process are used as an anode and a cathode, the main reactions are at the anode as follows [19-22]:





The performance of the EC process depends on many operational parameters such as pH of the solution, applied current to the reactor, conductivity of the (water/wastewater) solution, electrolysis time as well as electrode specifications such as arrangement of electrode, electrode shape, distance between the electrodes, etc. Main operational parameters influencing the EC efficiency is schematically given in Fig. 3. The effects of each parameters in details can be found elsewhere in the literature. However, in this study, effects of six of the parameters such as pH of the winery wastewater (by adjusting the pH with acid or base), arrangement of the sacrificial electrodes (parallel or serial connection to power supply), electrolysis time (duration of applying voltage to the wastewater), current density (applied current to the unit area of active electrode surface) and especially power supply type (by changing the polarity of the anodes and cathodes) were investigated.



Figure 3. Schematic display of the various operating parameters influencing the EC process performance.

2.1. Brief description of alternating pulse current electrocoagulation

Usually, DC is used in EC systems. In this case, an impermeable oxide layer may form on the cathode material as well as corrosion formation on the anode material due to oxidation. This prevents the effective current transfer between the anode and cathode, so the performance of EC reactor declines. These disadvantages of DC have been diminished by the addition of parallel plate sacrificial electrodes in the EC unit configuration. However, many have preferred

the use of AC in EC unit [7]. It is believed that the cyclic energization between the anode–cathode in AC system delays the cathode passivation and anode deterioration that are experienced in DC system, and thus, ensure reasonable electrode life [4]. A hypothesis for the lower electrode consumption with AC is that since DC only flows in one direction, there may be irregular wear on the plates due to the onslaught of the current and subsequent oxidation occurring in the same preferential points of the electrode. In the case of AC, the cyclical energization retards the normal mechanisms of attack on an electrode and makes this attack more uniform, thus ensures longer electrode life [23].

There are a few studies in which (AC) has been tested although typically DC has been used in EC systems. Vasudevan *et al.* [24] studied the removal of fluoride from water with DC and AC EC systems. They observed similar removal efficiencies with both technologies. However, energy consumption was slightly lower with AC technology. Eyvaz *et al.* [9] used APC in their study. APC enhanced removal efficiency compared to DC current. Pollutant removal decreases over the course of time with DC systems, possibly due to passivation of electrodes, whereas in an APC system this was not observed. Polarity reversal has also been suggested by other authors to reduce passivation of electrodes [25].

Schematic display of current waves of AC and APC systems are given in Fig. 4. An adjustable time relay plugged into the DC power supply was employed to obtain APC (It also represents AC in our study). According to EC unit with time relay system, turn on and turn off modes switch to positive pole to negative pole or reversion to it. For example, when the time relay is turned on in an EC reactor including two electrodes namely 1 (anode) and 2 (cathode), electrode 1 is then converted to cathode while electrode 2 is becoming anode. When the time relay is turned off, only DC system is in circuit, electrode 1 becomes anode this time. Current wave in real AC is shown as sine wave in Fig. 4.

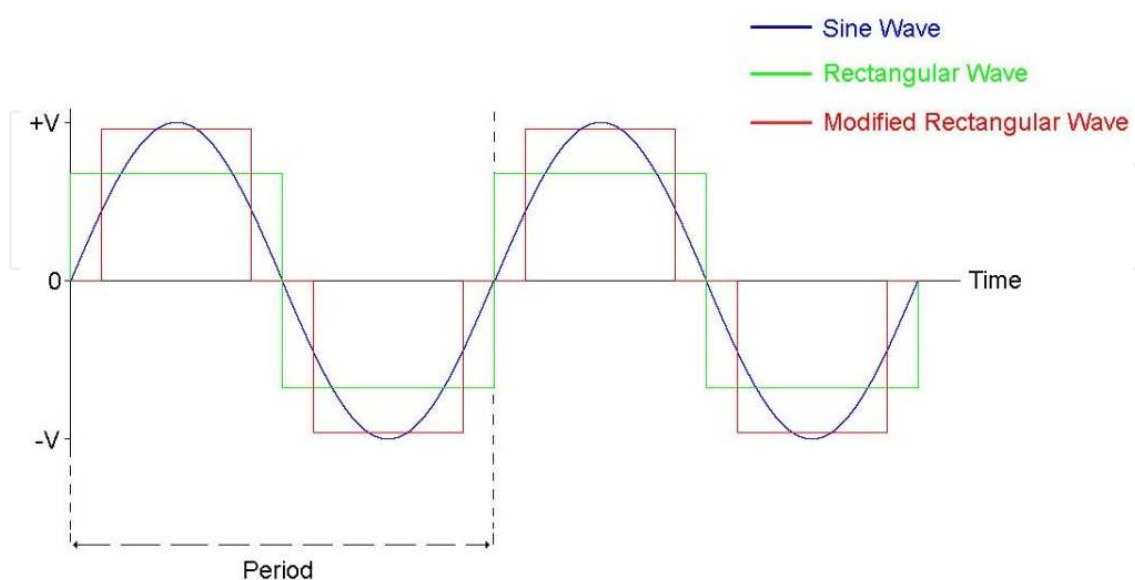


Figure 4. Schematic display of current waves of AC and APC systems.

3. Winery industry, winery wastewaters and treatment methods

Wine production processes generate organic and inorganic pollutions mostly associated with solid wastes and liquid effluents. The liquid effluents usually referred as “winery wastewater” are mainly originated in washing operations during grape harvesting, pressing and first fermentation phases of wine processing [26-29]. Winery wastewater is produced in significant volumes around the world [30-32]. Each winery is also unique in wastewater generation, highly variable, 0.8 to 14 L per litre of wine [33-35] and is characterized by high contents of organic material and nutrients, high acidity and large variations in the seasonal flow production [36, 37] and is generated mainly as the result of cleaning practices in winery, such as washing operations during crushing and pressing grapes, rinsing of fermentations tanks, barrels washing, bottling and purges from the cooling process. As a consequence of the working period and the winemaking technologies, volumes and pollution loads greatly vary over the year [35]. The organic matter might reach during vintage periods up to >30,000 mg/L chemical oxygen demand (COD), and the high sodium adsorption ratio (SAR>15) make such water inadequate to be disposed to common sewage systems [37,38].

Although different varieties of grapes and strains of yeasts result in different types of wine and consequently winery wastewaters with different characteristics, in general, the typical raw winery wastewater presents a pH between 3 and 4, COD ranges from 320 to 296,119 mg O₂/L and BOD₅ values around 125–130,000 mg O₂/L [32, 39]. The main organic compounds present in this kind of wastewaters are soluble sugars (fructose and glucose), organic acids (tartaric, lactic and acetic), alcohols (glycerol and ethanol) and high-molecular-weight compounds, such as polyphenols, tannins and lignin [39, 40].

Wine distillery wastewater, the product of the distillation of ethanol, wine and waste biological material, produces large volumes of liquid that involves unacceptable environmental risks [41-47]. The disposal of the untreated waste from the wine sector causing salination and eutrophication of water resources; waterlogging and anaerobiosis and loss of soil structure with increased vulnerability to erosion [33, 35].

Several winery wastewater treatments are available, and among them biological treatment methods have been recognized as a reasonable alternative way for a significant degradation of wastewater with high organic content, however, the presence of recalcitrant compounds for the microorganisms frequently makes impossible the complete treatment of a winery wastewater [27, 29]. The winery wastewater treatment technologies can be sorted as natural evaporation in ponds, evaporation–condensation with or without combustion, direct dispersion on soil as a fertilizer and intensification of the natural evaporation capacity of the ponds by means of sprinklers and panels as physicochemical methods; aerobic or anaerobic treatment, trickling filters, lagoons as biological methods [30, 47-49]. These methods classified as schematically in Fig. 5.

