Electrocoagulation: An Overview of the Technology for Livestock Farm Wastewater Treatment

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Abstract - *Livestock operations generate wastewater which is characterized by high biological oxygen demand and chemical oxygen demand concentrations, high levels of solids including fats, oils, and grease. Its high nutrient content, particularly phosphorus and nitrogen, is an important factor because of its adverse environmental impact. To reduce these, nutrient contaminants can either be captured or removed from liquid manure before disposal. Several techniques, including chemical, electrochemical, biological, and advanced oxidation, are used to treat this wastewater. Most of them have some limitations. Conventional and biological processes are time-consuming and cost-intensive, requiring a large treatment area, and generating large amounts of sludge. Lately, electrolysis has attracted attention as a potential strategy for wastewater treatment due to its environmental compatibility. Livestock waste chemistry differs considerably from industrial wastewater. Hence, the selection of electrode material with anode and cathode combination mode is critical to removing pollutants at low energy consumption. A total of 72 published articles were reviewed in this paper focusing on system configuration, contaminant removal, operation timing, and achievement of this electrocoagulation process. The commonly used electrode materials are aluminium, iron, and mild steel. In treating livestock wastewater, different combinations (Al-Al, Al-Fe, and Fe-Fe) and wiring modes of anode and cathode have been reported in the literature. It is anticipated that this study will guide researchers in the future as a milestone in the treatment of wastewater from livestock farms.*

Keywords – BOD, COD, electrocoagulation, electrode, TSS, livestock, wastewater

1. Introduction

Increasing growth of livestock industries both in size and number worldwide will generate huge amount of wastewater that characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD), nutrients, and organic and inorganic pollutants (Sarkar *et al*, 2006, Sengil and özacar, 2006; Tchamango *et al*, 2010). Water is an indispensable ingredient consumed in all processes of the concentrated livestock production facilities including dairy cows, beef cattle, hogs, sheep, goats, horses, and even poultry. A huge amount of water is required in flashing and cleaning, sanitization, heating, and cooling process. Approximately, 8% of the global water supply consumed by the livestock industries, with most of that water being used for concentrated, intensive, and feed-based production facilities (Schlink, 2010). The wet dairy operations are generally considered to be the largest water intensive livestock production industry generating huge amount of wastewater to be treated prior reuse and land applications.

It is reported that the dairy operation produces a huge number of wastewaters: ~0.2-10 L of waste/L of processed milk (Tchamango *et al*, 2010). Therefore, a considerable amounts of livestock related wastewater are generated each year that requires extensive treatment since untreated discharge of these pollutants will severely pollute receiving water bodies and crop/pasture land. The volume, concentration, and composition of the effluents generated in a dairy operation are mainly dependent on the type of manure handling and management methods being used, product being processed, and the amount of water being conserved. Similarly, swine wastewaters contain high concentration of N, P, and K nutrients. Thus, it warrants either capturing or removing the nutrient pollutants from swine liquid manure before discharging to water streams and crop-pasture fields.

Various techniques such as chemical, biological, advanced oxidation, and electrochemical are being used for treating the industrial effluent along with some limitations. The conventional methods of treating livestock wastewaters

include anaerobic lagoons, constructed wetlands, and storage with land application (Cronk, 1996; Mukhtar *et al*, 2009). The conventional and biological processes are time and cost intensive, require large treatment area, and generates large amount of sludge. Electrolysis has attracted attention as a potential technique for treating livestock liquid manure due to its versatility, simplicity, and environmental compatibility. Recently, electrocoagulation has shown the promise for treating industrial effluent and has been utilized in treating various industrial wastewater including urban, pulp and paper mill wastewater, tannery waste, textile, arsenic and chromium, restaurant, and oily wastewater (Zakeri *et al*, 2021; Pouet and Grasmick, 1995; Mahesh *et al*, 2006; Feng *et al*, 2007; Raju *et al*, 2008; Thella *et al*, 2008; Kumar *et al*, 2009; Stephenson and Tennant, 2003; Kobya *et al,*2003). The electrocoagulation systems have also shown potential in treating livestock wastewater.

Livestock wastewater chemistry differs considerably from industrial waste. The major advantages of electrocoagulation (EC) as compared to chemical coagulation are (Fayad, 2017; Khandeger and Saroha, 2013): 1) EC is relatively simple, easy to operate and manage, requires no addition of chemicals, and provides better removal capabilities for the same species than chemical coagulation, 2) EC removes many species that chemical coagulation cannot remove, 3) EC produces metallic and less sludge (oxides/hydroxide), readily settable, easy to de-water, and thus lowering the sludge disposal cost, 4) EC sludge is more readily filterable and can be utilized as a soil additive, 5) EC technique is simple in design, require little maintenance and needs minimal startup time; the process can be started by turning on the switch. In contrast, limitations of the electrochemical coagulation are as follows (Mollah *et al*, 2001, 2004): 1) the sacrificial anodes need to be replaced periodically, 2) depending on the design of the reactor this process requires minimal solution conductivity, limiting its use with less soluble solid waste, 3) in the case of removal of organic compounds, there is a possibility of formation of toxic chlorinated organic compounds from chlorinated waste, 4) An imperviable oxide film can form at the cathode which can resist the electric current flow, 5) the high cost of electricity can result in an increase in operational cost of EC. However, change of polarity and periodical cleaning of the electrodes may reduce this interference.

2. Materials and Methods

Since the nature of this study was review work, it has collected about 200 published articles and books on the subject. The purpose was to focus on system configuration, contaminant removal, operation time, and achieving this electrocoagulation process. As a result, out of 200 books, a total of 72 published articles and books related to the purpose of the study have been reviewed and the main contents of those papers have been discussed and finally tabulated.
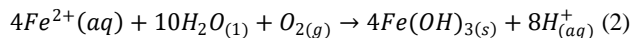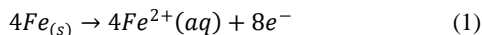
2.1. Electrocoagulation

Wastewater treatment by electrocoagulation is a modern treatment process that removes pollutants engaging both electro-oxidation and electrocoagulation (EC). This process primality destabilizes the suspended and blended or dissolved pollutants in wastewater medium when electric current is applied to the medium through anode and cathode. During EC process, ions also referred as coagulant agents are produced continuously from sacrificial electrodes (anode).

