Maintaining the Consistencies in Electropolishing Results by
Characterizing the Polishing Bath State as a Function of its Instant
Key Properties

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ABSTRACT

Maintaining the Consistencies in Electropolishing Results by Characterizing the

Polishing Bath State as a Function of its Instant Key Properties

Bivi Krishna

Electropolishing is an advanced industrial metal finishing in practice commercially since the mid-20th century, to treat the metals with electricity and industrial chemicals. The process has grown remarkably in the last 50 years; the medical and pharmaceutical industry's growth is a strong driving force for the electropolishing industry now.

The work detailed in this thesis focuses on maintaining the uniformities in electropolishing qualities by specifying the polishing bath state as an approximation of its fundamental properties. In light of the scarcity of precise information regarding the techniques to keep the electropolishing process in control as the polishing bath ages, this research will present the organized data for an ageing bath. A mathematical model constructed from the vital polishing bath properties measured on-the-spot is used to quantify the polishing deliverables concerning surface roughness as a function of its immediate critical bath properties. The work results demonstrate that the model can anticipate the polishing capabilities under selected polishing conditions for a given polishing bath state, fresh, aged or regenerated. This model-based technique reduces the trial and error-based efforts the polishing industry takes to figure out the suitable operating parameters to deliver the polishing results when the aged bath is no longer efficient.

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1 Introduction

1.1 Background

Electropolishing (EP) is an electrochemical metal polishing process that yields a smooth and shiny surface by controlled anodic dissolution [1]. The process lowers the surface roughness and refines the surface finish by up to 50%, levelling the microscopic peaks and valleys [2]. It is either applied as a substitute for the mechanical polishing or to remove the surface damages caused by mechanical polishing [3]. The physical properties of the metal remain unchanged after electropolishing. Moreover, the procedure eliminates the surface imperfections and makes the metal surface simpler to sanitize, thereby restraining the body from collecting contaminants [4]. Therefore, it is one of the well-liked finishes for food processing, medical and pharmaceutical applications considering the cleanability, sterility, permanence, and corrosion resistance [5][6][7][8]. Consequently, these aseptic benefits of electropolishing and the built-in pure nature of stainless steel make both the volume champions in the medical device market [6].

Several parameters determine the material removal during the electropolishing process. The polishing current, the period of exposure to the polishing current, the polishing bath efficiency and the metal surface state undergoing polishing are a few factors [1][5][9]. The desired surface finish is generally regulated by controlling the polishing current and the polishing time [10][11]. The surface finish's ultimate quality and consistency depend on how these variables stay in control [2][4]. Delivering the best results for electropolishing is therefore considered more of an art than science. The variable selection predominantly depends on the type of metal to be electropolished, and the surface finish required [12][13]. The electropolishing solutions used in the industry are always compatible with the respective metals

or alloys polished. The polishing bath used for stainless steel is mostly a mixture of phosphoric - sulfuric acids [9][14][15][16].

1.2 Research Problem

An electropolishing bath is a salient parameter that governs the electropolishing coherence as it is the medium where the entire chemical process occurs [5][9][15][16]. As electropolishing involves material removal, the metal ions are dissolved during the process and surges with the bath's increased use. The metal ions gradually end up as sludge at the polishing tank and influence the bath's chemistry [12][17]. This change in bath chemistry has a remarkable dominance on the polishing rates and results in increased roughness and reduced gloss if the bath is in operation for an extended time. The bath thus only has a restricted functional life, and hence polishing tasks must employ the proper bath for the process to conserve the polishing uniformities [2][9]. Stainless steel electropolishing dissolves free iron ions from the material surface and leaves a chromium-rich body resistant to corrosion [1][5][11][18]. Accordingly, the metal concentration building up in these phosphoric - sulfuric baths are steel components, mostly iron, followed by chromium and nickel [9][15][16].

Electropolishing businesses generally extend the term of use of the polishing bath to keep down the running costs. With the same polishing bath in operation for a long time, the polishing results start to show a decline and produce inconsistent and unpredictable outcomes. The expected surface finish or gloss values are no longer obtained [1][5][11][15]. There is little or no possibility in the industry to replace 100% or regenerate a specific portion of the bath at all times. Therefore, the shops employ many trials and run to find the best polishing parameters to compensate for the ageing bath. They use a higher polishing current or further lengthen the polishing durations for each workpiece to deliver the expected polishing results. This practice ultimately brings in increased electricity and operational costs [14][15][16].

Additional surface defects like shadows, smudges, surface waviness, uneven polishing, pitting, increased roughness also emerge from improper current densities, longer polishing durations and overheating of the bath. The contaminated bath also leaves metal salt residues on the surface, more challenging to remove, even with proper rinsing. The metal complexes that form during the process also play a notable role in altering the bath's concentration gradient, contributing to the decline of polishing qualities [9][15][16][19][20]. Therefore, this stage requires proper process control to retain the final quality of the polishing process.

1.3 Objectives and Methodology

With the demand from business competitions, the industries do not willingly disclose the process secrets they go around to maintain the polishing performances. As is known, the polishing shops generally engage the least number of controls, and this breeds in inconsistent and unpredictable qualities while operating with long-term exploited baths [2]. Moreover, comparatively, little literature is present relating to the essential mechanisms to regulate the polishing bath durability. This lack of information, to a great degree, restricts the extension of the polishing strategies. And as this problem is still inadequately explored, additional studies are required to operate quality controlled electropolishing systems that perform consistently.

The scarcity of precise information motivates this research to measure the polishing bath's instantaneous state on-site as the first step in reducing the trial and error process. A systematic approach is followed to examine how the dissolved metal ions dominate the bath properties and composition throughout the bath ageing. The study quantifies the influence of the ageing phosphoric - sulfuric acid on the Stainless-Steel polishing performances. The research established a mathematical model entailing six attributes built from the vital bath properties, allowing the interpretation of the workpiece's surface roughness under standard polishing conditions. The performance of the model projects the polishing qualities achievable

at a specific bath state. The model helps determine the bath stage where the polishing quality begins to suffer, thereby draining and restoring the aged bath with the fresh bath [21]. The multilinear model also remains logical for the regenerated polishing baths. This model-based approach is a practical and reasonable reversal technique for the electrolyte bath to sustain steady polishing results during accelerated polishing needs, thereby extending the operational life.

1.4 Thesis Overview

The thesis document is organized as below:

- Chapter 2 layouts a detailed literature review of electropolishing,

- Chapter 3 covers industrial electropolishing and standard practices they follow,

- Chapter 4 discusses the experimental apparatus and the procedures used for the various experiments,

- Chapter 5 presents the preliminary tests to determine the operating parameters for the main experiments and the corresponding results,

- Chapter 6 covers the main experimental methods and the respective results,

- Chapter 7 presents statistical analysis and a regression model constructed from the experimental data,

- Chapter 8 provides the conclusions and some future directions to the research.

2 Background to Electropolishing

2.1 History of Electropolishing

Electropolishing is not fresh to the field of Metal Finishing. A brief survey of the history of electropolishing should prove of some interest in the present thesis.

A known work on electropolishing was in 1910 when Chemist E. I. Shpitalskii was granted a patent (German Patent 225871) for the cyanide brightening process for silver and gold. The next twenty years saw no significant research until 1930 when a notable patent (French Patent 707526) was issued for the research laboratory of Société De Materiel Téléphonique in France. The patent was conferred to its Engineer Pierre A. Jacquet and his chief H. Figour for developing the electropolishing methods for nickel, copper, aluminum and molybdenum in a perchloric–acetic acid bath [22][23].

The patent remained overlooked for a long time by the other industries until 1935, when Jacquet [24] published his research on the electropolishing of copper in phosphoric acid. The development and industrialization of the process are primarily credited to this work. electropolishing soon gained a lot of interest, and a tremendous amount of work accompanied to explore the industrial implementations of the procedure [25][26].

Electropolishing has been used in full swing in the industry since the mid-20th century [27]. Various signs of progress were made to improve the practical technologies for the general use of the process. The publications and patent coverage now on electropolishing are extensive. The right mix of electrolytes, operating conditions, and the process itself is the subject of numerous trade secrets in the polishing industry. The process has improved and advanced over the years and remains the ultimate technique for producing super-smooth surfaces because of all the benefits it offers [5][28].