Advantages	Drawbacks
<ul style="list-style-type: none">☑ Needs simple equipments, designable for virtually any size,☑ Cost-effective, and easily operable,☑ The start-up and operating costs are relatively low,☑ Low maintenance cost with no moving parts,☑ No chemical addition is required,☑ Minimum chance of secondary pollution,☑ Needs low current, and it can be run even by green processes, such as, solar, windmills and fuel cells,☑ Effectively destabilize small colloidal particles,☑ Produces minimal sludge,☑ Lowering the sludge disposal cost,☑ Gas bubbles (produced during electrolysis) can enhance flotation,☑ Removes many species that chemical coagulation cannot remove,☑ More readily filterable and can be utilized as a soil additive,☑ Contains metal oxides that pass the leachability test,☑ Gives palatable, clear, colorless and odorless water.	<ul style="list-style-type: none">☒ The 'sacrificial anodes' need to be replaced periodically.☒ Requires a minimum conductivity depending on reactor design, limiting its use with water containing low dissolved solids.☒ In case of the removal of organic compounds, some toxic chlorinated organic compound may be formed in situ if chlorides are also present.☒ Wastewater with high humic and fluvic acid content may be amenable to the formation of trihalomethanes.☒ If phenols and algal metabolic and decomposition products are present, chlorine may lead to bad taste and odor.☒ An impermeable oxide film may be formed on the cathode that may interfere with the performance of the EC cell.☒ The cost of operating EC may be high in those are as where the cost of electricity is high.

Table 1. Advantages and drawbacks of the EC process.

COD and BOD of the winery wastewater can be removed significantly by biological treatment. However, the color of the wastewater remains dark brown as that before the treatment because of the non-biodegradable colored compounds such as melanoidins that can be degraded only 6–7% by biological treatment [47, 49-51]. EC process produces coagulants such as iron or aluminium (Al) hydroxides having a considerable sorption capacity by anodic dissolution and also pollutants are removed simultaneously by deposition on cathode electrode or by flotation due to the hydrogen gas produced at the cathode [47, 52-55]. Because the wastewater is not enriched with anions, the sludge produced in EC process is more compact than the sludge generated by chemical coagulation [47, 55]. Besides this, EC process has many advantages like simple equipment, easy operation, a shortened reactive retention time and less sludge amount when compared chemical coagulation [2, 47].

In recent years EC technique has been applied to the wastewaters generated from food industry such as distillery and fermentation [1, 49, 51, 56-58], dairy [59-61], potato chips manufacturing [21], pasta and cookie process [62], poultry slaughterhouse [63-65], and yeast [20, 66]. Although in literature, there are a lot of studies including various treatment methods shown in Fig. 5, there have been very few research [46, 47, 67] conducted about technical and economic analysis of EC process on winery industry wastewaters. Therefore, the purpose of this work is to examine the treatment performance of EC process employing Fe and Al electrodes on winery wastewater when investigating the APC on the overall EC efficiency.

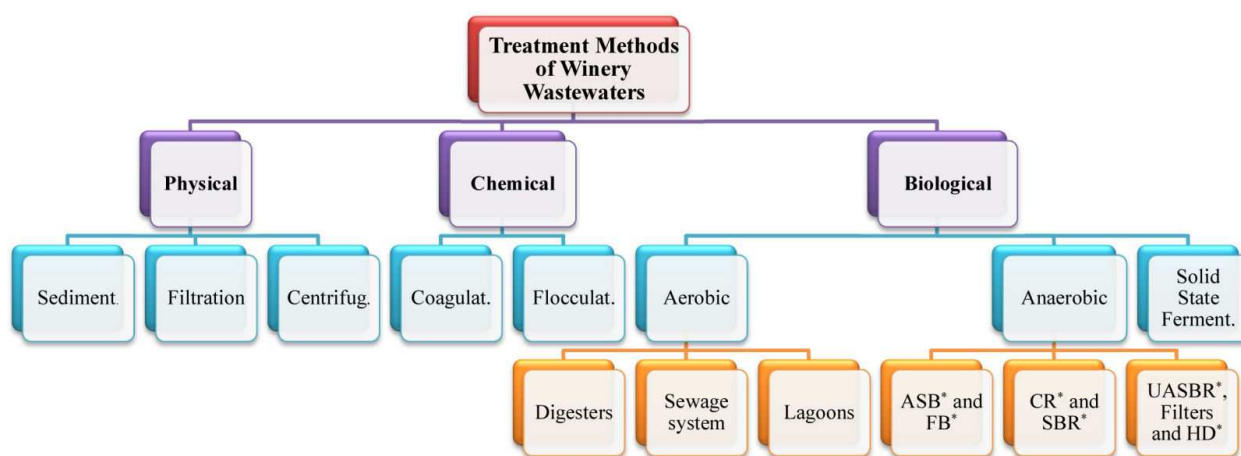


Figure 5. Schematic representation of various methods used in the treatment of winery wastewaters, *: ASB: Anaerobic sludge beds, FB: Fluidized beds, CR: Contact reactor, SBR: Sequencing batch reactor, UASBR: Upflow anaerobic sludge blanket reactor, HD: Hybrid digesters.

Pollutants	Electrode material	Operational parameters investigated	Summary of the work	Ref.
Winery	Aluminium, iron, stainless steel	Initial pH, current density and electrolysis time	<ul style="list-style-type: none"> When Fe electrodes were used under optimal conditions, the removal efficiencies of COD, color, and turbidity were calculated as 46.6, 80.3, and 92.3%, respectively. They were found as 48.5% for COD, 97.2% for color and 98.6% for turbidity, when Al electrodes were used. A new approach combining electrochemical methods with ultrasound in the strong electromagnetic field resulted in significantly better removal efficiencies for majority of the measured parameters compared to the biological methods, advanced oxidation processes or electrocoagulation. 	[47], [67]
Paper-pulp mill	Aluminium, iron	Initial pH, temperature, current density, treatment time.	<ul style="list-style-type: none"> Temperature has negative effect on the removal efficiency. Al–Al has a high efficiency in the color removal and Fe–Fe is effective in the COD and Phenol removal. Pimaric-type acids were removed with higher efficiency than abietic-type resin acids. EC had no significant effect on bacterial toxicity despite a high removal efficiency of resin acids and copper. The sludge aptitude to settling is better with Fe electrodes than with Al electrodes. 	[68-70]
Textile effluents, dyes	Aluminium, iron, stainless steel	Initial pH, current density, anode-cathode polarization	<ul style="list-style-type: none"> Anode–cathode polarization reduces the reaction for removing TOC and dye from aqueous solutions. 	[9], [71], [72]

Pollutants	Electrode material	Operational parameters investigated	Summary of the work	Ref.
		period, power supply type, electrode material, electrode connection mode.	<ul style="list-style-type: none">• EC employing SS electrodes was more economical; consumed less material and produced less sludge, and pH of the medium was more stabilized than EC with Fe electrodes.	
Boron removal	Aluminium, iron	Initial pH, current density, initial boron concentration, treatment time, temperature	<ul style="list-style-type: none">• 98 % removal of boron from produced water was achieved.• Adsorption is chemisorption and endothermic.• The effect of water purification for higher boron concentrations in the solution is better than for low ones.• For the iron and aluminium electrodes, pH = 6 is the most suitable value, and the aluminium anode is the best one for the boron removal.• The highest current density gave the quickest treatment for boron removal from synthetically prepared waters containing boron equivalent industrial wastewaters.	[73-75]
Landfill leachate	Aluminium, iron	Electrode material, current density, initial pH, operating time, Cl ⁻ concentration	<ul style="list-style-type: none">• Aluminum supplies more COD removal (56%) than iron electrode (35%) at the end of the 30 min operating time.• Coagulation and EC treatment mainly affected hydrophobic molecules and after treatment 30% of the initial BDOC quantity was removed.• Electrolysis (and as a consequence EC) increased the amount of hydrophilic organic compounds of lower apparent molecular weight.• Under conditions of iron electrode, 4.96 mA/cm² current density, 2319 mg/L Cl⁻ concentration, 90 min electrolysis time and unchanged the raw pH (6.4-7.3), the removal efficiencies of COD, NH₃-N, TP, BOD₅ and turbidity are 49.8, 38.6, 82.2, 84.4 and 69.7%, respectively.	[76-78]
Drinking water	Aluminium, iron, stainless steel	Anode metal type, NOM source, initial NOM concentration, co-occurring solutes, initial fluoride concentration, electrode connection type.	<ul style="list-style-type: none">• Between the three metals tested, iron was the least costly and most available material, it presented greater DOC removal, it showed no passivation layer and linear voltage ramp, and residual metal met guideline values.• Removal of fluoride was better for bipolar connection than for monopolar connection.• The operating costs for monopolar and bipolar connections were 0.38 and 0.62 US\$/m³, respectively, for the initial fluoride concentration of 10 mg/L.	[16], [79], [80]