Unlike chemical coagulation, in the electrocoagulation (EC) process coagulant is generated *in-situ* by chemical oxidation of an appropriate sacrificial anode material (usually aluminum or iron cations). This process involves many chemical and physical phenomena that compel consumable electrodes to release ions into the pollutants under treatment and spontaneously undergo hydrolysis/chemical reaction in wastewater forming various coagulant species. These are metal hydroxides precipitates (eliminates pollutants by adsorption or sedimentation) and various metal ions bested on electrodes materials.
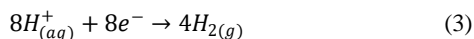
The production of metal ions involves five successive stages such as 1) Anode dissolution, 2) formation of OH^- ions and H_2 at the cathode, 3) electrolytic reactions at electrode surfaces, 4) adsorption of coagulant on colloidal pollutants, and 5) removal of colloids by sedimentation or flotation (Khandegar and Saroha, 2013). At the beginning of the EC process, Al and Fe ions were produced by anodic dissolution and reacted immediately with hydroxide ions in aqueous medium to produce aluminum hydroxide ($Al(OH)_2^+$ and $Al(OH)_3$) or iron hydroxide ($Fe(OH)_2$ and $Fe(OH)_3$), respectively. Subsequently, this process-initiated polymerization reactions when metallic hydroxide particles produced had reached sufficient concentration and sedimented as greenish and white gelatinous precipitate using mild steel and aluminum electrodes, respectively (Laridi *et al*, 2005; Ilhan *et al*, 2008). Electrocoagulation is an effective treatment because of the hydroxide absorption of the mineral surface, when metal hydroxides are used as coagulants, it is 100 times more in situ than in pre-precipitated hydroxides (Khandegar and Saroha, 2013; Mollah *et al*, 2004).

When aluminum and iron are used as anode material, the applied electrical current causes the dissolution of metal electrodes commonly aluminum (Al) and iron (Fe) into wastewater. The dissolved metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants (Bazrafshan *et al* (2013). According to Mollah *et al* (2001) oxidation of iron in an electrolytic system produces iron hydroxide, Fe $(OH)n$, where n = 2 or 3. Two mechanisms have been proposed for the production of Fe $(OH)n$; one is given below in reactions (1) – (4) and more details are given elsewhere by Mollah *et al* (2001).
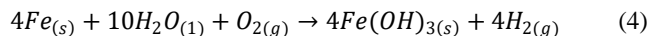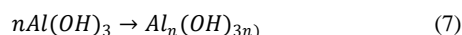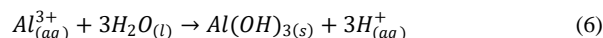
Anode:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}(aq) + 8e^- \qquad (1)$$

$$4Fe^{2+}(aq) + 10H_2O_{(1)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)} \quad (2)$$

Cathode:

$$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \qquad (3)$$

Overall:

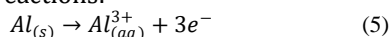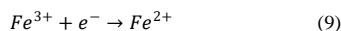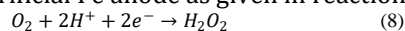$$4Fe_{(s)} + 10H_2O_{(1)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \qquad (4)$$

The $Fe(OH)_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater by complexation or by electrostatic attraction, followed by coagulation.

When an aluminum anode is used, the electrolytic dissolution of the aluminum anode produces cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ at low pH, which at appropriate pH values are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ according to the following reactions:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \qquad (5)$$

$$Al^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3H^+_{(aq)} \qquad (6)$$

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n)} \qquad (7)$$

A detailed explanation of the aluminum electrode reactions can be found in Mollah *et al* (2001). On the other hand, in the EF process; Fe^{2+} and H_2O_2 can be generated on-site electrochemically, either separately or concurrently. H_2O_2 can be electro-generated by the reduction of dissolved oxygen, and Fe^{2+} by the reduction of Fe^{3+} or the oxidation of a sacrificial Fe anode as given in reactions (8) – (10) below:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (8)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (9)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (10)$$

The reaction between H_2O_2 and Fe^{2+} produces hydroxyl radical, a non-selective strong oxidant, according to the reaction

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH + OH^- \qquad (11)$$
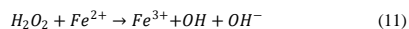
2.2. Influence of pH and conductivity

Among the parameters of the wastewater chemistry, the pH and conductivity of the wastewater under evaluation are two most critical factors that regulate electrodes dissolution, hydroxide speciation, and zeta-potential (degree of stability i.e. aggregation or repulsion) of colloidal particles. Fundamentally, Al and Fe electrodes work contrarily in an EC process with varying pH concentrations and consequently various species of metal hydroxides are forms. In a basic solution, $Al(OH)_4^-$ and $Fe(OH)_4^-$ relatively week coagulants compared to Fe(III) are formed (Fayad, 2017; Morgan and Lahav, 2007). In a wider range of pH (5 - 9), Fe(III) is more effective than Al(III) also efficient in a slightly basic pH. However, at an acidic pH, the forms of iron that dissolves from anode is Fe^{2+} (ferrous) and this dissolution of iron electrodes is significant even without

being operated by electricity (Sasson *et al*, 2009). Similar to non-electrochemical process, the reaction rate of Fe^{2+} oxidation to Fe^{3+} (ferric) in electrocoagulation was found strongly dependent on pH and oxygen saturation conditions of the solution.

With alkaline pH (7.6 – 14), Fe^{2+} ions are rapidly oxidized to Fe^{3+} (ferric) but the same reaction rate was much lower and almost negligible at pH below 4. An electrocoagulation system with aluminum electrodes (Al) and a starting acidic pH shows increase in final pH. In contrast, same electrocoagulation system with starting alkaline pH shows final pH unchanged. Mouedhen *et al*, (2008) reported a sharp increase in the release of Al ions in the pH range 2-3 and determined as beyond pH 3 the variation of dissolved Al was negligible. He also concluded that in highly acidic (pH 2) or alkaline solutions (pH 12), the pH remains unchanged and the voltage requirement of the electrolysis system are positively correlated with the electrical conductivity of the solutions.