2.2 Electropolishing Process

Electropolishing is an electrochemical metal finishing process that produces a shiny, smooth, ultra-clean surface by removing a thin layer of the material to level the micro-peaks and valleys [1][9][11]. The surface finishing is achieved by the combination of two different mechanisms, anodic levelling (macro-smoothening) and brightening (micro-smoothening) [29][30]. Fig. 2.1 represents a metal surface before and after the electropolishing process [31].
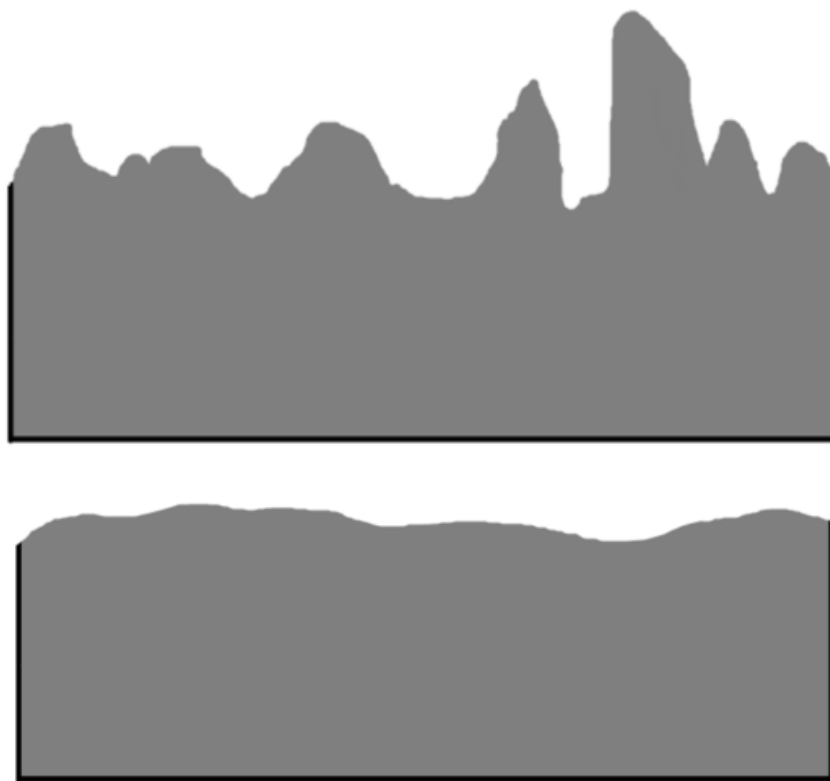
Figure 2.1 Surface profile before and after electropolishing.

Figure 2.2 represents the schematic of a typical electropolishing cell [32]. The metal workpiece to be electropolished is connected to the positive terminal of the DC power supply and the negative end to the cathode material. Both electrode materials are submerged in the electrolyte solution, forming a complete circuit. An electrical current passing from the anode to the cathode causes the ions on the metal surface to dissolve into the electrolyte. The process

results in oxygen evolution at the anode and hydrogen at the cathode [1][10][33]. The primary chemical reaction occurring during the electropolishing process is represented by Equation 1.1 [34]. This equation denotes that the metal ions are removed from the anodic workpiece, dissolving them into the electrolyte solution [5][9][35].

$$\text{Metal} - \text{Electrons} \rightarrow \text{Metal ions} \qquad\qquad [1.1]$$

Figure 2.2 Typical electropolishing setup.

The quantity of the metal dissolved is proportional to the amount of the electricity passing through the electrolyte. Faraday's Law of electrolysis demonstrates that the amount of

metal removed from the metal surface is calculated as indicated by Equation 1.2 [1][28][36][37].

$$\text{Amount of material removed, } m \propto \text{Amount of charge passed, } Q \qquad [1.2]$$

Understanding the concept of differential rates of removal of the metal ions is essential for accomplishing good electropolishing results. The right delivery of quality, efficiency and reduced cost is obtained by appropriately managing the process parameters. The metal removal rates can be controlled, ensuring that the polishing requirements are achieved [5][33][34][37].

2.3 Basic Principle of Electropolishing

According to Jacquet [38], the metal surface is a cluster of peaks and valleys at the electron-microscope level, where the real mechanism of the electropolishing process occurs.

Figure 2.3 indicates the low and high current density areas in the workpiece and the relative consequence on the electropolishing results [36]. An insulating viscous liquid layer develops on the anodic metal surface on applying a voltage to the electropolishing cell. This film has a higher electrical resistance and viscosity than the rest of the polishing bath. The layer is thicker on the valleys, and thus the resistance at the peaks is lower than the valleys. As current travels through the path of lower resistance, the peaks (A-B) become the very high current density areas and dissolve rapidly. The lesser current density areas, the valley (C-D), receive fewer current and display minor metal dissolution. In turn, this mechanism evens out and smooths the surface at the micron level [36][37][38].
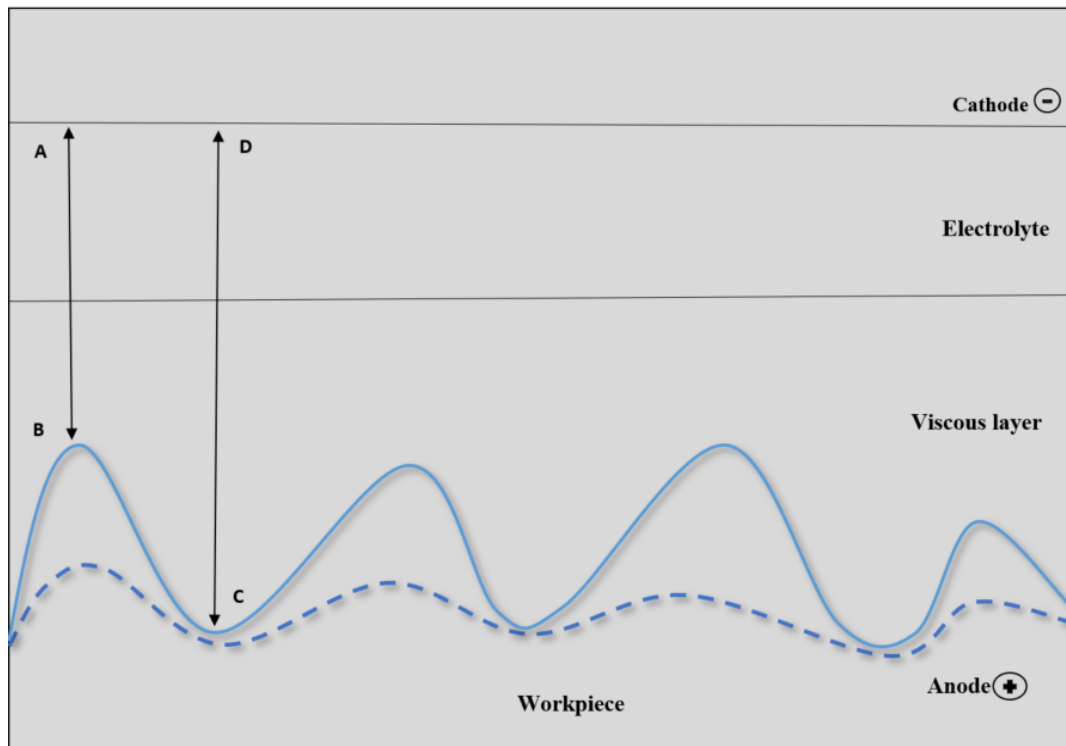
Figure 2.3 Electropolishing mechanism.

2.4 Current - Voltage Relationship in Electropolishing

Jacquet [38] also investigated the electropolishing by observing the current-voltage Characteristics. They found that the polishing operation requires the proper balance between voltage and current and that it is feasible to derive pitting, polishing or gas evolution, as shown in Figure 2.4 [36]. When the current density is too low, etching occurs, resulting in non-specific removal of metal. If the current density is too high, both the valleys and the metal surface peaks will be dissolved faster, resulting in pitting and gas evolution. A grasp of current-voltage combined effects is essential to high-quality electropolishing [1][28][36][37][38][39][40].
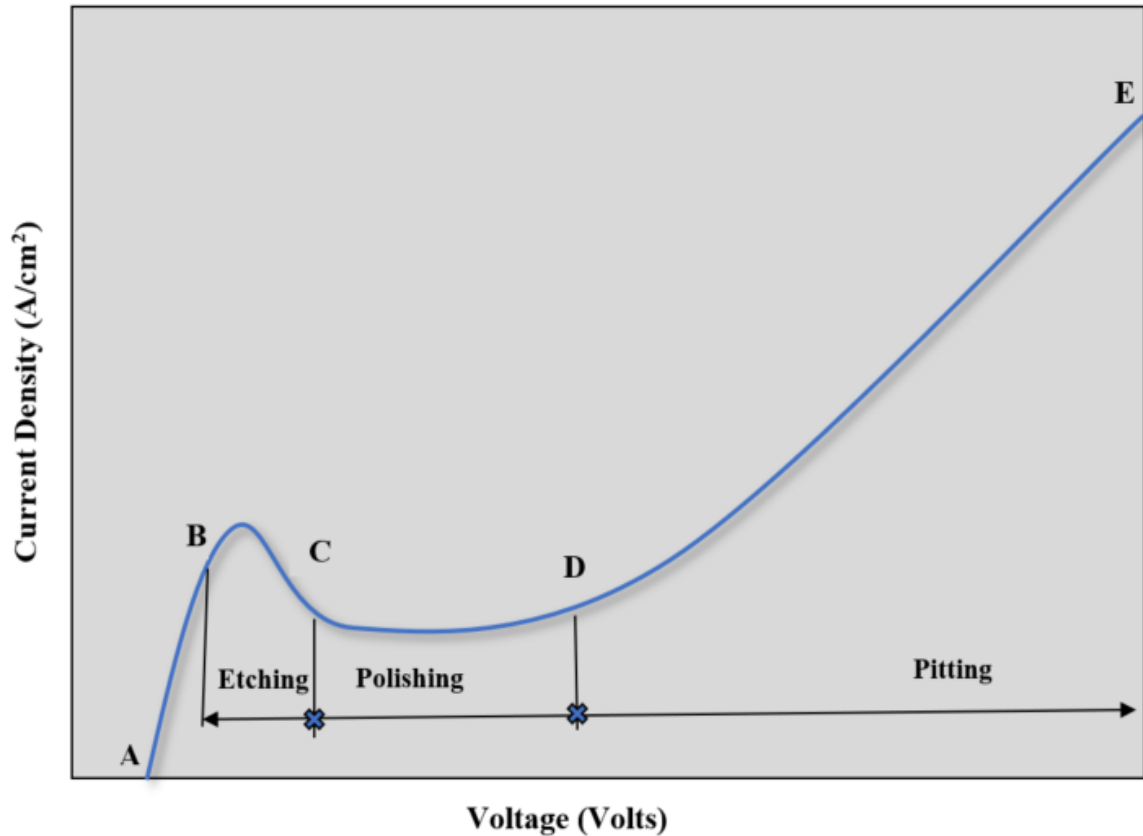
Figure 2.4 General relationships between current and voltage.