Pollutants	Electrode material	Operational parameters investigated	Summary of the work	Ref.
			<ul style="list-style-type: none"> The residual arsenic concentration was maintained below the limiting value recommended during a period of 16 h of continuous mode operation for EC-MF system. 	
Olive mill	Aluminium, iron	Electrolysis time, current density, chloride concentration, initial pH, settling time, electrode material and polarization, amount of hydrogen peroxide, addition of coagulant-aid	<ul style="list-style-type: none"> EC can remove more than 70% of COD, polyphe-nols and dark color. EC treatment makes good solid matter and turbidity removal efficiency, 71% and 75%, respectively. EC in the absence of coagulant aid and oxidant is not too efficient for the treatment of this type of wastewater. 	[81-83]
Oily wastewaters	Aluminium, iron, steel	electrode connection mode, current density, initial oil concentration, pH, NaCl dosage	<ul style="list-style-type: none"> The best performance was obtained using mild steel MP electrode system. EC process operated under the optimal conditions involves a total cost of 0.46 US\$ per cubic meter of treated oily bilge water. The oil removal efficiency showed its best values at high current density values, high initial oil concentration with an emulsion of pH around 7. Sacrifice anode like Fe found to be more effective than Al for the removal of sulfide species and organic matters. 	[55], [84], [85]
Poultry slaughterhouse, manure	Aluminium, iron	Stirring speed, current density,	<ul style="list-style-type: none"> It has been possible to decrease COD of poultry slaughterhouse wastewater about 2170 mg/L to a less than 300 mg/L in a matter of 30 min. under stirring speed of 150 rpm, initial pH 3 and a current density of 1.0 mA/cm² conditions. Aluminum electrode performed better in reducing the COD, with a removal efficiency as 93% in 25 at low initial pH, such as 3, and current density of 150 A/m². On the other hand, iron electrode was more successful in removing oil-grease with 98% efficiency, irrespective of the initial pH. From economic point of view, iron electrode is clearly preferable; the total operating cost is between 0.3 and 0.4 \$/m³, which is nearly half that of aluminum electrode. 	[63], [64], [76]

Pollutants	Electrode material	Operational parameters investigated	Summary of the work	Ref.
Electroplating/ metal	Aluminium, iron	Electrode material, current density, wastewater pH, conductivity, initial metal concentration	<ul style="list-style-type: none">• Under the optimal conditions, about 90% of COD and 92% of residual color could be effectively removed from the UASB effluent with the further contribution of the EC technology used as a post-treatment unit.	[86-88]
			<ul style="list-style-type: none">• The Fe–Fe and Fe–Al electrode combinations were more effective for the removal of Cu, Cr and Ni from metal plating wastewater.• At the current density of 25 mA/cm² with a total energy consumption of 49 kWh/m³, more than 96% removal value was achieved for all studied metals except Mn which was 72.6%.	

Table 2. cont. A brief literature review of EC efficiency on the treatment of different waters/wastewaters containing various organic/inorganic pollutants.

4. Materials and methods

4.1. Materials

4.1.1. Winery wastewater used in this study

The wastewater used in this work was taken from an equalization tank of a wine factory located in the city of Tekirdağ (in TURKEY), producing approximately 350 m³ of wastewater daily. The characteristics of the wastewater are presented in Table 3.

Parameter	Value
pH	5.2
COD, mg/L	20,400 ± 1,100
BOD ₅ , mg/L	11,120 ± 1,055
TOC, mg/L	4,230 ± 940
TSS, mg/L	1,045 ± 85
Turbidity, NTU	1,600 ± 510
Color, Pt-Co	5,300 ± 100
Conductivity, µS/cm	2,800 ± 93

Table 3. Characteristics of the winery wastewater used in this study

4.1.2. EC setup and electrode connection modes

EC reactor was made from plexiglas reactor with dimensions of $130 \times 130 \times 120$ mm and operated in batch mode. Al and Fe electrodes with effective area of 143 cm^2 were used and the distance between the electrodes was 20 mm. Electrodes were connected to a digital DC power supply (Maksimel, Ankara, Turkey) in various electrode connection modes of which details are given below. A time relay (Siemens Sirius, Germany) was used with DC power supply to change polarity of the electrodes when performing APC experiments.

4.1.3. Monopolar electrodes in parallel connections (MP-P)

To improve the performances of an EC it may be necessary to interchange the polarity of the electrode intermittently. However, a two-electrode EC cell is not suitable for wastewater treatment, because for a workable rate of metal dissolution the use of electrodes with large surface area is required. Performance improvement has been achieved by using EC cells with monopolar electrodes either in parallel or series connections [3]. In the MP-P system, anodes and cathodes are in parallel connection, the current is divided between all the electrodes in relation to the resistance of the individual cells. Hence, a lower potential difference is required in parallel connection, when compared with serial connections. MP-P connection mode is given in Fig. 6.

4.1.4. Monopolar electrodes in serial connections (MP-S)

In the MP-S system, each pair of sacrificial electrodes is internally connected with each other, because the cell voltages sum up, a higher potential difference is required for a given current. MP-S connection mode is given in Fig. 7.

4.1.5. Bipolar electrodes in serial connections (BP-S)

In the BP-S system, there is no electrical connection between inner electrodes, only the outer electrodes are connected to the power supply. Outer electrodes are monopolar and inner ones are bipolar. This connection mode has simple setup with and has less maintenance cost during operation. BP-S connection mode is given in Fig. 8.

4.1.6. Time relay device

An adjustable time relay (3RP1525-1BW30 Siemens Sirius Time Relay $20 > 240 \text{ VAc/Dc}$) plugged into the DC power supply was employed to obtain APC. It represents AC in our study. According to EC unit with time relay system, turn on and turn off modes switch to positive pole to negative pole or reversion to it. For example, when the time relay is turned on in an EC reactor including two electrodes namely 1 (anode) and 2 (cathode), electrode 1 is then converted to cathode while electrode 2 is becoming anode. When the time relay is turned off, only DC system is in circuit, electrode 1 becomes anode this time.

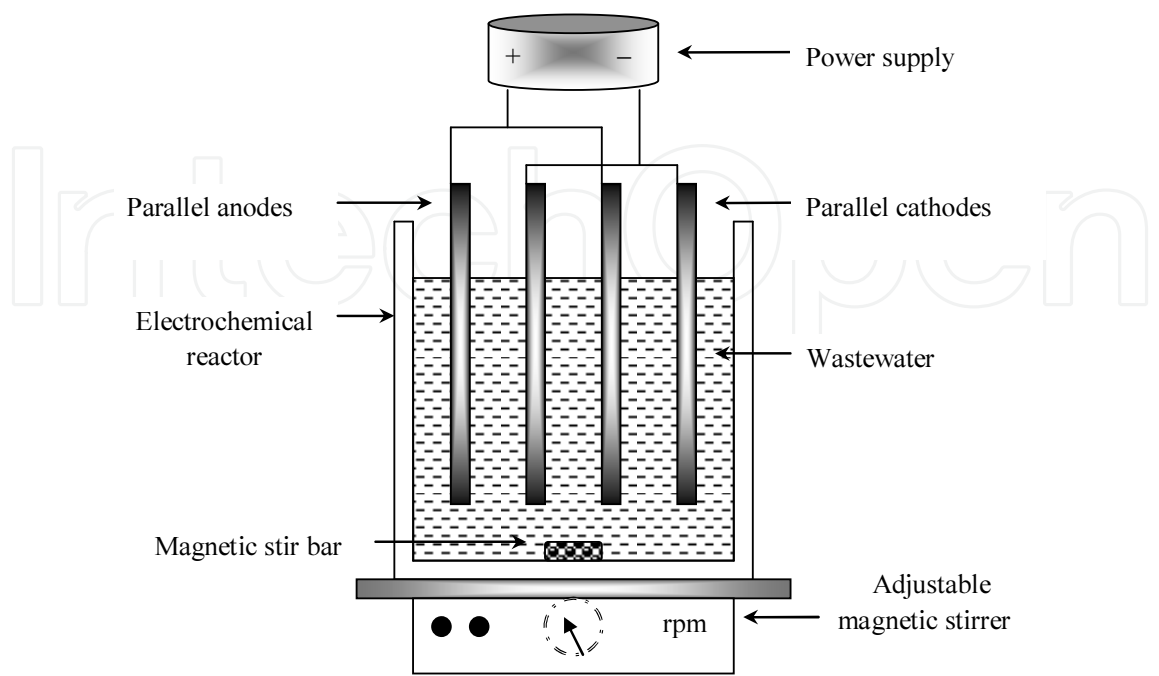


Figure 6. EC reactor with MP-P electrodes [89].