2.3. Electrode's gap

The gap between two electrodes is another critical parameter that steers the pollutants removal efficiency during EC process. In an EC process, the electrostatic field depends on the gap between anode and cathode and voltage drop increases linearly with increases in inter-electrode gap according to the following relationship:

$$V = IR = \frac{i \times d}{A \times \sigma} \qquad (12)$$

Where, i is the current (A), d is the gap between two electrodes (m), A is the effective anode surface (m^2), and σ is the specific conductivity (S/m).

2.4. Operating cost

Cost of operation generally consists of electrical energy, electrodes, labor, maintenance, sludge disposal costs. Principally, electrical energy and electrodes consumption for treating per unit of liquid manure are determined by the following relationship (Kobya and Demirbas, 2015; Kobya *et al*, 2006).

$$Operating\ Cost = \propto \times Cost_{Energy} + \gamma \times Cost_{Electrodes} \qquad (13)$$

$$Cost_{Energy} \left(\frac{kWh}{m^3}\right) = \frac{V \times i \times t_{EC}}{Vol_{waste}} \qquad (14)$$

$$Cost_{Electrode} \left(\frac{kg}{m^3}\right) = \frac{i \times t_{EC} \times M_w}{z \times F \times Vol_{waste}} \qquad (15)$$

Where, α and γ are unit price of electricity and electrodes; V is the applied voltage, i is the current (A), t_{EC} is the operating time (s or h), and Vol_{waste} is the volume of liquid manure processed.

3. Results

Since the nature of the paper is review work, the results of the review were arranged in the form of two tables and discussed separately. Recently, EC treatment technology has been utilized in treating various industrial wastewater including urban, pulp and paper mill wastewater, tannery

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waste, textile, arsenic and chromium, restaurant, and oily wastewater (Zakeri *et al*. 2021; Zhang *et al*, 2020, 2018; Benazzi *et al*, 2016; Kumar *et al*, 2009; Raju *et al*, 2008; Thella *et al*, 2008; Feng *et al*, 2007; Mahesh *et al*, 2006; Stephenson and Tennant, 2003; Kobya *et al,* 2003). The performance of the electrolysis system depends on wastewater chemistry which dictates the selection of an appropriate electrocoagulation hardware system suitable for wastewater types. In spite of the considerable success of electro-coagulation as a possible technique for treating industrial wastewater, this technology was not widely for treating the livestock wastewater based on literature. Most of the EC research paper dealt with dairy waste used wastewater prepared artificially either from milk powder or effluents directly from milk processing plants. The process that used real-world lagoon effluents is extremely scarcely described in the literature. Every wastewater and its chemistry are different and thus, compounds that contributes to COD concentration in wastewater. The Table 1 shows the major constituents of the livestock wastewater and Table 2 shows major constituents of the swine, poultry and other wastewater. Therefore, it is important to review the effect of different electrodes materials, operating parameters including current density, pH, electrical conductivity, and solids contents of livestock wastewater (dairy, swine lagoon waste, and poultry wastewater) that achieved best pollutants efficiency.

Sengil and özacar (2006) studied the EC treatment of wastewater from a dairy exhaust aiming COD and oil-grease removal with mild steel electrode. The optimum values for current density, pH, and electrolysis time for 18,300 mg COD/L and 4570 mg oil–grease /L were 0.6 mA/cm^2, 7, and 1 min, respectively. The overall COD and oil–grease removal efficiencies were 98 and 99%, respectively, with mean energy consumption of 0.003 kWh/kg of COD. Tchamango *et al* (2010) used aluminum electrodes in treating artificial dairy effluents and reported removal efficiencies of 61, 81, and 100%, for COD, TN, and turbidity, respectively.

Bensadok *et al* (2011) conducted an experiment using batch electrochemical technique with Al-Al electrodes to remove COD, phosphate and turbidity from dairy effluents (milk liquid fractions). They reported that the removal efficiencies of water quality parameters were dependent on the composition of the electrode's material. An optimal value of current density, initial pH, NaCl concentration and electrolysis duration were 0.5 mA/cm^2, 6.6, 1.5 g/L and 2 min, respectively. Results indicated that the removal efficiency of COD, phosphate and turbidity attained respectively 80, 59 and 96%. Corresponding energy consumptions were 0.03 and 0.04 kWh/kg for COD and phosphate removal, respectively.

Swine liquid manure collected from primary lagoon was treated with electrocoagulation techniques with three different electrode combinations (Al-AL, Fe-Fe, and Al-Fe) in batch study under varying electric potential (Rahman and Borhan, 2014). The removal efficiencies of TP, COD, and TOC were positively correlated with increasing treatment times and applied current densities (5, 10, and 21 mA/cm^2) for each electrode materials. Aluminum electrodes outperformed iron and hybrid (Al-Fe electrodes) in removing TP at all current density levels tested. Overall, use of hybrid electrodes resulted in improved COD removal. For the same treatment times (1200s) and current density (21 m/cm^2), hybrid electrodes removed about 100% COD, which are about 1.9 and 1.3 times higher than those of aluminum and iron electrodes, respectively. Iron electrodes showed the highest removal efficiency (85%) for total organic carbon (TOC) at 21 mA/cm^2 current density and 1200 s treatment time. Overall, lower specific electrical energy consumptions (SEECs) per kg of pollutants (TP, COD, and TOC) were estimated for the aluminum electrodes than the other electrodes combination.

Thapa *et al* (2015) treated feedlot runoff with aluminum (Al-Al), iron (Fe-Fe), and hybrid (Al-Fe) electrodes arranged in parallel at different electrical voltage potentials (5, 10, and 15 Volts) for up to 30 min in a batch at room temperature under laboratory condition. The electrical conductivity (EC), total phosphorus (TP), total nitrogen (TN) and chemical oxygen demand (COD) concentrations were reduced significantly irrespective of electrode types. Overall, TP reduction was higher (100%) followed by COD (50-75%) and TN (25-60%) concentration. He indicated that Al electrodes were more effective than the other two electrodes for TP reduction at all applied potentials and COD reduction was better at lower applied potential. Hybrid (Al-Fe) electrodes outperform other two electrodes combination in removing TN. The speed of the nutrient removal and energy consumption were increased with increasing voltage level.