There are three major regions on the curve identified as unstable dissolution with etching (B-C), a stable plateau with polishing (C-D) and dissolution with pitting (D-E). The metal surface conserves its existing appearance up-to-the point B. Variations in both voltage and current and a concurrent fall in current density is found in the region (B-C). The metal surface shows signs of etching here. The current density remains constant, and the voltage increases over the regime (C-D). The polishing effect occurs in this region. The first bubbles of gaseous oxygen appear on the workpiece at the point D. The dissolution of metal is accompanied by the evolution of oxygen at higher voltages in (D-E). Pitting occurs as the oxygen bubbles get trapped on the metal surface [28][36][37][38][39][40].

2.5 Differences Between Electropolishing and Mechanical Polishing

The difference in the finish for two surfaces polished to the same finish using mechanical polishing and electropolishing can only be identified under high magnification [41], as shown in Fig. 2.5 [42].
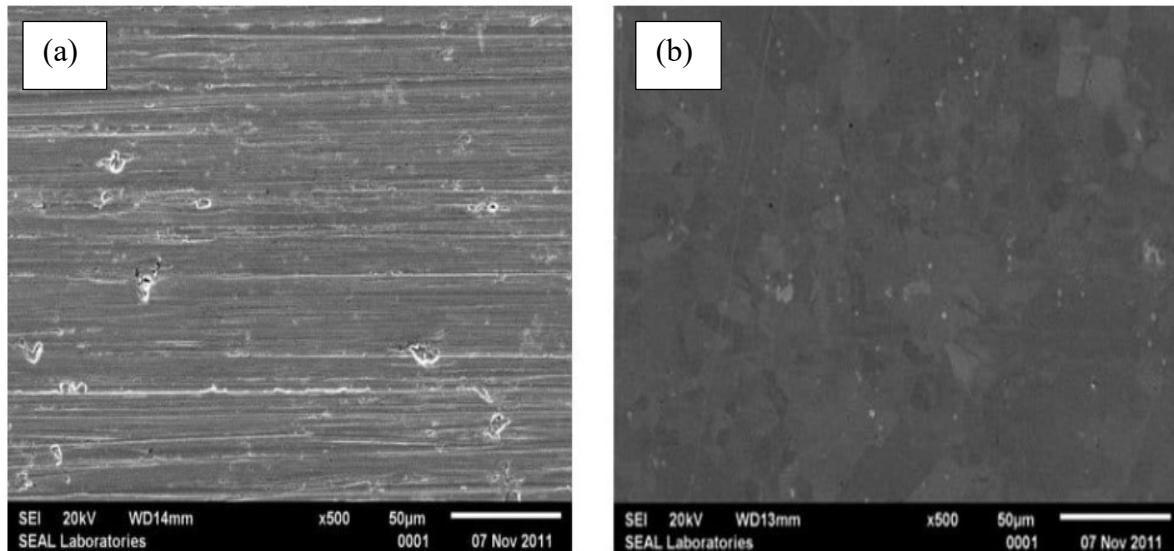
Figure 2.5 Mechanically polished and electropolished surfaces under magnification.

The significant differences between electropolishing and mechanical polishing are [41][42][43]:

- The electropolished surface has a high degree of smoothness and reveals the actual crystal structure. The mechanically polished metal body contains embedded abrasives, scratches, cuts and strains.

- Electropolishing removes microscopic peaks by dissolving the metal surface and cleans the valleys, thereby reducing corrosion rates. Mechanical polishing does not remove inclusions but pushes them further into the body and even collects the abrasive materials, creating damage and corrosion spots.

- Belts and wheels with abrasives are used to polish a surface mechanically, while an electrolyte solution and polishing current is used to remove the surface material during electropolishing.

- Mechanical finishing requires a lot of intense labor, whereas electropolishing greatly reduces labor costs.

- Electropolishing holds the real mechanical strength of the metal, but mechanical polishing significantly lowers the tensile strength.

- The electropolished finish is superior to the most widely used mechanical finish 2B for stainless steel.

- Electropolished surface bears a high cost than using 2B, but it is worth the added value due to the more attractive, smoother and firmer surface finish offered.

2.6 Properties of Electropolishing

The electropolishing process is an ultimate cleaning technique that is economical, highly flexible, and vital to conserve metal quality. It is the most used, relatively quick and contactless surface finishing process, best known for the bright and highly reflective finish it delivers [11][12]. The electropolished part reflects the light rays in parallel lines, and images are visible on the surface as from a mirror. The light rays get reflected in a random pattern from an unpolished or rough surface, and thus no image is seen or appears matte [44][45]. Fig. 2.6 illustrates the light reflection from polished and unpolished surfaces [45].
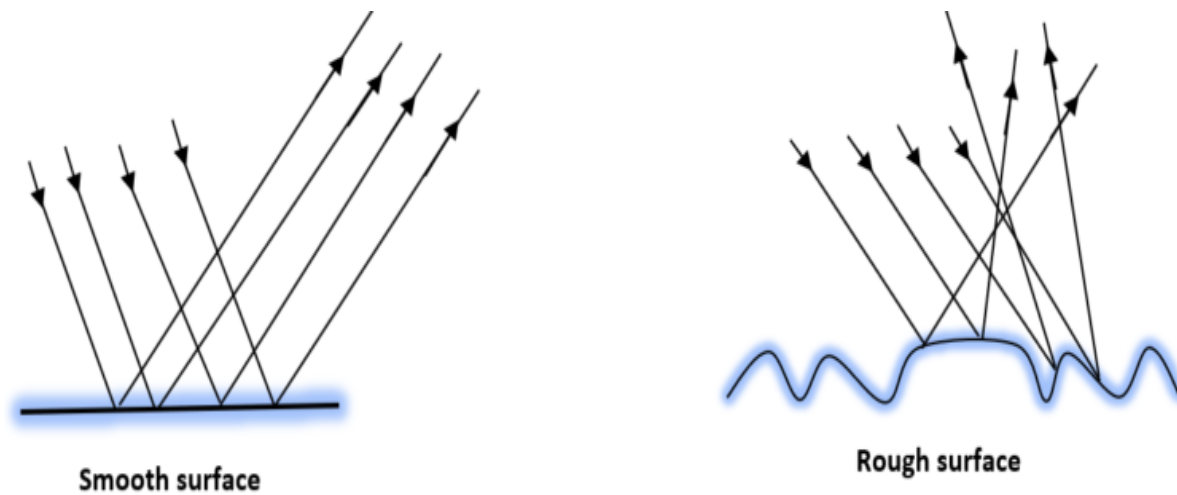
Figure 2.6 Light reflection from polished and unpolished surfaces.

Electropolishing potentially increases the material properties and the physical appearance of the workpiece. It results in a few positive changes in the metal body; the more valuable and viable are the metallurgical gains [1][9][15][28][46]. Overall, the process makes the metal parts smooth with a shiny look without any surface defects. The method also dissolves the outer layer of the metal body, removing the embedded impurities and thereby enhancing the corrosion resistance [3][12][18][47].

The electropolishing process can be applied to metal parts of any size or geometry and offers many advantages across various industries. Table 2.1 lists the primary distinguishable attributes of the electropolishing process that are highly beneficial for part-manufacturing in today's marketplace. These metal improvement benefits offer great promise for design, production and cost-savings [46][47][48][49][50][51][52][53].

Table 2.1 Properties of electropolishing.

Category	Post-electropolishing gains
Aesthetics	• Yields a bright and smooth surface finish. • Eliminates or minimizes scratches and stains. • Brings out metal's natural shine and improves reflectivity.
Mechanical	• Retains the natural grain structure and properties of the metal. • Holds the real fatigue strength of a metal part. • Relieves the stress off-the metal surface. • Lessens the coefficient of friction for the surface.
Corrosion Resistance	• Removes free iron or foreign material from the metal surface. • Generates a chromium-rich surface that is resistant to corrosion. • Eliminates the imperfections to prevent the moisture accumulation that leads to corrosion. • Removes the existing rust and oxides on the surface.
Cleanability	• Lessens product contamination and resists the build-up of unpleasant particles and bacteria. • Reduces the cleaning time by more than 50 percent and helps to maintain a hygienically clean surface. • Imparts non-stick qualities to the metal surface.
Other	• Reveals flaws in metal surfaces undetectable by other means. • Simultaneously deburrs along with polishing. • Polishes areas inaccessible by other methods. • Prepares surfaces for plating, welding and anodizing.

2.7 Limitations of Electropolishing

As with most processes, electropolishing also has a few drawbacks that include the following [5][13][22][32][54]:

- The low applicability of the electrolyte, as different metals require distinct polishing solutions.

- Most of the electrolytes used for polishing has a finite operational life.

- The regeneration of electrolytes used for polishing is difficult and limited in application.