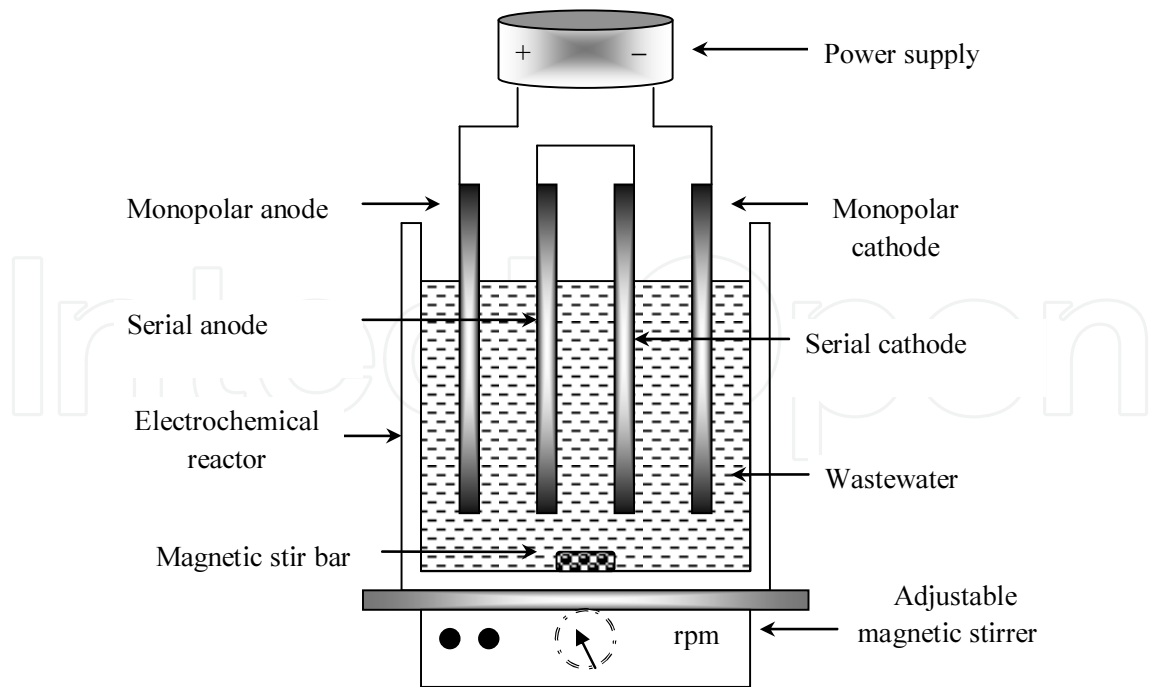


Figure 7. EC reactor with MP-S electrodes [89].

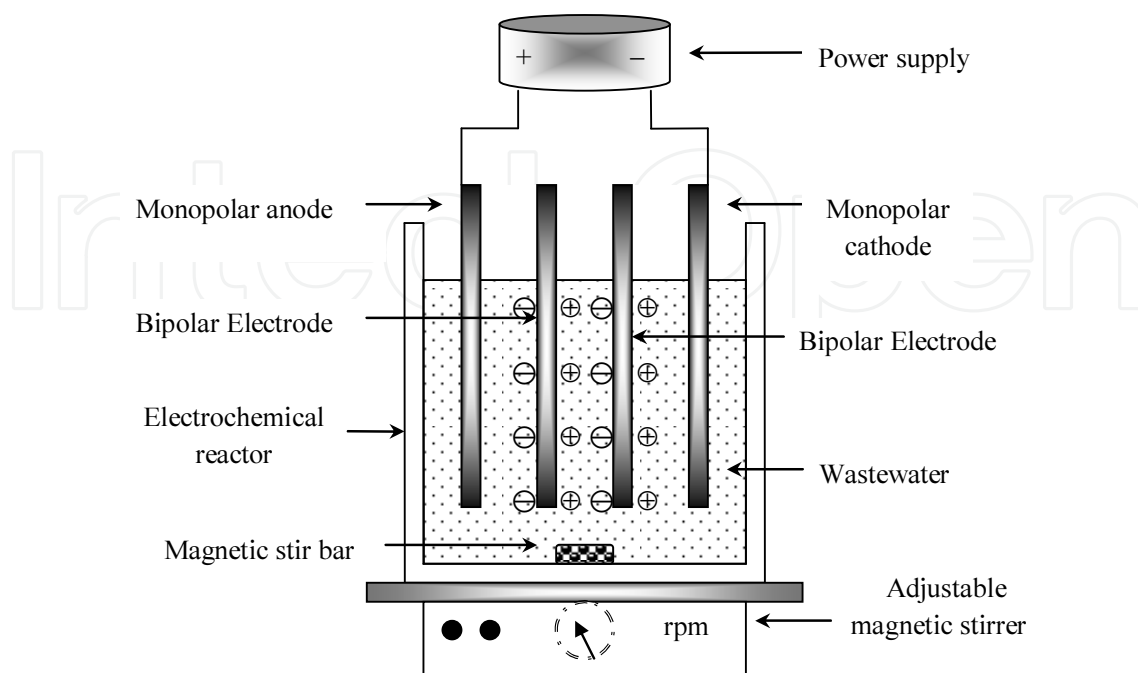


Figure 8. EC reactor with BP-S electrodes [89].

4.2. Methods

All experiments were performed at constant temperature of 25°C. In each run, 1,500 mL of winery wastewater was placed into the reactor. Magnetic stirring (250 rpm, Velp Are) was applied to provide a homogenous solution in the reactor. Conductivity was 2.800 $\mu\text{S}/\text{cm}$ that was the conductivity of the wastewater itself where no supported electrolyte was added. The current and pH were adjusted to the desired value before the process. After each run, electrode surfaces were removed by dipping for 1 min in a solution prepared by mixing 100 cm^3 of HCl solution (36.5%) and 200 cm^3 of hexamethylenetetramine aqueous solution (2.80%) [71] and washed thoroughly with demineralized water to remove any solid residues on the surfaces, dried and re-weighted. The solution was filtered through a filter paper (Whatman 40 ashless-NJ, USA) after each run and then analyzed. The solid residue was dried until constant weight was obtained for the calculation of sludge amounts. The experiments were performed in three replications used to compute the mean value and standard deviations. Therefore large amounts of data were collected; analyzed and figured for pH, current density and time experiments; only on effects of COD removal efficiencies; so, all of the graphics could not be presented here due to the limited space in the chapter. Electrode and energy consumptions, sludge formations and operating costs are given in Tables. Economic data used for the evaluation of the total operating costs dye given for the first quarter of 2013, Turkey market, in Table 4.

Item with warranty period	Cost
Power supply and installing, \$, 5 years	10,000
EC tank and installing, \$, 10 years	500
Maintenance and depreciation, \$/m ³	0.005
Electricity, \$ /kWh	0.17
Labor costs, \$/m ³	0.1
Aluminium electrode, \$/kg	0.5
Iron electrode, \$/kg	0.5
Chemicals (acid, salt, etc.), \$/m ³	0.04
Sludge disposal cost, \$/kg	0.012

Table 4. Economic factors used in the total operating cost calculations.