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Table 1. Summary of the electrolysis and electrocoagulation techniques to treat dairy wastewater.

Brief description of the EC system configurations under evaluation	Operation parameters			Wastewater characteristics				Removal Efficiency (%)	Energy	Source
	Current density/ voltage	Operation/ retention Time	Liquid manure Type	pH	EC (mS/cm)	Target pollutants	Initial values (mg/L)			
Fe-Fe electrodes (10cm × 8.5 cm× 0.2 cm) were used. Electrode distance = 2 cm.	20 V	60 min	Dairy wastewater	3.0	--	COD TSS BOD	-- -- --	920% 87% 87%	--	Zakeri *et al*. 2021
Low carbon steel electrodes (7cm × 4 cm× 0.5 cm) with an effective surface area of 38 cm^2; substrate was agitated with a magnetic stirrer bar at 150 rpm	--	100 min	Dairy manure	6.0	0.32	Phosphorus	115	97%	NR	Zhang *et al*, 2020
Sequential Electrocoagulation/Electro-oxidation **Electrocoagulation (EC):** Two Al plate as mono-polar anode and cathode with a gap of 5 mm. **Electro-oxidation (EO):** Two cylindrical electrodes made of expanded platinized titanium and the electrodes were separated by 0.5 cm.	30 mA/cm^2	21 min	Dairy wastewater treatment plants	6.55	3.93	COD	EC EO EC+EO	46% 35% 66%	NR	Chakchouk *et al*, 2017
Four electrodes (two anode and two cathode) Size = 150mm×70mm×2mm Gap = 1mm (10 – 30mm) Total submersed area = 0.021 m^2. A peristaltic pump adjusted three residence times (30, 60, 90 min)	13.3 mA/cm^2	90 min	Synthetic dairy wastewater (SDW: 2 g of whole powder milk in 1-L of water)	6.0	1.49	Color Turbidity TOC COD	-- -- -- --	94% 93% 65% 95%	--	Benazzi *et al*, 2016
Electro-Fenton of dairy wastewater Volumetric ratio (H$_2$O$_2$/wastewater) = 0.907; Molar Ratio = 3.987; Size = 20 mm×5 mm×2mm; Gap = 30 mm; Effective area = 1 cm^2	55 mA/cm^2	86 min	H$_2$O$_2$ + dairy lagoon wastewater At a ratio 0.907 mL/L	7.48	0.21 mS/cm	COD	2527	97%	--	Davarnejad and Nikseresht 2016
A 1-L plastic container with 0.8L liquid manure. Four- electrode types (Stainless steel (SS), aluminum (Al), low carbon steel (LCS), and grey cast iron (GCI)).	263 mA/cm^2	100 min	Dairy slurry mixed with tape water (1:2)	6.4	0.32	TP	100	SS 90% Al 96% LCI 97% GCI 77%	583-826 Wh/g of P removal with cast iron	Zhang *et al*, 2016

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Electrode setup	Current / Voltage	Time	Wastewater	pH		Parameter	Initial	Removal	Energy	Reference
Anode and cathode size (70mm×40mm×5mm) with an effective area of 38 cm2 and paired with same type of material. Electrode gap = 40 mm.										
4 Al electrodes (150 mm×70mm×2 mm) with gap = 10 mm connected in parallel monopolar mode Submerged Area: 0.021 m^2	10V 1330 mA/cm^2	90 min	Dairy wastewater	6.0	1.49	Color Turbidity TOC COD	-- -- -- --	94% 93% 65% 69%	1.88 kWh/ m^3	Benazzi *et al* 2016
Continuous flow Al -Al (-- mm×-- mm×10 mm) with gap = 10 mm connected in bipolar mode Submerged Area (69.2 cm^2): 0.0069 m^2	200 mA/cm^2	60 min	Dairy wastewater	8.0	4.7	COD TSS	-- --	93% 99%	13.57 kWh/m^3	Aoudjehane and Benatallah 2015
Eight Parallel iron Plate monopole Electrodes 130 × 200 × 1.5 mm) with Gap = 6-14 mm;	6.16 mA/cm^2	21 min	Dairy Effluents	5.0-9.0	NR	COD Turbidity TSS VSS pH		57% 99% 92% 97% 10	--	Valente *et al* 2015
Sequential Electrocoagulation/Electro-oxidation **Electrocoagulation:** 55 cm^2 Al plate and large surface area of Fe mesh as mono-polar anode and cathode. **Electro-oxidation:** Two DSA electrodes (Ti/IrO$_2$-Ta$_2$O$_5$ and Ti/IrO$_2$-SnO$_2$–Sb$_2$O$_5$) were prepared by the Pechini method.	9.09 mA/cm^2	120 min	Dairy wastewater from washing cows before milking and milking instruments, and shed cleaning)	8.3	2.36	Turbidity COD TOC	3900 3859 1062	100 90 98	NR	Borbon *et al*, 2014
Electrocoagulation: Two Al anodes and three Fe cathodes were connected in bipolar mode; 0.0016 m^2 effective electrodes area **Advance oxidation process:** Fenton ((H$_2$O$_2$) 30% w/v and FeSO4·7H2O 99.5% at a ratio of 5:1; Ozone dosing (250mg/h from an ozone generator)	5 mA/cm^2	75 min	Dairy exhaust wastewater	4.4	3.67	COD	5902	70%	7 kWh/m^3	Torres-Sánchez *et al*, 2014