- Various chemicals used for polishing are harmful acids that are toxic, flammable or even explosive.

- The polishing process results in a large volume of sludge from the metal dissolution, harmful to the environment.

- The dirty polishing baths may leave embedded impurities and a long-lasting impact on the metal surface.

- The polishing shops must dispose of the used baths and the metal sludges according to the local regulations.

- The rinse water waste also must be carefully handled as it contains metal ions and diluted acid contents.

- The polishing process itself results in a highly inflammable evolution of hydrogen at the cathode if not controlled.

- The polishing process cost is usually a little high though it saves a substantial amount of money in the long run.

- Electropolishing does not cover the rough surface defects, heavy scratches, pits or inclusions on the raw metal.

The industry always takes up electropolishing as an essential process for metal finishing as the advantages still outnumber the drawbacks.

2.8 Applications of Electropolishing

A significant deal of interest has evolved over recent years in producing extremely clean and corrosion-resistant components for use. electropolishing demonstrates to be an effective method for this purpose. Parts are often mechanically finished and then electropolished to a surface with a low roughness value [55][56]. The end assessment of the results consists of evaluating both surface appearance and surface chemistry. The former ascertains the polishing efficiency; the latter ensures that the polished surface is proper and protected as much as possible [11][51][57].

The applications of electropolishing has a link to its benefits. The quality of the finish required varies with the respective application. It is feasible to attain a high surface sanitation and sterility rate, as the electropolished surface is effortless to clean [5][50]. This quality is the most crucial parameter in the food and beverage processing, medical and pharmaceutical industries.

The food touches the metal elements, and thus it must not cause contamination or any changes in taste or colour of the food product [5][9][11][48][58][59][60]. Medical device manufacturing is highly regulated and thus requires the utmost attention to sanitation and safety. For internal or external use, devices must be clean, defect-free, and align with regulators like the FDA. Electropolishing meets the vital needs and stringent requirements for surgical instruments, implants and the other tools required for the medical, pharmaceutical and dental fields [61][62][63][64][65][66][67].

Many metals and their alloys can be electropolished using different electrolytes and the latest metal handling methodologies available now. As a result, electropolishing is used in a

broader discipline than ever before, with manufacturers demanding improved surface properties for their products. It is the popular finishing treatment across various industries for diverse applications. Table 2.2 lists a few sectors that favour electropolishing due to the multiple benefits offered [68][69][70].

Table 2.2 Major industries using electropolishing and the associated benefits.

Industry	Reasons for electropolishing
Medical, pharmaceutical, dental	• Expedited cleaning, exceptional levels of non-contamination. • Enhanced surface appearance, lowered risk of sharps and burrs. • Less friction of parts due to microscopically smooth surface.
Food, beverage, meat, poultry	• Smooth and cosmetically pleasant surface. • Outstanding aseptic and hygienic properties. • Absolute and effectual cleansing of the surface.
Semi-conductor	• Polishes delicate parts with minimized risk of damage. • Anti-corrosive qualities with a superior finish.
Automotive, aerospace, marine	• Smooth, shiny, appealing, easy-to-clean micro-finish. • Deburrs small metal components like fasteners, wire racks and blades. • Eliminates weld coloration and improved corrosion resistance at the joints. • Reduces burrs and cracks and provides optimal part function.

Industry	Reasons for electropolishing
Household appliances, machine-parts, nuclear	• Effortless clean-up, non-stick, non-contaminating surface. • Appealing finish with high levels of corrosion resistance. • Deburrs and eases the stress from the internal surface.
Vacuum chambers, filter housings, pipes and piping	• Better polishing without altering the precise dimensions. • Preserves the interior against rust and other types of corrosion. • Effectively polishes metal components of any size and shape.

2.9 Metals and Alloys that Work with Electropolishing

Electropolishing is the most preferred metal finishing process, controlled and applied to a more comprehensive range of metals. Mostly all metals and alloys are electropolished using distinct electrolytes with varying degrees of success these days [1][5][12][51][71]. The results of electropolishing gets better with the more clean, homogenous, the fine-grained scale-free structure of the alloy [9][16][19][20]. The various grades of stainless steel, mostly 300 and 400 series, are the most common alloys that are commercially electropolishing today [5][12][71][72][73][74]. Table 2.3 lists the popular metals and alloys that are electropolished.

Table 2.3 Metals and alloys that are commercially electropolished.

Metals or alloys			
stainless steels	Nickel alloys	Tool steel	Carbon steel
Nitinol	Titanium	Copper	Aluminum
Inconel	Nickel	Molybdenum	Niobium

Gold	Brass	Silver	Hastelloy
Carbon steel	Cupronickel	Bronze	Kovar
Leaded steel	Beryllium	Copper alloys	Tungsten
Tantalum	Cobalt chrome	Columbium	Vanadium
Antimony	Cobalt	Chromium	Bismuth

2.10 Electropolished Stainless Steel Alloys

Stainless steels are alloys of iron and carry at least 10.5% chromium, that protects iron from rusting. It is ideal for many applications where both strength and corrosion resistance are desirable. stainless steel is superior due to its resistance to corrosion and staining, better gloss, and low maintenance. Additionally, the polished material has a surface that is easy to clean and sterilize and does not require a surface coating. The alloy is available in the market as sheets, plates, bars, wires and tubes [74][75]. The intended use of each class of stainless steel is determined by the varying ratios of its separate constituents. Corrosion resistance is enhanced by adding more amounts of chromium, nickel and molybdenum. Other components of stainless steel include carbon, manganese, sulphur, phosphorus, silicon etc. [76][77][78]. Table 2.4 presents the various grades of stainless steels that are commercially electropolished [79].

Table 2.4 Electropolished stainless steel types.

stainless steel Types
Austenitic stainless steel 304
Austenitic stainless steels 316 and 316 L
Ferritic stainless steels 430 and 434
Martensitic stainless steel 420
Duplex stainless steel 2205

Precipitation-hardening stainless steel 17-4	
Austenitic Steel Nitronic 60	

Stainless steel type 304 and 316 are the two most used grades. Type 316 electropolishes better than type 304. It contains molybdenum, and that offers its vastly superior corrosion resistance. Grade 316L has low carbon content and thus is softer. It is preferred for its weldability, machinability and corrosion resistance. The manufacturing industry, therefore, uses 316L and is the choice for medical implants [80][81][82][83]. The constituents of grade 316L stainless steel is included in Table 2.5 [84].

Table 2.5 Composition of AISI 316L stainless steel.

Component	Weight %
Iron	65
Carbon	0.03
Chromium	17
Nickel	12
Molybdenum	2.5
Manganese	2
Silicon	1
Sulphur	0.03
Phosphorus	0.045

2.11 Effect of Electropolishing on Stainless Steel

It is useful to determine why many equipment manufacturers primarily undertake the electropolishing of stainless steel. The primary benefit of the process is improved aesthetics by eliminating surface imperfections. The capabilities to the areas hard to access with mechanical polishing, all with fewer labour prices, make electropolishing the preferred technique [3][12]. The bacterial contamination levels are inevitably lowered, and it is easier to maintain high levels of cleanliness in these polished areas. Consequently, electropolished stainless steel offers a better surface finish, more convenient to clean. This property makes stainless steel prevalent for its use in the food processing, pharmaceutical and medical industries [8][50][60][62].

While treating an alloy like stainless steel, the added feature is the preferential dissolution of one or more constituents. All stainless-steel grades are iron-based alloys and contain considerable amounts of chromium and nickel. The different components exhibit varying removal rates; iron ions are separated more rapidly than the nickel and chromium ions. The electropolishing of stainless steel leaves a chromium enriched surface; this aids the lower rates of corrosion offered by the alloy [1][5][11][80]. A thin passive oxide layer forms when the chromium on the stainless-steel surface comes in contact with oxygen. Electropolishing enhances the passive oxide layer and optimizes the corrosion resistance properties. Therefore, the intrinsic strength and inherent corrosion resistance of stainless steel make it the appropriate material for many equipment manufacturers [3][9][36][74][79].

3   Electropolishing in the Industry

3.1 Electropolishing Facility

Various types of electropolishing apparatuses are available with their respective precisions to address customer-specific needs. The design varies with the polishing tank size, electrode positioning, and the size or shape of the part to be polished [85].

A typical electropolishing setup consists of a DC power supply and a tank fabricated with steel to hold the electrolyte bath. A part or group of metal parts to be electropolished is charged positive, fixtured to racks and immersed into the bath. The fixture rack is, in turn, installed to the positive side of the power supply. A cathode or series of cathodes is lowered into the polishing bath and connected to the power source's negative pole. When current is applied, the metal ions separate from the metal part and move towards the cathode. The metal ions dissolve in the electrolyte, and oxygen is liberated at the metal surface, promoting the cleaning process [12][27][33][86]. A schematic of a typical electropolishing system is shown in Figure 3.1 [87].