Measurements of COD and total suspended solids (TSS) were performed according to the procedure of Standard Methods (2005). The pH and conductivity of solutions were measured using a multi meter (Hach Lange HQ40d-Düsseldorf, Germany). An UV spectrophotometer (HACH Co., model DR5000-Düsseldorf, Germany) was employed to measure color and turbidity of the wastewater. The initial pH was adjusted to a desired value using NaOH (Merck-Darmstadt, Germany) or H₂SO₄ (Merck-Darmstadt, Germany).

Pollutant removal efficiencies are calculated as follows:

$$\% \text{ Removal efficiency} = \frac{C_0 - C}{C_0} \times 100 \tag{14}$$

where C is COD, color or turbidity value of treated aqueous solution (mg/L, Pt-Co or NTU) and C₀ is the initial relating concentrations (mg/L, Pt-Co or NTU).

5.Results and discussions

5.1. Determining the optimum experimental parameters to comparison DC & APC systems

5.1.1. Effects of initial pH

The EC process is highly dependent on the initial pH of the solution [3]. In aluminium case, precipitation mechanism of monomeric and polymeric Al(OH)₃ species at pH 4.0–6.5 and adsorption mechanism of Al(OH)₃ and polymeric Al(OH)₃ species at pH > 6.5 are effective on the removal of pollutants. However, in the iron case, good removal efficiency can be achieved

on floc formation at pH 6–8 [89-91]. Five pH values (4, 5, 6, 7, 8, and 9) were selected to investigate the optimal pH at which maximum removal efficiencies, minimum electrode and energy consumptions were observed for three electrode connection systems as well as both of the electrode material, Fe and Al. The effects of pH have been investigated at constant current density of 40 mA/cm² and 60 min of operating time. Because there were a lot of parameters (such as pH, current density, operating time, electrode material, electrode arrangement, and current type) of which effects were investigated on the great number of process outputs (such as COD, turbidity and color removals; energy and electrode consumptions; sludge amount, and total operating cost), large amounts of data were collected, therefore, only some of them are given as figures; as for the others, they are presented in tables. However, effects of APC are analyzed and discussed in much more details in the following sections. The effects of initial pH on COD removal are featured in Fig. 9. In both cases of different electrode materials, no great differences are observed between connection modes. As seen from the figure, the highest COD removal efficiencies were observed at pH 5 for Al electrode and at pH 7 for Fe electrode, where also maximum turbidity and color removals as well as minimum energy and electrode consumptions with minimum sludge formations (Table 5) were achieved. According to the Fig. 9, COD removal efficiency increased when pH increased from 4 to 5 and then it decreased at higher pH values, until pH 9. In similar trend, Fe electrode shows maximum performance for COD removal at pH 7, (maximum turbidity and color removals were also obtained at these pHs: 5 and 7, as seen in Table 5). It was concluded that colloid particles were destabilized by the metal ions produced by anodic dissolution and these ions reacted with organic pollutions by adsorption or co-precipitation while they were precipitating in the form of hydroxides at these pH values [54, 71]. According to Table 5 where the optimum pHs are presented for both electrodes, Fe and Al electrodes show similar performances with all connection modes on the removal of color and turbidity. Additionally, almost equal amounts of sludge revealed. However, MP-S and BP-S systems exhibit high consumptions as the consequence of the serial connection requiring higher potential. When electrode consumptions are compared, more electrode material is consumed in iron case than that of aluminium. The lowest total operating cost was gained with MP-P mode as expected.

5.1.2. Effects of current density

Current density is the most important parameter for controlling the reaction rate within the reactor in all electrochemical processes. It is well known that the magnitude of current density determines the amount of Al or Fe ions released from the electrodes and the formation rate of $\text{Me}(\text{OH})_n$ (coagulant production rate) [92, 93] and adjusts the rate and size of the bubble production, and hence affects the growth of flocs [3, 94, 95]. In this research, all the experiments were applied under pHs 5 and 7 for Al and Fe electrodes, respectively with 60 min of electrolysis time to examine current density effects. Fig. 10 depicts the current density effects on COD removal. The removal percentages reach maximum at 40-50 mA/cm² and stay constant or decrease at higher current densities. Increment in current density raised the formation of hydroxide flocs and promote the removal efficiency by coagulation but meanwhile it causes an increase in energy consumption. However, after a certain value of current density, cathode passivation occurred and dissolution of anode material stopped or reduced and also floc

formation and removal efficiencies decreased. The turbidity and color removal efficiencies were also came in sight the same trend with current density as COD removal efficiency. Because the lower current density with higher removal efficiencies is preferable, depending on the results, 40 mA/cm² was chosen as the appropriate current density value for the following time experiments. The other results belong to this value are shown in Table 6.

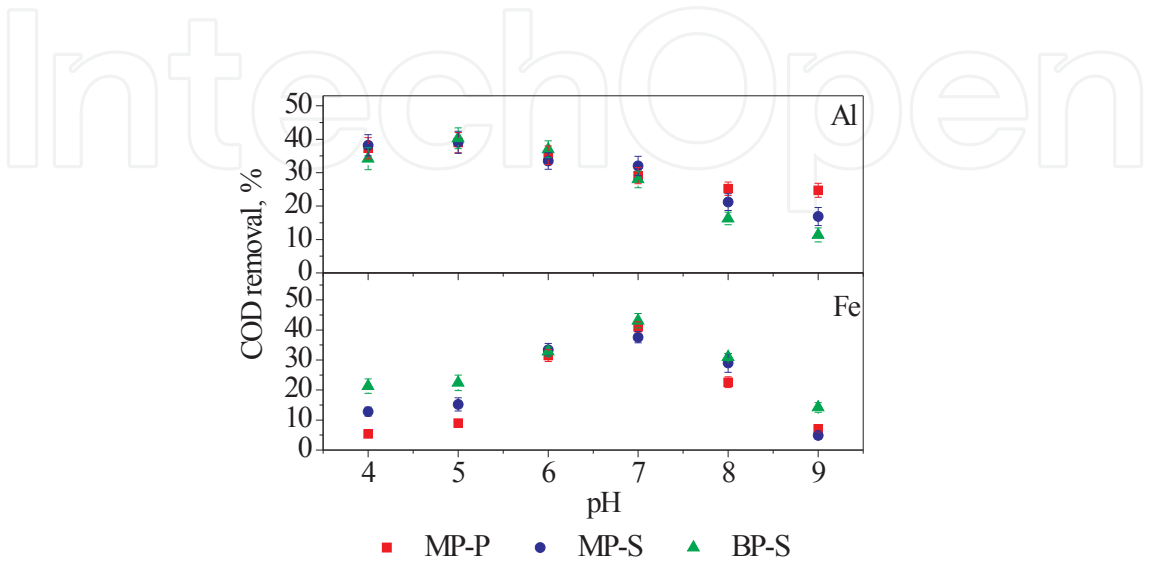


Figure 9. Effects of initial pH on removal efficiencies for Fe and Al electrodes with different electrode arrangements (current density of 40 mA/cm²; operating time of 60 min).