Four Al -Al (80 mm×85 mm×3mm) with gap = 10 mm connected in bipolar mode Submerged Area (69.2 cm²): 0.0069 m²	3000 mA	75 min	Dairy exhaust wastewater	6-7.5	0.8	COD Oil/grease TSS	1070 ppm 500 ppm 1500 ppm	87% 48% 93%	113 kWh/kg	Sharma 2014 Bipolar
Four Al -Al (100 mm×50 mm×1mm) with gap = 10 mm connected in monopolar mode Submerged Area (100 cm²): 0.01 m²	7V (0-30V; 0-2 A)	10 min	Dairy exhaust wastewater	5-7	1.7	COD Turbidity	8000 ppm 367 NTU	99% 98%	0.00011 kWh/kg COD	Shivayogima th and Naik 2014 monopolar
Two parallel plate electrodes of identical sizes Al-Al (90 mm × 25 mm × 1.5 mm); Gap =8 mm.	1-3.6 mA/cm²	1-5 min	Feedlot runoff	8.02	3.6	TP COD TN	49 ppm 263 ppm 33 ppm	100% 78% 56%	24 kWh/kg 61 kWh/kg 650 kWh/kg	Thapa *et al*, 2014
Three pairs of Al and Fe plates used alternately using a pole changer to generate Al and Fe coagulants; Submerged Area: 100 cm²	15 mA/cm²	20-30 min	Dairy Effluents	6.5-7	0.94	COD Turbidity pH	1200-1900 520-560 6.5-7	79% NR NR	8.43 kWh/m³	Yavuz *et al* 2014
Six parallel plate electrodes (Gap = 20 mm) in bi-polar connection; Al-Al (15×15×25 mm); Submerged Area (14×20mm): 0.028 m²	0.5 mA/cm²	Up to 60 min	Dairy Effluents (milk processing factory)	7.24	8.07	COD BOD TSS Fecal coliforms	6114 ppm 2919 ppm 734 ppm 3.3×10⁶ fc	90-100%	0.095 kWh/L	Bazrafshan *et al* 2013
Two Fe-Fe or Al-Al with size 50mm×10mm×1mm	30mA/cm2	30 min	synthetic wastewater	various	--	COD P-PO₄	6760 ppm --	-- 94%	--	Smoczynski *et al*, 2013
Three pairs of parallel plate electrodes (Gap = 20, 40, 60 mm); St-St (150 mm×400 mm); Al-Al (150 mm×400 mm; Fe-Fe (150 mm×400 mm)	10-30 V (30V)	0-120 min	Dairy wastewater (mixture of milk and water from containers and floor cleaning)	7.4-7.7	1.8-2.2	COD	1350 1596 1605	62% 79% 82%	NR	Ghahremani *et al* 2012
Eight Parallel iron Plate monopole Electrodes 130 × 200 × 1.5 mm) with Gap = 6-10 mm);	5 mA/cm²	5-30 min	Dairy Effluents From milk processing plants	5-9	NR	COD Turbidity TSS	1727-4780 268-438 300-604	58% 95% 95%	NR	Valente *et al* 2012
Parallel plate electrodes (Gap = 20mm) Al-Al (30×150×2mm); Pt-Ti (30×150mm grids); Submerged Area: 12×10⁻⁴ m²	0.5 mA/cm²	2 min	Dairy Effluents (milk liquid fractions)	6.6	3.1	COD Phosphate Turbidity	7560 ppm 41 ppm 1545 NTN	80% 59% 96%	0.03 kWh/kg 0.04 kWh/kg	Bensadok *et al* 2011
Two parallel plate electrodes (Gap = 10 mm)	12.3 mA/cm²	74 min	Dairy Effluents	6.5	NR	COD TS	3900 ppm 3090 ppm	68% 54%	1.32 kWh/kg	Kushwaha *et al* 2011

Electrode	Current density	Time	Effluent	pH		Parameter	Initial	Removal	Energy	Reference
Al-Al (100 mm×85 mm×1mm); Submerged Area (9.5×8.5 cm²): 0.008 m² NaCl added = 2 g L⁻¹	0-20V; 0-5A		(milk power homogenized in DI water)			TN TUR	113 ppm 1744 NTU	91% 99.8		
Four Fe-Fe (100 mm×85 mm×1mm) parallel plate electrodes (Gap = 10 mm) connected in parallel and in bipolar mode; Submerged Area (9.5×8.5 cm²): 0.008 m², NaCl added = 2 g L⁻¹	27.0 mA/cm² 0-20V; 0-5A	50 min	Simulated dairy Effluents (milk power homogenized in DI water)	7	0.22	COD TS TN TUR	3900 ppm 3090 ppm 113 ppm 1744 NTU	70% 48% 93% ~100%	2.76 kWh/kg	Kushwaha *et al* 2010
Two Parallel plate Electrodes (Gap = 5mm) Al-Al (100mm×50×40mm); immersed in 50 mm depth with a submerged area: 0.002 m²	4.3 mA/cm²	30 min	Artificial dairy effluent prepared- mixing 5 milk powder (2.5, 5, 10 and 20 g/L) tap-water	6.8-7	0.6-1.6	COD Phosphorus Nitrogen Turbidity	NR	61% 89% 81% 100%	NR	Tchamango *et al*, 2010
The EC Unit with Iron Electrodes, Built on a Filter Press Frame	--	--	Dairy lagoon effluents after chemical pretreatment to coagulate and separates solids.	7.8	7605	NO3-N KDN TP SRP	0.18 ppm 631ppm 37 ppm 4.2 ppm	78% 50% 96% 99.6%	--	Mukhtar *et al*, 2009
Four Parallel Plate Electrodes (Gap = 20mm) in bi-polar connectiom Fe-Fe (100×50×20mm) Submerged Area: 0.033 m²	0.6 mA/cm²	1 min	Dairy Effluents (dairy exhaust fractions)	6-7.5	1.2	COD Oil-grease TSS	18300 ppm 4570 ppm 10200 ppm	98% 99% NR	0.003 kWh/kg	Sengil and özacar 2006
Electrolysis: Two parallel plate Cu-Cu suspended vertically Size: 1m long; Gap = NR Depth of electrodes: 1.5 m **Storage length** effect and **aeration**: 0.8-1.0 L/s by an electric motor	3.1 mA/cm²	33 weeks	Cattle Slurry in a Tank	6.8	NR	Coliform Ammonia H₂S CH₄ CO₂ N₂O	10⁴ TCB/g 15 g/kg 2000 ppm 2200 ppm 8500 ppm 20 ppm	50% NS 92.5% 50% 50% 100%	8 kWh/m³	Skjelhaugen and Donantoni, 1998

Key: '--' Not reported; NS= not significant; EC= Electrical conductivity; EO = Electro-oxidation; TP = total phosphorus; COD = chemical oxygen demand; BOD = biological oxygen demand; TN = total nitrogen; TSS= total suspended solids; NR = Not reported; DSA = dimensionally stable anodes.