The polished metal parts are runs through a sequence of cleaning and drying steps to remove the polishing bath traits to make the resulting surface look bright and clean [5][9][11][33][86]. The quality standards defined for the considered use are evaluated using additional gadgets. A visual check of the electropolished parts is enough to assess the brightness or clarity in some cases, while others require a dedicated instrument to determine the surface profile [37].
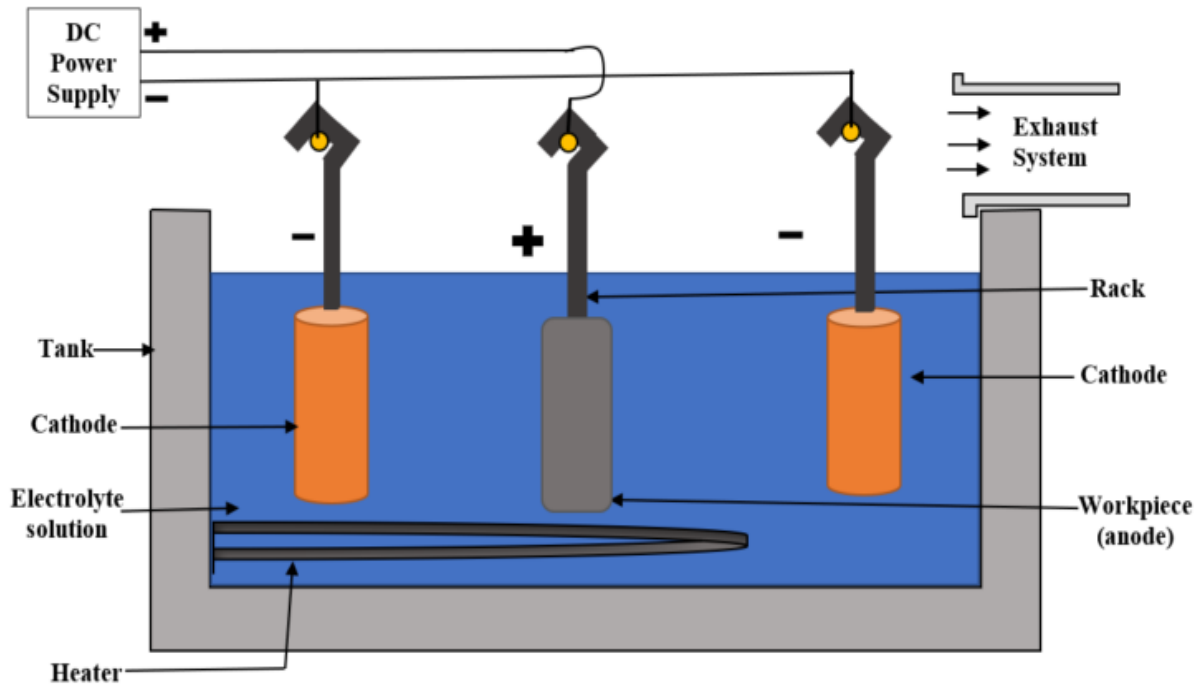
Figure 3.1 A typical electropolishing system.

3.2 Steps Involved in Electropolishing

The widely used standard for electropolishing, ASTM B912, defines three necessary stages for the process [88][89]. These stages are essential in obtaining the best polishing results for stainless steel alloys and are carried out in different tanks. Figure 3.2 shows the flowchart representing the three primary operations of a typical electropolishing process [11]. The steps involved are [9][11][19][37]:

- Metal surface preparation

This phase removes the surface soils, such as grease, oil, fingerprints, and other contaminants; otherwise, they interfere with the process consistency and cause etching or pitting.

- Electropolishing

The actual polishing process is performed in this phase to make the surface bright and smooth, followed by an electropolishing rinse.

- Post-treatment

This stage rinses and removes the bath residue and the by-products of the electropolishing reaction, causing subsequent staining and corrosion if not properly cleaned, and finally dries the metal surface.

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┌──────────────────────┐       ┌──────────────────────┐
│  Metal Preparation   │──────▶│   Alkaline cleaning  │
└──────────────────────┘       └──────────────────────┘
                                          │
                                          ▼
                               ┌──────────────────────┐
                               │   Cold water rinsing  │
                               └──────────────────────┘
                                          │
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                               │ Pickling/Acid descaling│
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                               │   Cold water rinsing  │
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┌──────────────────────┐       ┌──────────────────────┐
│    Electropolishing  │──────▶│    Electropolishing  │
└──────────────────────┘       └──────────────────────┘
                                          │
                                          ▼
                               ┌──────────────────────┐
                               │        Rinsing        │
                               └──────────────────────┘