	Al			Fe		
Parameter	MP-P	MP-S	BP-S	MP-P	MP-S	BP-S
Initial pH	5	5	5	7	7	7
Current density, mA/cm ²	40	40	40	40	40	40
Operating time, min	60	60	60	60	60	60
Initial voltage, V	28	84	85	28	84	85
Final voltage, V	29	85	87	29	85	87
Initial COD, mg/L	20,400	20,400	20,400	20,400	20,400	20,400
Initial color, Pt-Co	5,300	5,300	5,300	5,300	5,300	5,300
Initial turbidity, NTU	1,600	1,600	1,600	1,600	1,600	1,600
COD removal, %	39	39.1	40.3	41	37.6	43.1
Color removal, %	70	69.1	71	73.2	69.1	73.2
Turbidity removal, %	86.3	85.2	82.1	81	80.6	81
Energy consumption, kWh/kg COD	6.83	20.19	19.93	6.49	20.99	18.64
Energy consumption, KWh/m ³	36.20	107.34	109.25	36.20	107.34	109.25

	Al			Fe		
Energy cost, \$/kg COD	1.16	2.35	3.39	1.16	3.57	3.17
Energy cost, \$/m ³	6.15	18.25	18.57	6.15	18.25	18.57
Faraday (charge loading), coulomb/m ³	47.40	47.40	47.40	47.40	47.40	47.40
Electrode consumption, kg Al or Fe/m ³	0.40	0.45	0.45	0.88	0.89	0.87
Electrode cost, \$/m ³	0.20	0.23	0.23	0.44	0.45	0.43
Sludge formation, kg/m ³	9.86	9.93	10.17	10.73	10.06	11.16
Sludge formation, kg/kg COD removed	1.86	1.87	1.87	1.92	1.97	1.90
Sludge disposal cost, \$/kg	0.12	0.12	0.13	0.13	0.12	0.13
Operating cost, \$/kg COD removed	0.83	2.35	2.32	0.82	2.47	2.19
Total operating cost, \$/m ³	6.62	18.74	19.07	6.86	18.96	19.28

Table 5. Optimum results obtained from pH experiments.

5.1.3. Effects of operating time

Operating time is another important factor in EC process, which is necessary to provide sufficient current applied to the electrodes where the metal ions generated by the dissolution to form metal hydroxide species. Therefore reasonable electrolysis times should be applied in the EC reactor. To investigate the effects of operating time on the EC, optimum parameters obtained from the former pH and current density experiments were used: pHs 5 and 7 for Al and Fe, respectively; 40 mA/cm² of current density. Influence of the operating time on COD removal and the other results at the appropriate electrolysis time are presented in Fig. 11 and Table 7 respectively.

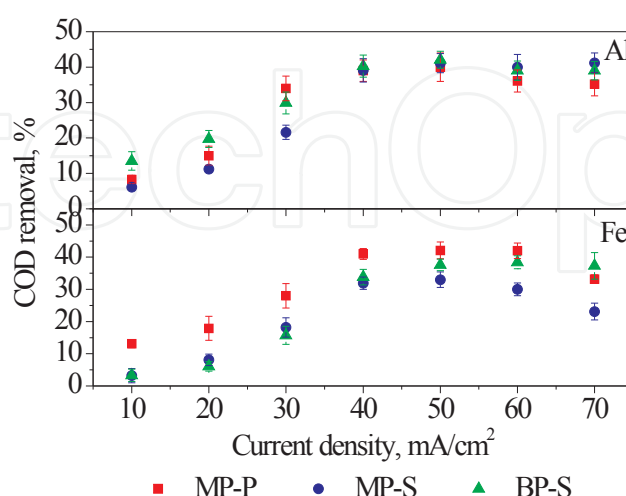


Figure 10. Effects of current density on removal efficiencies for Fe and Al electrodes with different electrode arrangements (initial pH of 5 for Al and 7 for Fe; operating time of 60 min).

Parameter	Al			Fe		
	MP-P	MP-S	BP-S	MP-P	MP-S	BP-S
Initial pH	5	5	5	7	7	7
Current density, mA/cm ²	40	40	40	40	40	40
Operating time, min	60	60	60	60	60	60
Initial voltage, V	28	84	85	28	84	85
Final voltage, V	29	85	87	29	85	87
Initial COD, mg/L	20,400	20,400	20,400	20,400	20,400	20,400
Initial color, Pt-Co	5,300	5,300	5,300	5,300	5,300	5,300
Initial turbidity, NTU	1,600	1,600	1,600	1,600	1,600	1,600
COD removal, %	39	39.1	40.3	41	37.6	43.1
Color removal, %	70	69.1	71	73.2	69.1	73.2
Turbidity removal, %	86.3	85.2	82.1	81	80.6	81
Energy consumption, kWh/kg COD	6.83	20.19	19.93	6.49	20.99	18.64
Energy consumption, kWh/m ³	36.20	107.34	109.25	36.20	107.34	109.25
Energy cost, \$/kg COD	1.16	2.35	3.39	1.16	3.57	3.17
Energy cost, \$/m ³	6.15	18.25	18.57	6.15	18.25	18.57
Faraday (charge loading), coulomb/m ³	47.40	47.40	47.40	47.40	47.40	47.40
Electrode consumption, kg Al or Fe/m ³	0.40	0.45	0.45	0.88	0.89	0.87
Electrode cost, \$/m ³	0.20	0.23	0.23	0.44	0.45	0.43
Sludge formation, kg/m ³	9.86	9.93	10.17	10.73	10.06	11.16
Sludge formation, kg/kg COD removed	1.86	1.87	1.87	1.92	1.97	1.90
Sludge disposal cost, \$/kg	0.12	0.12	0.13	0.13	0.12	0.13
Operating cost, \$/kg COD removed	0.83	2.35	2.32	0.82	2.47	2.19
Total operating cost, \$/m ³	6.62	18.74	19.07	6.86	18.96	19.28

Table 6. Optimum results obtained from current density experiments.

As seen from Fig.11, COD removal efficiencies of both electrodes in three connection modes increases until a certain operating time value, then, remain steady or decrease. Here, two explanation may be done: Firstly, for an electrolysis time beyond the optimum electrolysis

time, the pollutant removal efficiency does not increase as sufficient numbers of flocs are available for the removal of the pollutant [1], secondly, removal efficiency does not increase, on the contrary, it decreases due to the anodic passivation and cathodic polarization which can impede the performance of EC [9, 96]. This situation is also valid in the case of the current density experiments. The optimum operating times (chosen as 90 and 105 min for Fe and Al, respectively), at which the maximum pollutant removals and minimum energy/electrode consumptions were gained, is presented with experimental results in Table 7. Because the removal efficiencies in the Table are close to each other, MP-P connection mode with minimum total operating cost is preferred for the follow-up experiments of the comparison of DC and APC.

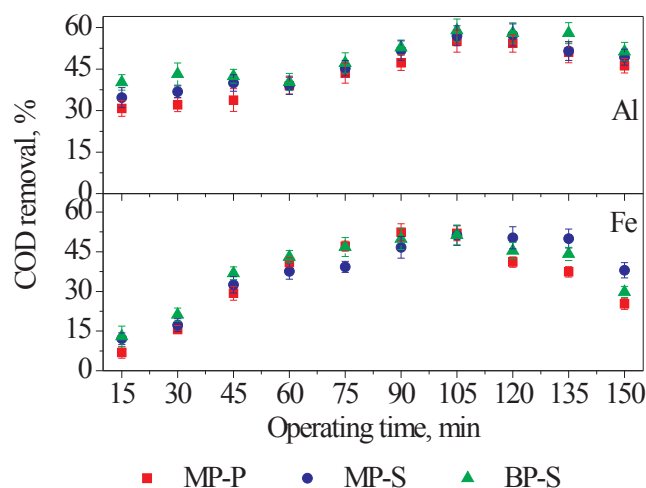


Figure 11. Effects of operating time on removal efficiencies for Fe and Al electrodes with different electrode arrangements (initial pH of 5 for Al and 7 for Fe; current density of 40 mA/cm²).