Table 2. Summary of the electrolysis and electrocoagulation techniques to treat swine, poultry and other waste.

System Description	Operation parameters			Wastewater characteristics					Removal Efficiency (%)	Energy kWh/kg kWh/L	Source
	Current density/ voltage	Time	Waste Type	pH	EC mS/cm	TSS mg/L	Target compounds	Initial Values (ppm)			
Fe electrodes mono-polar parallel connection, 1 cm apart from each other in 500mL cylindrical glass beaker with DC power source; 1.5 gm/L NaCl added for providing sufficient electrical conductivity.	13.78 V	60 min	Domestic graywater	8.2	0.8	--	COD	180	70% 0.48 kWh/kg COD removed	--	Bajpai and Katoch 2021
Two parallel plate low carbon steel (LCS) electrodes of identical sizes (70 mm × 40mm × 5 mm); Gap= 40 mm. Effective area 38 cm^2	26.3 mA/cm^2	100 min	Upper layer of a swine deep pit barn	8	1.95	2.12	TP	439-770	73-86%	56-83W h/g-P removal	Zhang *et al*, 2018
A continuous flow EC reactor consisted of Al-Al and Fe-Fe electrodes with 130 mm H × 70 mm W × 12 mm D and Gap of 20 mm. HRT = Al = 31.8–88.2 mL/min HRT = Fe = 61.8–118.2 mL/min	16-58 mA/cm^2	32-88 62-118 min	Swine manure treatment systems	6 Al 7 Fe	6.4 6.8	NR	TP	73 65	93% 96%	2.2-15.3 2.1-17.2 kWh/L	Mores *et al*, 2016
EC cell size: 80 mm L×80 mm W×10 mm H Four parallel plate monopolar Al-Al electrodes ((50 mm × 60mm × 3 mm) Gap/spacing = 11 mm Effective electrode area = 90 cm2	30 mA/cm^2	30 min	Screened livestock effluents	8.4	--	2340	Color COD	Dark grey 2200	93% 95%	NR	Tak *et al*, 2015
Ten Parallel Plates Electrodes (Gap = 15mm) Pb-PbO$_2$ (300×300 mm); Ti-IrO$_2$ (340×190 mm)	20A-5V	--	Liquid hog manure	--	--	--	Odor Bacteria	--	2fold reduction	NR	Bejan *et al*, 2015
Two parallel plate electrodes of identical sizes; Al-Al (90 mm × 25 mm × 1.5 mm); Gap =8 mm.	6.9 mA/cm^2	5-60 min	Swine liquid manure	8.4	6.7	980	TP COD TOC	35.3 1577 490	100% 77% 69%	39 11 38 kWh/kg	Rahman and Borhan 2014
Two rectangular cathodes (steel, 1.2 mm thick) on either side of one anode (Ti, 1 mm thick) arranged in parallel Gap: 10 mm; Anode area = 480 cm^2	12VDC-30A (7VDC)	360 min	Leachate from swine slurry	NR	0.996	NR	NH$_4$-N OP STOC Color	849 180 1378 3392	99% 59% 64% 93%	NR	Cho *et al*, 2010

			composting system								
Two parallel rectangular Al –Al and Fe-Fe plates Size: 50 mm×180mm×5 mm; Gap: 62 mm; effective area: 0.006 cm²	15mA/cm²	20 min	Poultry wastewater (anaerobically pretreated)	5.0	1.5-2.5	NR	COD Color	NR	90% 92%	NR	Yetilmezsoy *et al*, 2009
Eight iron or aluminum plates connected in monopolar (MP) or bipolar (BP) fashion. In MP, four plates are individually connected to the power. Thus, there were four anodes and four cathodes. In BP, only outer two plates are physically connected to the power Size: 1000mm×1100mm; Gap=150mm	0.3 A	60/90 min	Screened wastewater from poultry slaughter house	6.11-6.5	0.33-0.5	1440	BOD Oil-grease SCOD TCOD TSS Turbidity	2700 720 1290 2700 1440 --	86 99 50 82 89 90	NR	Asselin *et al*, 2008
Two parallel plate electrodes (Gap = 5 mm) Fe-Pt-Ir (150 mm×35 mm×1 mm); Fe-Fe (150 mm×35 mm×1 mm);	40 mA/cm²	180 min	Screened swine manure	8.5	250mM	NR	NH_4-N TP	2000 400	97% 98%	60 kWh/kg	Ikematsu *et al*, 2007
Eight Parallel Plates Electrodes (Gap = 15mm) Al-BP (0.011 m²); Fe-MP (0.011 m²)	0.5A Al-BP 2A Fe-MP	30 min	Liquid swine manure	6.4	13.2	7.2	COD BOD	992 77	65-68% 87%	NR	Laridi *et al* 2005
Two cylindrical parallel electrodes (length 1.5 m with dispersion area of 0.11×2 m² (gap = 50 m)	1.56 mA/cm²	90 d	Stored swine slurry	7.0	NR		Odor NH_4 FC ATP	--	84% NS NS NS	0.038 kWh/L	Ranalli, 1996

Key: EC= Electrical conductivity, '--' Not reported; NS= not significant; EC= Electrical conductivity; TP = total phosphorus; COD = chemical oxygen demand; SCOD= Soluble Chemical Oxygen Demand; TCOD= Total Chemical Oxygen Demand; TSS= total suspended solids; BOD = biological oxygen demand; ATP= Adenosine triphosphate; NR = Not reported.