┌──────────────────────┐       ┌──────────────────────┐
│    Post-Treatment    │──────▶│   Nitric acid cleaning│
└──────────────────────┘       └──────────────────────┘
                                          │
                                          ▼
                               ┌──────────────────────┐
                               │   Cold water rinsing  │
                               └──────────────────────┘
                                          │
                                          ▼
                               ┌──────────────────────┐
                               │    Hot water rinsing  │
                               └──────────────────────┘
                                          │
                                          ▼
                               ┌──────────────────────┐
                               │        Drying         │
                               └──────────────────────┘
```
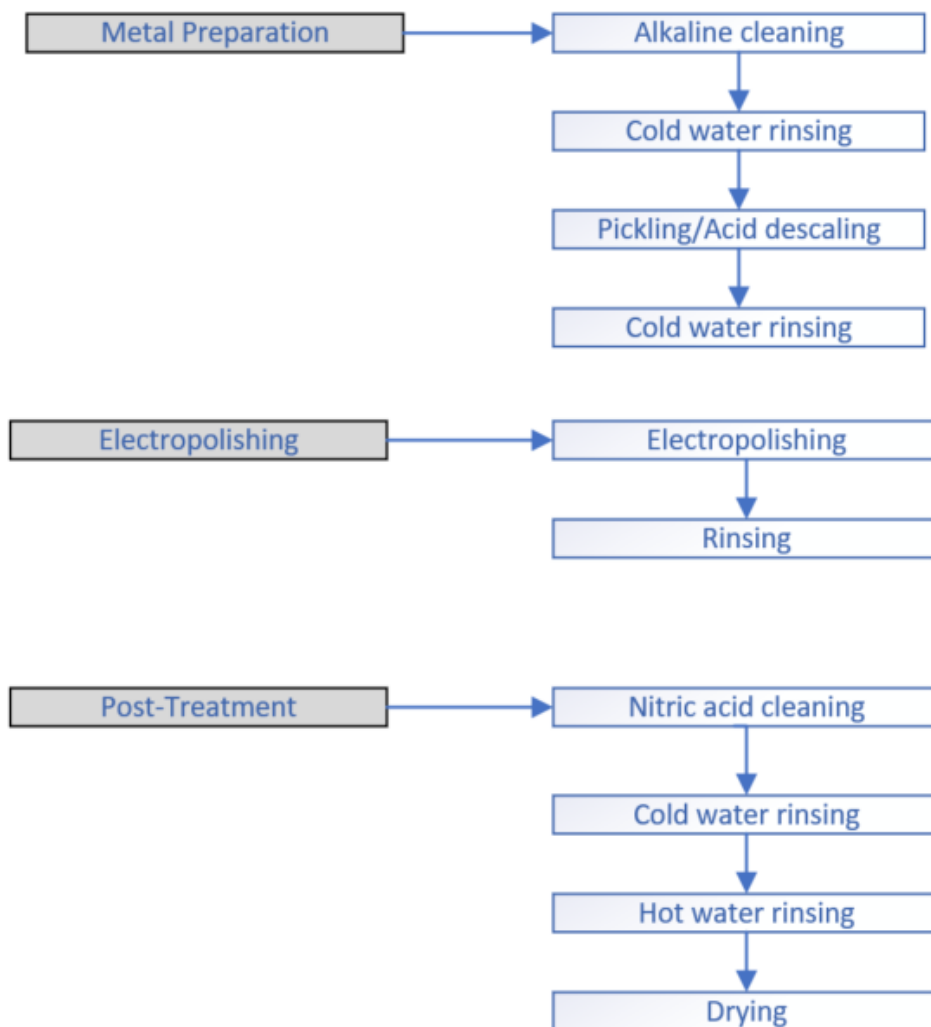
Figure 3.2 Flowchart representing the electropolishing process steps.

3.2.1 Metal surface preparation

Sufficient surface preparation ahead of electropolishing is indispensable for quality polishing outcomes, like other metal finishing treatments. The first tank uses traditional

cleaning methods, such as vapor degreasing, alkaline or solvent cleaning. The surface is made free of shop dirt, oil, grease, grit, oxides, fingerprints, etc. If not removed, the contaminants diminish the final finish quality and impose a big problem for various industries like medical, pharmaceutical, etc. The incorrect cleaning results in metal parts being refused due to sub-standard polishing, and thus, the unneeded contacts are avoided with the pieces after they are cleaned. The alkaline cleaners are relatively cheaper when compared to the cost involved in re-polishing. The alkaline cleaning tanks are always maintained with adequate alkalinity to preserve the performances so that the cleaning process doesn't affect the work quality [9][11][19][37].

The next tank in this stage employs a cold-water rinse. This rinse eliminates the contaminants and the residues from the previous operation by dilution and restrains the alkaline drag-in into the next tank. The alkali concentration slowly elevates in this tank and presents a neutralizing impact on the acid descaling process that follows. Therefore, fresh makeup water is fed to the rinse tank regularly to sustain adequate water stability. Spray rinses or any other system involving water volume control is used to avoid water wastage and to prevent overcharging the waste treatment system [9][11][19][37].

The pickling or acid descaling procedure is similar to the alkaline cleaning and eradicates the oxides on the surface from the former approaches such as welding, cutting etc. The oxides present on the metal body influence the quality of the surface finish recommended for medical and pharmaceutical applications. This process also neutralizes the alkaline film left by the cleaning operation. The alkaline drag-in from the cleaner tank, if not, destroys the acid stability in the electropolishing tank, yielding quality issues. The procedure selected for the acid descaling must be adaptable with the electropolishing bath. Care is taken to ensure that the ions from the acid descaling tank do not reach the following station [9][11][19][37].

This cold-water rinsing process is similar to the alkaline cleaner rinse and takes out the acid residues that are effortless to remove compared to the alkaline remnants. The rinsing process is hence fulfilled in short rinse times or applying low flow rates [9][11][19][37].

3.2.2 Electropolishing

The metal ions dissolve from the anodic workpiece during the electropolishing process, building-up a metal sludge in the polishing tank. All constituents of the stainless steel alloy, iron, chromium, nickel, manganese etc., undergo dissolution, resulting in a controlled levelling and smoothening of the metal surface. Some side reactions also occur, forming a few other by-products in the electrolyte that hinder the polishing results if not controlled [9][11][19][37].

The racks carrying the polished metal parts are raised and rinsed with water using an appropriate method such as a spray nozzle before moving into post-treatment tanks. This rinsing process prevents the drag-out of the electropolishing solution. The rinse water goes into the electropolishing bath, and this drag-in of excessive water poses harmful effects on the polishing qualities causing etching or loss of finish. Polishing shops typically heat the electropolishing system when not in operation, either overnight or on weekends, to concentrate the electrolyte bath. The polishing tanks also take-in moisture from the atmosphere, and therefore the tank is covered when not in use, or the solution is pulled-out and placed separately. The bath is either regenerated or disposed of when the polishing bath's metal content is high [9][11][19][37].

3.2.3 Post-treatment

The metal parts are rigorously rinsed after the electropolishing process to eradicate the electrolyte residues. Some electropolishing solutions are highly viscous and difficult to rinse, especially when the bath is aged. The short post-treatment rinse in nitric acid dissolves the chemical by-products which are formed during the polishing process. The by-products are the

phosphates and sulphates of the transition metals and are difficult to remove with simple water rinses. These by-products, if not removed, degrades the polished appearance and provide sites for subsequent bacterial contamination and corrosion [9][11][19][37].

The short cold-water rinses with lower flow rates remove the nitric acid solution residue, which is much easier to remove than the alkaline or electropolishing residues. Drag-in of the nitric acid to the next tank meant for hot water rinse may cause staining on the polished metal parts, and therefore the acidity in this rinse tank is maintained in limits [9][11][19][37].

The hot water rinsing eliminates the last traces of possible chemicals and raises the temperature to flash dry the samples before removing them from the racks. Attention is paid to ensure that the nitric acid or the electropolishing solution reaching this tank is within the permissible level. The hot water rinse tank is replaced totally or partially with fresh make-up water to avoid this problem [9][11][19][37].

The parts that do not dry with hot rinsing require additional drying stations like heated air chambers, centrifugal dryers etc., to rapidly evaporate the residual moisture to prevent further staining [9][11][19][37].

3.3 Operating Parameters for Electropolishing

Several process parameters are critical in controlling the final quality of electropolishing. The optimum electropolishing with regards to quality, effectiveness, and cost is achieved by adequately handling the process parameters. An alteration in any of these essential variables affects the process outcomes and produces inconsistent qualities [1][2][13][28][33]. The following are the crucial parameters for any successful electropolishing process [5][9][11][19][20][34]:

i.   Polishing current

The applied current controls the material removal rates during the electropolishing process.

ii.   Polishing duration

The metal removal rates during electropolishing is proportional to the polishing times.

iii.   Polishing bath

A suitable electrolyte with the proper concentration and composition balances the polishing quality.

The operating conditions for electropolishing are comparatively broad, and the most favored parameters vary with the polished metal. The users must experimentally determine the ideal control parameters on trial workpiece samples before designing and establishing proper electropolishing systems [20]. The process also varies with the metal's initial surface conditions and the required final finish [90]. Table 3.1 lists the other variables that govern the electropolishing process [5][8][28][74].

Table 3.1 Other parameters that influence electropolishing.

Metals	
Anode – cathode distance	Bath age
Bath temperature	Agitation of bath
Workpiece geometry	Arrangement of workpiece

3.4 Electrolytes Used for Electropolishing

The electropolishing process removes the metal ions from the surface and provides the metal with a bright finish. The procedure depends on the electrolysis principle and involves the polishing current and the electrolyte solution [1][5][11][39]. The acids dissociate into ions solution, and the cations move to the cathode, while anions move to anode during the process. The mobility of these ions in the electrolyte solution determines the polishing rate during the

process [1][2][5]. Hence, a well-maintained electropolishing solution is essential for the desired surface finish [9][15][16][19][79][91].

According to Lyczkowska-Widlak et al. [9], the electrolytes used for the electropolishing process performs the following functions during the electropolishing process:
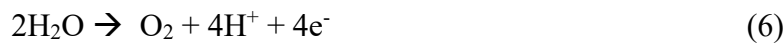
- Acts as the medium where the chemical reaction occurs.

- Removes the metal ions from the processing zone of the process.

- Enables the transport of electric loads.

The electrolyte bath used in the industry is mostly unique to the metal or the alloy's chemical composition [5]. The success of the polishing process lies in using the right bath and its efficiency maintained throughout the process [1][5]. The properties and composition of the electrolyte solution are crucial in delivering the best results [11][15][16][92]. Different electrolytes, as well as require distinct operating conditions in terms of the voltages and polishing times for accomplishing the polishing process [11]. Therefore, the polishing shops also rely on a few other factors while choosing the electrolytes, such as the throwing power, the costs, usage and disposal rules, etc. [5]. Almost all the electropolishing solutions used commercially are often mixtures of concentrated acids with high viscosity [1][5][9][11]. The electrolytes, hence, need the utmost care while using and disposing of, agreeing with the local health, safety and environmental regulations. Thus, it is essential to know the polishing bath chemistry while planning the whole electropolishing process [11][35].

3.5 Widely Used Electrolytes for Stainless Steel

The proper conditions to carry out the chemical reactions that occur during the electropolishing process is provided by the electrolyte bath [5][9]. The viscous mixture of phosphoric - sulfuric acid is used for the stainless steel polishing on an industrial scale [1][11]. The bath's appropriate electrical conductivity is established by sulfuric acid, while phosphoric