	Al			Fe		
Parameter	MP-P	MP-S	BP-S	MP-P	MP-S	BP-S
Initial pH	5	5	5	7	7	7
Current density, mA/cm ²	40	40	40	40	40	40
Operating time, min	105	105	105	90	90	90
Initial voltage, V	28	84	85	28	84	86
Final voltage, V	29	85	88	29	85	90

	Al			Fe		
Initial COD, mg/L	20,400	20,400	20,400	20,400	20,400	20,400
Initial color, Pt-Co	5,300	5,300	5,300	5,300	5,300	5,300
Initial turbidity, NTU	1,600	1,600	1,600	1,600	1,600	1,600
COD removal, %	55.1	57	59	52.4	46.7	49.9
Color removal, %	96.3	92.1	94.7	81.4	76.7	81.1
Turbidity removal, %	97.7	97	95.4	90.8	88.2	91.5
Energy consumption, kWh/kg COD	8.45	24.23	23.97	7.62	25.35	24.71
Energy consumption, KWh/m ³	63.36	187.85	192.29	54.30	161.01	167.68
Energy cost, \$/kg COD	1.44	4.12	4.07	1.30	4.31	4.20
Energy cost, \$/m ³	10.77	31.93	32.69	9.23	27.37	28.51
Faraday (charge loading), coulomb/m ³	82.94	82.94	82.94	71.10	71.10	71.10
Electrode consumption, kg Al or Fe/m ³	0.75	0.75	0.77	1.33	1.30	1.30
Electrode cost, \$/m ³	0.37	0.37	0.39	0.66	0.65	0.65
Sludge formation, kg/m ³	13.49	13.87	14.31	13.52	12.33	12.98
Sludge formation, kg/kg COD removed	1.80	1.79	1.78	1.90	1.94	1.91
Sludge disposal cost, \$/kg	0.16	0.17	0.17	0.16	0.15	0.16
Operating cost, \$/kg COD removed	1.02	2.81	2.77	0.95	2.97	2.89
Total operating cost, \$/m ³	11.45	32.62	33.39	10.20	28.31	29.46

Table 7. Optimum results obtained from operating time experiments.

5.2. Comparison of DC & APC systems

As encountered as a problem, cathode passivation, in the current density and operating time experiments, it may be described schematically as given in Fig. 12 similar to the results given in Table 8. To compare DC and APC system, MP-P connection mode selected for both electrode material. Current density and operating time experiments were repeated with time relay integrated with DC power supply to generate polarization between anodes and cathodes at certain intervals. Time relay was set to 300 Hz⁻¹ [9] meaning anode–cathode polarization period of 10 min. The results are depicted in Figs. 13 and 14 for current density and operating time, respectively. As seen in the figures, removal efficiencies are not stopped or decreased at or after a certain current density or time value, moreover, at the same values APC sounds superior to DC. To make a local comparison between APC and DC, the results of APC are presented at optimum experimental conditions that formerly determined for DC system employed Fe or

Al electrodes in MP-P connection mode in Table 8. Moreover, few reports in literature about power supply effects on EC process are presented with overall results in Table 9.

Parameter	Al		Fe	
	DC	APC	DC	APC
Initial pH	5	5	7	7
Current density, mA/cm ²	40	40	40	40
Operating time, min	105	105	90	90
Initial voltage, V	28	28	28	28
Final voltage, V	29	29	29	29
Initial COD, mg/L	20,400	20,400	20,400	20,400
Initial color, Pt-Co	5,300	5,300	5,300	5,300
Initial turbidity, NTU	1,600	1,600	1,600	1,600
COD removal, %	55.1	77	52.4	75
Color removal, %	96.3	99	81.4	99
Turbidity removal, %	97.7	99	90.8	99
Energy consumption, kWh/kg COD	8.45	6.05	7.62	5.32
Energy consumption, kWh/m ³	63.36	63.36	54.30	54.30
Energy cost, \$/kg COD	1.44	1.03	1.30	0.91
Energy cost, \$/m ³	10.77	10.77	9.23	9.23
Faraday (charge loading), coulomb/m ³	82.94	82.94	71.10	71.10
Electrode consumption, kg Al or Fe/m ³	0.75	0.85	1.33	1.36
Electrode cost, \$/m ³	0.37	0.43	0.66	0.68
Sludge formation, kg/m ³	13.49	18.10	13.52	18.16
Sludge formation, kg/kg COD removed	1.80	1.72	1.90	1.78
Sludge disposal cost, \$/kg	0.16	0.22	0.16	0.22
Operating cost, \$/kg COD removed	1.02	0.74	0.95	0.67
Total operating cost, \$/m ³	11.45	11.55	10.20	10.27

Table 8. Comparison of DC and APC at the same experimental conditions.

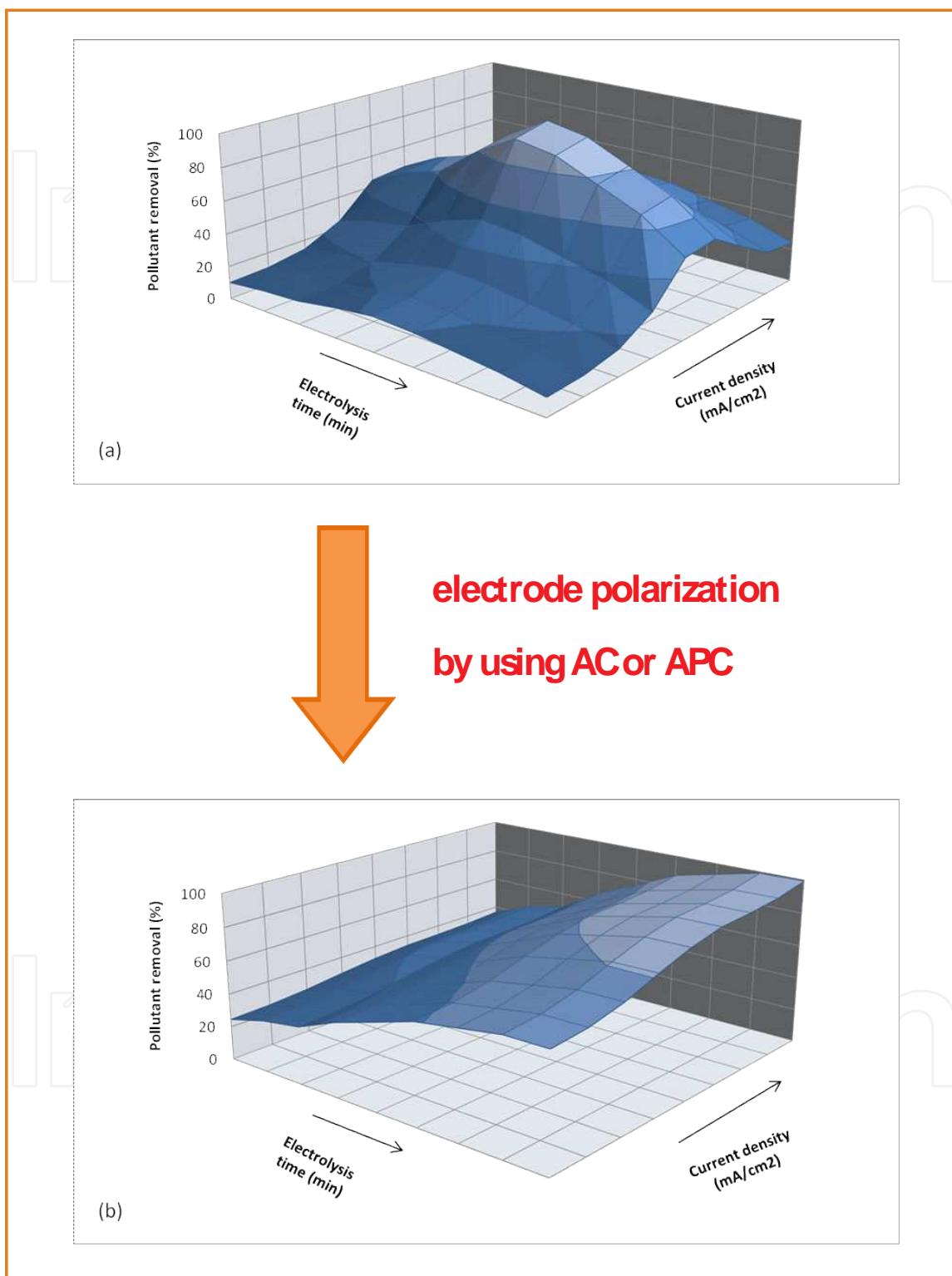


Figure 12. (a) General trend of pollutant removal efficiency changing with respect to current density and operating time in EC using DC power supply (one-way current), (b) Improved removal efficiency behaviour with respect to current density and operating time in EC using AC power supply or APC (two-way current).