4. Discussion

Removal of nutrients using the electrical coagulation method is strongly dependent on the electrical conductivity of the aqueous medium. In addition, pH, particle size, COD loading rates, electrodes nature and area, and catalytic activity of the anodes also affect the process. Inherently, higher TP reduction was likely due to formation of abundant amount of insoluble metal phosphate when OH⁻ released from the cathode that react with the soluble phosphate ions already contained in the feedlot runoff (Thapa *et al*, 2015) and swine liquid manure medium (Rahman and Borhan, 2014) during electrolysis process according to equations 8-12 (Nguyen *et al*, 2014; Inan and Alaydin, 2014). The TP reductions were primarily due to the production of Al or Fe ions in an anode. The hydroxide ion produced in cathode is immediately react with metal ions in the runoff and produce metallic hydroxides. Subsequently, this process, initiated polymerization reactions (two or more small, similar molecules are combined to larger molecules) when metallic hydroxide particles produced had reached sufficient concentration. In the end, it is deposited as sediment and thus decrease amount of total phosphorus from the solution (Nguyen *et al*, 2014; Inan and Alaydin, 2014 ; Laridi *et al*, 2005; Ilhan *et al*, 2008).

The removal of COD depends upon the wastewater medium and treatment conditions such as coagulant dose released from electrocoagulation system and chemistry of the medium including pH, oxidizable carbon compound in the liquid and with suspended solids, etc. The Fe-Fe electrodes performed best in removing COD followed by Hybrid (Fe-Al) and Al-Al electrodes at high current density levels. The COD removal efficiencies of hybrid electrodes were in-between Fe-Fe and Al-Al. Laridi *et al*. (2005) stated that at 1500 and 2000 mA current levels iron electrodes resulted in significantly greater COD reductions than that of aluminum using swine liquid manure for an 1800s treatment time. It was demonstrated in a bench scale study using neutral and alkaline textile wastewater that the Fe-Fe was more efficient than Al-Al electrodes in removing COD and electrode's efficiency was reversed when wastewater medium was acidic (Kobya *et al*, 2003). In our study, the final pH recorded for all electrode types were ranged from 9-9.5. Thus, slightly basic swine liquid manure with iron-based electrodes (Fe-Fe and Fe-Al) electrodes resulted higher COD reduction than Al-Al electrodes (Rahman and Borhan, 2014).

With acidic pH (4-6), the Al electrodes showed higher COD and color removal (in poultry water) due to the amphoteric character (ion that can react both as an acid as well as a base such as copper, zinc, tin, lead, aluminum, and beryllium) of Al(OH)3 which does not precipitate at <2.0 pH. Similarly, at high pH (>10), increasing Al(OH)3 solubility may lead to the formation of AlO_2^- of which does not help for water treatment (Yetilmezsoy, 2009). Inherently, electro-coagulation is considered as an accelerated corrosion process in which a metallic surface is continuously corroded by other metal it is in contact with, due to an electrolyte and the flow of an electrical current between the two metals (caused from an external source of electromotive force (EMF)). The reaction rate principally governs by the removal of hydrogen ions [H+] through H_2 evolution/generation from electrodes material under use. With Al electrode, the speed of this reaction is high at low pH (close to 4). At this pH value, an insoluble metal oxide compound is formed facilitating complete reaction with organic compound Moreno-Casillas *et al*, 2007). In contrast, too high pH will increase metal hydroxide (Al(OH)3) solubility and thus lead to the formation of soluble metal oxide (AlO2) (Adhoum and Monser, 2004). Unlike Al, the Fe electrodes the formation of the flocs usually occurred at pH values higher than 7.5.

4.1. Effect of functional parameters on the system's performance

The electrocoagulation process in terms of speed and effectiveness in treating animal wastewater are mainly depends on the electrical conductivity and pH of the solution, current density, electrode passivation, arrangement and shape of electrodes, type and mode of power supply, gap or the distance between the electrodes, agitation speed, electrolysis time, initial pollutant concentration, and retention time.

4.1.1. Electrical conductivity

Electrical conductivity of the solution is most important parameter that maneuvers the speed of electrocoagulation process. Along with pH, the pollutants removal efficiency and operating cost are directly related to the solution conductivity. The wastewater solution must have a minimum threshold level of conductivity for the flow of the electric current and optimum pH for better removal efficiency. The conductivity concentrations of a solution determine the maximum possible current could be applied/passing through it. Generally, a salt (sodium chloride or sodium sulfate) is used to raise the conductivity of liquid wastewater to an optimum level. Thus, there is an increase in the current density when the conductivity of the wastewater increased at constant cell voltage or decreased in the cell voltage at constant current density (Bayramoglu *et al*, 2007; Merzouk *et al*, 2011). Studies with liquid swine and dairy manure demonstrated that the EC of electrolysis samples decreased significantly in the treated wastewater and decreasing rate were inversely correlated to the applied electrical potential. Similar results were also perceived by other researchers while treating industrial wastewater (Kim *et al,* 2013). The decrease in EC contents during electrolysis was possibly due to the loss of electrolyte ions in the wastewater, transformation of chlorine ion into chlorine gas after playing the role of electron donor and after converting anodically to chlorine which is further converted to hypochlorous acid in the aqueous solution (Krstajić *et al,* 1987).

4.1.2. pH of the solution

A pH 6.0 is optimal for both Al and Fe based electrodes (Inan *et al,* 2004). The pH of the wastewater solution is a

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critical operational parameter in electrocoagulation process. The maximum pollutant removal efficiency is obtained at an optimum solution pH for a particular pollutant and electrode. The precipitation/sedimentation of a pollutant begins at a particular pH. The pollutant removal efficiency decreases by either increasing or decreasing the pH of the solution from the optimum pH. In a neutral and slightly acidic solution (treating medium), aluminum (Al-Al) based electrodes performed better in removing COD than that of iron (Fe-Fe) electrodes. In contrast, iron-based electrodes performed better in alkaline solutions (Inan *et al,* 2004; Kobya *et al,* 2003). The highest removal efficiencies for COD and turbidity were achieved with aluminum in acidic wastewater (pH ~ 2-4) and iron electrode were found more effective in neutral and alkaline wastewater (pH ~ 6-9). Verma *et al.* (2013) studied the removal of hexavalent chromium from synthetic solution using electrocoagulation and found that the pH of the solution has a significant effect on the Cr (VI) removal efficiency. They performed the experiments at different pH of the synthetic solution and obtained the maximum chromium removal efficiency at the pH 4. They further reported that the pH of the synthetic solution after the EC process increased with an increase in the electrolysis time due to the generation of OH⁻ in the EC process.