acid oversees the anodic layer formed on the workpiece, thereby aiding the polishing process [9]. Moreover, both the acids provide the anions for the metal ions dissolved during the process [5]. Preferentially iron, followed by chromium and nickel, dissolve in the bath during the electropolishing of stainless steel alloys [9][14][15][48]. The equations from 3 to 7 represent the dissolution of the metal ions and the evolution of gases during the process. The process liberates oxygen at the anode and hydrogen at the cathode.

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

$$Cr \rightarrow Cr^{3+} + 3e^- \qquad (4)$$

$$Ni \rightarrow Ni^{2+} + 2e^- \qquad (5)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (6)$$

$$2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2 \qquad (7)$$

The literature reveals that other electrolyte combinations are also used for electropolishing stainless steel. Table 3.2 tabulates the different electrolyte mixtures for stainless steel. Most of them are hazardous and generate sludges [5][10][11].

Table 3.2 Commonly used electrolytes for stainless steel polishing.

Electrolyte bath	Source
Phosphoric acid	[93]
Phosphoric-sulfuric acid	[94]
Phosphoric-sulfuric-chromic acid	[95]
Sulfuric-citric acid	[96]
Phosphoric-chromic acid	[97]

Sulfuric-glycolic acid	[98]

3.6 Significance of Polishing Bath

A significant challenge faced by the electropolishing industry is the extended use of the polishing bath solutions without renewal or a replacement. The bath contamination increases with the operation times due to the metal ions [5][9][15][16][99][100]. The increased metal ion concentration alters the bath chemistry, which in turn has an impact on the polishing qualities. The roughness and gloss of the final finish are affected when the bath contamination crosses a definite level [11][19][101][102]. The bath's extended use also contributes to the emergence of additional surface defects like shadows or smudges on the metal surface, resulting from the bath's improper composition. This problem makes it essential to maintain a controlled concentration and composition for the polishing baths during the electropolishing process to deliver consistent polishing results [1][9][15][16][103][104][105].

Moreover, the content of the dissolved metal ions in the electrolyte bath influences the current density during the polishing process. Improper and uncertain polishing finishes result from variations in current densities [9][15]. The procedure uses the concentrated acid mixture characterized by high viscosity values, and the dissolved metal content further increases the bath viscosity [1][5]. The surge in metal ions also changes the bath density, and therefore, a highly contaminated bath is identified by high values of viscosity and density [9][19][106][107]. Polishing bath overheats due to bath density changes, and as conductivity depends on the concentration, the changes in both density and temperature change the bath conductivities [15][19][20].

The critical key element for the electropolishing industry is maintaining the quality of the polished surfaces [1][2][11]. When the bath contamination increases, a longer polishing duration or a higher polishing current is needed to keep the polishing deliverables. Increased

current densities and extended polishing durations lead to increased electricity costs resulting in higher operating costs. Operating with higher polishing currents as well leads to overheating the electrolyte, worsening the existing problems [9][15][16].

3.7 Bath Control Operations in the Industry

The electropolishing shops use the polishing baths until and after they get too contaminated. As the polishing qualities start to diminish drastically after a threshold level of bath contamination, the process has to be operated at the right conditions to produce consistently good results [11][15][16][19]. As discussed earlier, the shops start with the trial and error approach to identify the operating parameters to make-up for the bath contamination. The operating parameters adjusted accordingly are the polishing duration or the polishing current. However, as time goes by, this approach either gets slow or doesn't work anymore. At this point, the industry adopts an alternate procedure to keep the bath age to a desirable value. The choice of this strategy depends on the convenience of control and handling and varies with different electropolishing installations. The polishing units usually accomplish this by one of the following methods [11][19][20]:

- Allow the bath to operate until a level at which the electrolyte bath produces an insoluble sludge of metal ions at the bottom of the polishing tank, which is then separated at regular intervals. The change of solution level is made-up with the addition of fresh solution.

- Operate the bath with no decanting until the metal content reaches a certain pre-determined level. The bath is then regenerated by replacing a specified volume of the bath with an equivalent fresh solution.

3.8 Relevant Studies in the Past

The review of the relevant literature finds that extensive work has been done in the field of electropolishing; however, only a scant number of studies are available that addresses the techniques to keep the electropolishing process in control as the bath ages.

According to the literature, there are a few approaches for managing the polishing consistencies in the long run. Chatterjee [5] put forward one practical method, where they investigated how the polishing quality in terms of the brightness drops as the polishing bath's metal content exceeds six wt. %. The author recommends maintaining the metal ions in the bath below five wt. % during the process to have consistent results.

Lyczkowska-Widlak et al. [9] consider determining the bath life by the amount of the current passed through the unit volume of the bath since its first use. The author suggests that the electrolyte solution's durability ranges from passing up to 100 - 180 Ah/ dm^3 of polishing current. They proposed removing 30-50% of the bath volume after processing roughly 80 Ah/ dm^3 polishing current and then augmenting with fresh solution.

Although there is much research concerning various aspects of electropolishing, the studies concerning the quantitative data for the polishing baths available to design proper polishing systems are limited. More research is required to quantify the bath age as a quality control parameter to describe the resulting polishing efficiencies. As far as known, no one, to the best of our knowledge, has monitored the systematic changes in the bath with the passage of a specific amount of polishing current to relate it to the respective polishing qualities. This study aims to investigate the evolution of dissolved metal ions, acid composition and bath properties in an ageing phosphoric - sulfuric acid bath. Organized experiments with a simple test set-up is used to identify the mechanisms involved in bath ageing. The bath properties (conductivity, specific gravity and viscosity) are measured during bath ageing at regular intervals. The polishing results achieved under standard polishing conditions are determined at

various bath ages by executing standard polishing tests. The trend is identified, and a multilinear regression model is designed from the measured data to explain the bath results delivered at a given bath state.

4   Experimental Set-up and Procedure

All the electropolishing experiments are conducted under a ventilated fume hood, considering the harmful gases emitted during the reactions. The experiments are executed following the training offered at Concordia University, WHMIS, hazardous waste disposal, corrosive substances, and minor spills response. Personal protective equipment like gloves, safety goggles and protective clothing are used while preparing the electrolytes and during the experiments.

4.1 Experimental Set-up

4.1.1 Characteristics of electropolishing vessels

Table 4.1 lists the two different apparatuses used for the electropolishing experiments:

Table 4.1 Electropolishing cells used for experiments.

Preliminary experiments	Main experiments
500 mL glass beaker	5 litre glass vessel with dimensions (22.9 x 22.9 x 12.7) cm

4.1.2 Characteristics of electrodes

Two kinds of 316L grade stainless steel working electrodes are used, depending on the tests performed. Table 4.2 presents the electrodes used for the specific polishing tests.

Table 4.2 Various electrodes used for experiments.

Working electrode	Dimensions	Source	Counter-electrode	Pseudo-reference electrode
Rectangular pieces	(45 x 10 x 1) mm	Cut out from a stainless-steel sheet from McMaster-Carr	Stainless steel sheet	Stainless steel wire
Square bar	(75 x 75 x 6) mm	McMaster-Carr		

The stainless-steel sheet used as the counter-electrode is rolled and positioned inside the glass bowl covering the circumference. This shape and positioning of the counter-electrode provide even current densities to the working electrode. A pseudo-reference electrode is used only for the standard electropolishing tests. A stainless-steel wire used as the pseudo-reference electrode provides a stable potential to monitor the working electrode potential. Figure 4.1 displays the electropolishing cell, electrodes and the solution used for the main experiments.
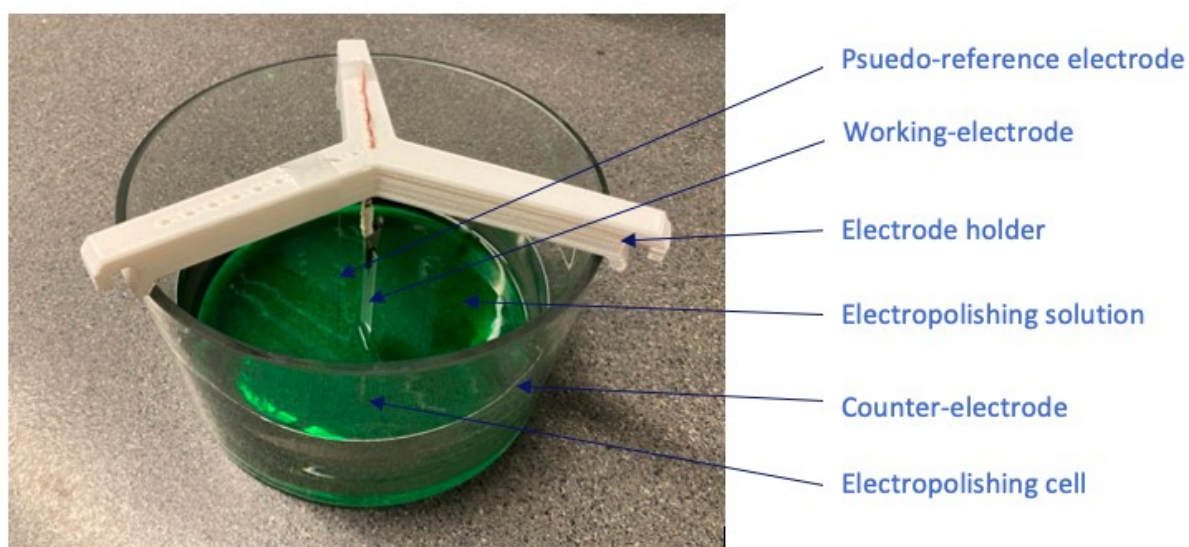
Figure 4.1 Electropolishing vessel with electrodes and solution.

The working electrode and the pseudo-reference electrode are held in position at a specified distance from each other using an electrode holder made of polylactic acid (PLA) plastic, 3D printed in an ultimaker 2+ printer. This holder prevents any electrode movements during the experiments. The electrolyte is poured slowly into the beaker after all the required electrodes are submerged in the polishing solution. The terminals from the DC power supply are connected to complete the circuit. Alligator clips connect the positive terminal to the working electrode workpiece and the negative terminal to the counter-electrode.

4.1.3 Characteristics of electrolyte

The solution used in the polishing cells is a mixture of phosphoric - sulfuric acid. This polishing mixture is among the most preferred solutions for the electropolishing of all grades of stainless steel. The solution we used represents the EPS 4000 used in the electropolishing industry, which is also a mixture of phosphoric - sulfuric acid, and the composition is similar [108]. The commercial EPS 4000 solution is proprietary, and the exact formula is not disclosed. Therefore, an acid-base titration-end point detection method that uses methyl orange and phenolphthalein indicators is used to approximate the phosphoric - sulfuric acid ratio in the industrial solution, the procedure included in the appendix. The electrolyte solution is prepared in the lab based on the estimated composition of EPS 4000 from the titration result. The initial solution comprises 50% phosphoric acid, 35% sulfuric acid and the remaining deionized water. Table 4.3 tabulates the component configuration in 100mL of the electrolyte solution, as identified from the titration method.