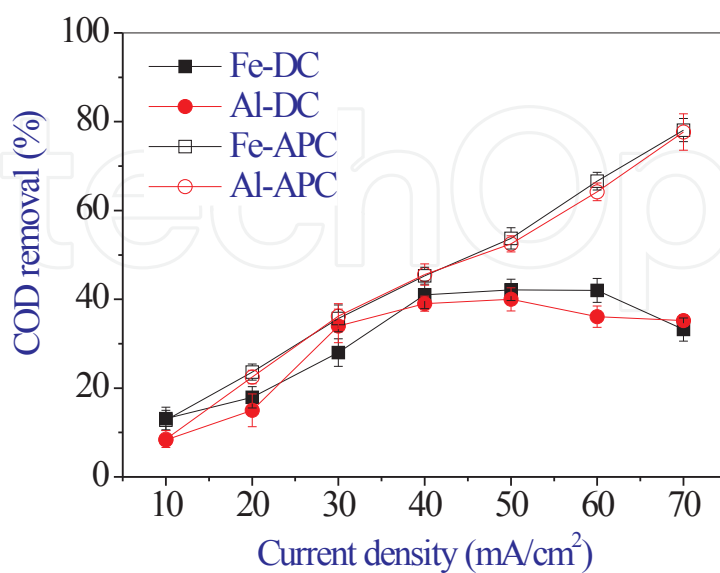


Figure 13. Comparison of DC and APC for two electrode materials in view of COD removal performances at different current densities.

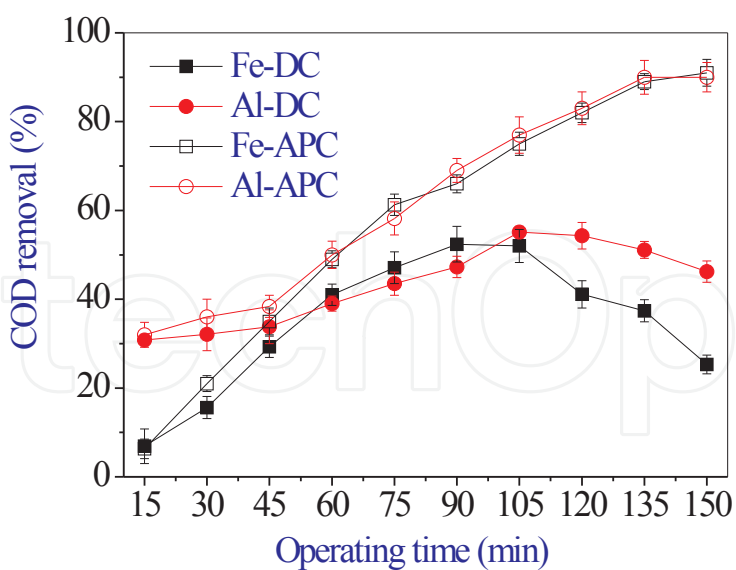


Figure 14. Comparison of DC and APC for two electrode materials in view of COD removal performances at different operating times.

Pollutants	Electrode material	Operational parameters investigated	Summary of the work	Ref.
Cr (VI)	Aluminium, iron	Initial pH, current density, reaction time, initial Cr (IV) concentrations, solution conductivity, electrical energy consumption, type of circuit	<p>The APC mode was found to be more efficient than the DC mode with a lower anode over-voltage, slower anode polarization and passivity, and lower tank voltage.</p> <p>The operating time is 3–25% less when APC mode is used.</p> <p>The APC mode minimizes waste and increases sludge stability.</p> <p>In the APC mode, the “water recovery” was very significant, measuring as high as 0.92 m³/m³ wastewater. For DC mode, the water recovery was less than 0.5 m³/m³ of wastewater.</p>	[11]
Cadmium	Aluminium	Initial pH, current density, initial Cd concentrations, effect of coexisting ions	<p>The optimized removal efficiency of 97.5% and 96.2% was achieved for AC and DC source at a current density of 0.2 A/dm² and pH of 7.0 using aluminum alloy as anode and cathode.</p> <p>For both AC and DC electrolysis the adsorption of cadmium preferably fitting Langmuir adsorption isotherm better than Freundlich isotherm.</p>	[10]
Cadmium	Zinc	Initial cadmium ion concentration, initial pH, current density and temperature.	<p>The optimum removal efficiency of cadmium is 97.8% and 96.9% with the energy consumption of 0.665 and 1.236 kWh/m³ was achieved for AC and DC source at a current density of 0.2 A/dm² and pH of 7.0</p> <p>For both AC and DC electrolysis the adsorption of cadmium preferably fitting Langmuir adsorption isotherm.</p>	[97]
Synthetic Methyl Orange wastewater	Aluminium	Initial pH, initial MO concentration, solution conductivity	<p>Electrocoagulation with periodic electrode reversal (PREC) can effectively retard cathodic polarization and anodic passivation.</p> <p>Decolorization of MO wastewater is described well by a first-order reaction equation. The rate constant was fitted to be 0.183 min^{−1} for PREC, an increase of 20% compared to the EC.</p>	[12]
Dianix Yellow CC, Procion Yellow dyes	Aluminium	Initial pH, current density, operating time, frequency of anode-cathode polarization.	<p>Higher removal efficiencies of TOC and dye can be acquired in shorter operation times by using APC system.</p> <p>Removal efficiencies increase in APC system after optimum operation time belongs to DC system as well.</p>	[9]

Table 9. A brief literature review of some studies on power supply effects on EC performance

4. Conclusions

The EC technique has gained a remarkable attention in the wastewater treatment applications due to its benefits including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness. The EC process contains an in-situ generation of metal hydroxide ions by electrolytic oxidation of the sacrificial anode. These metal hydroxide ions act as coagulant and remove the pollutants from the solution by sedimentation. Majority of the studies reported in the literature have traditionally used DC in the EC process. However, the traditional process also has the serious disadvantages of cathodic passivation which can impede the electrolytic process in a continuous operation. The use of DC leads to the corrosion formation on the anode due to oxidation. An oxidation layer also form on the cathode reducing the flow of current between the cathode and the anode and thereby lowering the pollutant removal efficiency and highering the operational cost. Therefore, in this research an almost new method, APC electrocoagulation was used to overcome the cathode passivation. A real high strength industrial wastewater, winery wastewater, was selected as the model electrolytic solution. In the EC reactor, aluminium and iron were used as sacrificial electrodes separately in three different connection modes namely, monopolar – parallel, monopolar-serial, and bipolar serial connections. DC was obtained from a DC power supply operated at galvanostatic mode while APC was obtained by a time relay device integrated with the DC power supply. COD, color, and turbidity removal efficiencies were considered when DC and APC were compared technically. Furthermore, various cost items were used to calculate the total operation cost of both DC and APC systems by means of pollutant removals. A comprehensive literature survey from numerous references is also stated on EC and power supply effects. According to the experimental results, the following conclusions may be exposed:

- Higher removal efficiencies can be acquired in both same and shorter operation times by using APC system. In the same operating time, conditions, APC provide 40% more COD removal than DC. Similarly, APC reach 30 % more faster to DC' s COD removal performance. Thus, it can be said that anode–cathode polarization reduces the reaction time which is necessary for metal hydroxides removing the pollutants.
- COD, turbidity and color removal efficiencies increase until a certain current density and operation time and then they decrease so long as DC system goes on working. It may be due to the cathode passivization arisen from accumulation of contaminants on the cathode material. Therefore, electrode surfaces are needed to be cleaned and then put into use again. However, removal efficiencies increase in APC system after optimum operation time belongs to DC system as well. Thus, APC system can prolong the electrode life in each batch round of EC process.
- ACP can be easily obtained by a simple time relay device from the existing DC power supply and can be used in EC applications.
- ACP provides regular polarization to each electrode in the EC reactor, so, the sacrificial electrodes could be consumed in reasonable similar times.

- Fill-and-draw periods of reactor could be easily increased for batch EC processes by using time relay to eliminate cathode passivation. An increasing in fill-and-draw periods is important to decrease operating costs for batch processes.
- According to the results of the study, color and turbidity can be removed successfully from winery wastewaters but remained COD concentration is still too high for discharge. So, EC process should be applied with other treatment technologies such as anaerobic treatment that can remove the high COD concentrations.

Based on the promising results achieved in this research, different electrode materials can be used together by changing the anode-cathode polarization; ACP system can be also evaluated for different wastewater types or electrolytic solutions in further researches.

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