4.1.3. Current density

Current density is one of the most crucial and steerable factors that control electrocoagulation system by depicting the amount and speed of coagulant release into the treating media, bubble production rate, and thus ultimate effectiveness of the electrocoagulation process. The current densities applied to the electrolysis system were directly proportional to the energy consumption and sludge generated. The increase in current densities increases the anode dissolution rate according to Faraday's law of electrolysis and thus guiding to release hydroxide ions to surrounding media. It is well-known that current not only determines the coagulant dosage rate but also the bubble production rate and size and the flocs growth (Valente, 2015). This ultimately providing more oxidizing power to decompose the organic pollutants present in the effluent and increases the pollutants removal speed. However, an increase in current density above the optimum current density does not result in an increase in the pollutant removal efficiency as sufficient numbers of metal hydroxide flocs are available for the sedimentation of the pollutant.

4.1.4. Gap between electrodes

An optimum gap between electrodes is another important factor since it governs flocs formation, hydrogen bubble distribution in the electro-flotation process, and operational cost of the system. The pollutant removal efficiency as accomplished by the formation of metal hydroxides within the effluent, increases until the inter-electrode gap between anode and cathode reached an optimum. This is because of the fact that the electrolytic

oxidation led flocs formation which is a function of electrostatic fields and the gap between the electrodes. Generally, a gap of 6 mm to 14 mm (0.8mm to 10mm is more typical) was maintained in electrocoagulation process found in the literature while treating dairy wastewater. Reduced gap between electrodes keeps energy consumption of EC operation low.

4.1.5. Electrolysis time

The pollutant removal efficiency also varies with the electrolysis time (referred as contact time) and also is a function of current density and adjusted pH. Generally, the pollutant removal percentage increases with an increase in contact time. This is due to the fact that that the mass of a substance deposited at an electrode during electrolysis is directly proportional to the quantity of charge passed through the electrolyte (Faraday's Law of Electrolysis). Therefore, increasing the contact time in the electrocoagulation process gives rise to a higher concentration of free ions inside the system and consequently an increased flocs and removal efficiency. However, the pollutant removal percentage increases linearly with the electrolysis time up to a certain point and then become flat. Beyond this optimum contact time, removal efficiency does not increase with increase in contact time. This due to that fact that at this point, the pollutant removal efficiency does not increase as sufficient numbers of flocs are available for the removal of the pollutant.

4.1.6. Initial concentration of pollutant

The pollutant especially COD removal percentage were found to be ranged from 18 to 90% when initial COD concentration of the aminol wastewater were ranged from 500 to 20,000 mg/L. In general, for a particular current density, the pollutant removal efficiencies were found to be decreased with a high initial concentration of the pollutant. This is because the number of metal hydroxide flocs formed by a particular electrolysis system and operating condition may not be sufficient to sediment the greater amount of pollutant at higher initial concentrations (Khandegar *et al*, 2013; Kobya *et al*, 2006; Daneshvar *et al*, 2006).

4.1.7. Electrode materials

Selection of electrode materials is dependent on the wastewater chemistry (pH, EC, oxidizable carbon compounds such as organic acid, halogenic compounds and organic nitrogen) and reactivity of target organic and inorganic compounds/ pollutants contained in it and the charge dose in terms of metal oxide ions (Fe(II) and/or Fe(III); Al(OH)2 and Al(OH)3)) that delivered by the electrodes materials. Compounds that contribute to water pollution (COD) are biodegradable organic compounds (protein, lactose, and fats), non-biodegradable compounds (rubber tires, plastic, fiberglass, metals, etc.,) and inorganic oxidizable compounds (nitrogen and phosphorus). The constituents, chemistry, and the compound that influences the COD concentration in dairy wastewater is different.

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Therefore, to achieve a best result for target pollutants such COD, TP, TSS, color etc., a combined system incorporating both Al and Fe electrodes could be a best choice.

4.1.8. Effect of agitation speed

The agitation ensures mixing and prevents forming concentration gradient in the electrolysis reactor. The agitation also enforced a velocity in the electrolysis chamber that creates a uniform the movement of the generated ions for proper mixing that facilitates faster reaction. However, agitation speed beyond certain point, the flocs get destructed by collision with each other instead of gaining floc size and untimely reduces pollutant removal efficiency.

4.1.9. Electrode degradation

As stated by Tietje-Girault *et al.* (2007), electrodes degradation mainly depends on 1) activity and surface area changes due to catalysis, blockage, and potential-distribution, 2) adsorption/desorption of reactant, product, intermediates, contaminants, 3) film formation/removal (passivation or polymerization), and 4) phase transformation (solid–solid, intercalation, dehydration). The passivation or polymerization recognized to be a process that retards the performance of an electrocoagulation system. Electrode passivation is the process of growing a film which is basically an oxide layer on the electrode surface restricting amperage and the required anode electrode dissolution in the electrolytic solution and thus the effective current flow between the anode and cathode. The electrodes should be free from any passivating materials and should be cleaned periodically to ensure anodic dissolution at a constant rate. The electrode passivation can be removed by routine mechanical cleaning suing H_2SO4 and HCl Acid. Also, passivation can be reduced by changed the polarity of the anode and cathode.

5. Conclusion

The increasing growth of livestock industries is generating huge amounts of wastewater that is characterized by high COD, BOD, nutrients, and organic and inorganic pollutants to the environment. The nature of pollutants, their concentrations, treatment methods and appropriate disposal methods vary mainly depending on the type of livestock effluents and manure management methods. Additionally, the selection of a wastewater treatment technique is dependent on various pollutant types, concentrations, and volume to be handled. Electrolysis especially electrocoagulation has been found to be a widely used appropriate method to treat various types of livestock wastewater. Recently, electrolysis process showed various advantages including environmental capability, energy efficiency, simplicity, easy to operate, cost-effectiveness, and produce decreased amount of sludge. In this article, the effect of various operating parameters on the system's performance were discussed to increase the system's performance. Additionally, future studies to improve the performance of electrolysis are recommended, such as (1) study the influence of shape and geometry of the electrodes; (2) effect of UV light and Cl; and (3) reduce the electrode passivation in reducing operating cost, etc. which will be helpful for future researchers as well as in management of livestock industries.

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