Table 4.3 Composition of the electrolyte solution used.

Constituents	Amounts (mL)
Phosphoric acid	50
Sulfuric acid	35
Deionized water	15

Industries maintain the total acid content in the polishing bath above 50% and not over 90%, the balance being water. The water content in the solution is kept relatively at lower levels as the baths containing less water polish at lower current densities [98][109]. The concentrations of the sulfuric - phosphoric acid used for the electrolyte preparation are 96.8% and 85%, respectively.

4.1.4 Equipment

i.   Power source

The B&K Precision Model-9117, multi-range programmable DC power supply is used for all the experiments. It is a single output high power supply capable of delivering up to 80V or 120A at a maximum power output of 3000W. The user-friendly controls and a numeric keypad with an easy-to-read display allow for an easy configuration from the front panel [110]. A fluke 87V True RMS digital multi-meter is connected parallel with the electropolishing cell to monitor the cell voltage.

ii.   Profilometer

The Mitutoyo Surftest SJ-210 Series-178, contact-type portable profilometer shown in Figure 4.2 quickly and accurately determines the surface roughness of stainless-steel pieces. The roughness tester displays the mean roughness value (Ra) in micrometre. This gauge is

small, lightweight and is extremely easy to use. It uses a stylus tip to make direct contact with the surface of the stainless-steel workpiece. The instrument shows the surface roughness waveforms on the colour LCD screen. The cut-off length set in the device determines the distance the stylus has to travel on the workpiece to measure the surface roughness, which usually depends on the workpiece area [111].

Figure 4.2 Mitutoyo portable profilometer.

iii.   Viscometer

The Cannon-Ubbelohde viscometer shown in Figure 4.3 measures the kinematic viscosity of the highly viscous electrolyte solutions used for the experiments using a capillary-based method. This instrument has a reservoir on one side and a measuring bulb with a capillary on the other. The electrolyte is introduced into the reservoir and is sucked down the capillary and measuring bulb. The liquid is permitted to travel back through the measuring bulb and the time it takes for the fluid to pass through two calibrated marks is a measure for viscosity. The device has a third arm ranging from the end of the capillary and open to the outside. Thus, the pressure head only depends on a fixed height and remains independent of the total volume of liquid [112].

Figure 4.3 Ubbelohde viscometer.

iv.   Conductivity meter

The Thermo Scientific Orion benchtop conductivity meter shown in Figure 4.4 measures the electrolyte solution's conductivity. The meter provides a temperature compensated conductivity reading with different reference temperatures. It has a quick to navigate setup menu and a large, informative LCD screen that displays the conductivity readings. The sensor probe is placed in the solution to measure the conductivity value [113].

Figure 4.4 Thermo scientific benchtop conductivity meter.

4.2 Electropolishing Procedure

The utmost aim of the electropolishing process is to improve the overall product finish quality. Therefore, it is essential to prepare the metal parts before the treatment and clean the electropolished parts.

4.2.1 Metal surface preparation

The stainless steel samples are prepared for the electropolishing experiments by the following procedure:

- Degrease the workpiece in soap water for 15 minutes in the ultrasonic bath (Branson Model 1510 ultrasonic cleaner).

- Rinse the workpiece with water to remove the soap.

- Clean the workpiece in acetone for 15 minutes in the ultrasonic bath.

- Clean the workpiece in deionized water for 15 minutes in the ultrasonic bath.

- Rinse thoroughly with water.

- Dry the workpiece using air.

The initial roughness of the sample is measured using the profilometer. An identification number is engraved above each stainless steel workpiece. The polishing area is adjusted by measuring $1cm^2$ and insulting the sample's remaining area with the teflon tape. This technique helps in avoiding improper electropolishing at the phase boundary, where the electrolyte touches the workpiece.

4.2.2 Electropolishing

All the electrodes are lowered into the electropolishing vessel with the help of the electrode holder. The required amount of the electrolyte solution is filled in the cell. The power supply is set to the required operating voltage or current, and each experiment is carried out for

the fixed polishing durations monitored with a stopwatch. The voltage or the current for the test is maintained at the required level by monitoring using a multi-meter.

4.2.3 Post-treatment

The samples are polished for the required polishing durations, the power supply is turned off, and the anode workpiece is removed from the electropolishing bath. After removing the teflon tape, the polished piece is transferred to a beaker to rinse it free of the electrolyte as quickly as possible. Running cold water rinses ensure thorough removal of all acid residues. The pieces are now air-dried and used for recording the surface roughness values using the profilometer. The surface morphologies are later characterized using scanning electron microscopy (Hitachi S-3400N SEM). The samples are stored in labelled plastic bags.

5   Identifying the Operating Parameters

This study phase experimentally determines the operating conditions on trial workpieces before the main electropolishing experiments. The critical control parameters considered here are the operating voltage, polishing time and the inter-electrode gap.

5.1 Materials and Methods

5.1.1 Materials

Table 5.1 lists the electropolishing cell and the electrodes used for the preliminary experiments.

Table 5.1 Apparatus and electrodes used for preliminary tests.

Polishing cell	Working-electrode	Counter-electrode	Pseudo-reference electrode
500 mL glass beaker	Rectangular pieces, (45 x 10 x 1) mm	Stainless steel sheet	Stainless steel wire

5.1.2 Operating voltage and polishing time

The test identifies the right voltage and polishing duration for the stainless-steel workpieces to achieve the best polishing qualities in surface roughness and gloss. The samples are polished at different voltages for varying durations to evaluate the polishing efficiencies. The desired testing voltage is set on the DC power supply and is monitored using the multi-meter. The experiment is timed using a stopwatch for fixed polishing times. Table 5.2 lists the different combinations of voltages and polishing durations used for the experiments.

Table 5.2 Test combinations for the voltages and polishing times.

Operating voltage (volts)	Polishing time (minutes)
2	2
2	5
2	8
2	10
5	2
5	5
5	8
5	10
8	2
8	5
8	8
8	10
10	2
10	5
10	8
10	10

5.1.3 Operating inter-electrode gap

The experiments determine the right inter-electrode distance between the working electrode and the pseudo-reference electrode for the stainless-steel workpieces to achieve the best polishing qualities in surface roughness and brightness. The different test sets are executed at the identified voltage and polishing durations and the polishing efficiencies are evaluated for each of the inter-electrode test combinations. The test voltage is set on the DC power supply

and the test is executed for the required time. The voltage value is monitored using the multi-meter, and the current drawn is observed on the power supply. The designed experiments are timed using a stopwatch. Table 5.3 lists the different combinations for the experiments.

Table 5.3 Test combinations for the inter-electrode gaps.

Operating voltage (volts)	Polishing time (minutes)	Inter-electrode gap (mm)
5	10	5
5	10	10
5	10	15
5	10	20

The power supply is turned off once the polishing time is up. The electrode holder and the counter-electrode are raised out of the electrolyte solution. The used electrolyte solution is poured into the storage can for proper disposal. The workpiece is placed in a beaker, and adequate cleaning is carried out to remove the bath's traces. The polished samples are dried using air and are stored for surface roughness measurement using the profilometer. The counter-electrode is cleaned and is put back into the beaker to be used for the next experiments.

5.2 Results and Discussions

5.2.1 Operating voltage and polishing time

Electropolishing the stainless steel samples at a voltage of 5 volts for 10 minutes delivers the best polishing results regarding improved surface finish and gloss. The workpieces polished at 2 volts performed the best at 10 minutes but did not possess a shiny finish. Operating at 8 volts for 5 minutes resulted in the workpiece dissolution; the workpiece corners

get rounded, though polishing imparted a glossy finish. The sample area exposed to polishing almost eroded while operating at 10 volts for 2 minutes. The remaining experiments for 8 and 10 volts are not performed as the workpieces would not have endured the tests. This behavior is anticipated as more material is removed over time as the longer the workpiece undergoes the polishing process, and eventually erodes the metal. Figure 5.1 displays the electropolished stainless steel samples with the various combinations of voltages and polishing times.
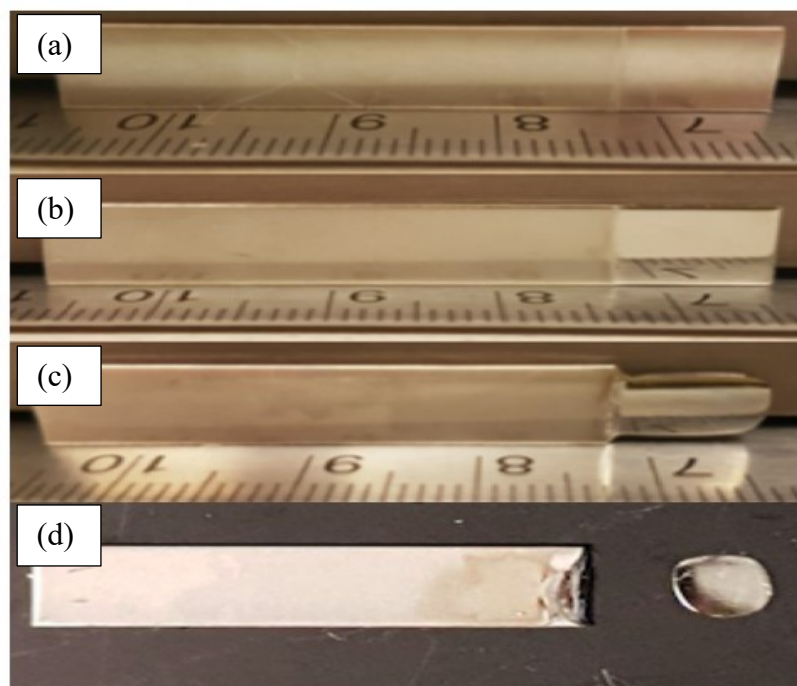
Figure 5.1 Stainless steel samples polished at:(a) 2V for 10min;(b) 5V for 10min;(c) 8V for 5min; and (d) 10V for 2min.

5.2.2 Operating inter-electrode gap

The initial surface roughness Ra for the stainless-steel workpieces is 0.823 μm (standard deviation = 0.0007 μm). A shiny-smooth surface finish is achieved with an electrode gap width of 15 mm for the operating voltage of 5 volts for 10 minutes. The inter-electrode gap of 10 mm also reduced the metal surface roughness considerably but did not have a shiny finish. The metal surface did not polish evenly for the smallest inter-electrode gap of 5 mm though the

surface roughness reduced. This occurs because the gas evolved during the polishing process cannot efficiently dissipate from the narrow working gap. At the large gap width of 20 mm, the electropolished surface has the highest roughness due to the lower current density owing to the high gap resistance. Figure 5.2 shows the values of surface roughness, Ra obtained with distinct interelectrode gap widths.
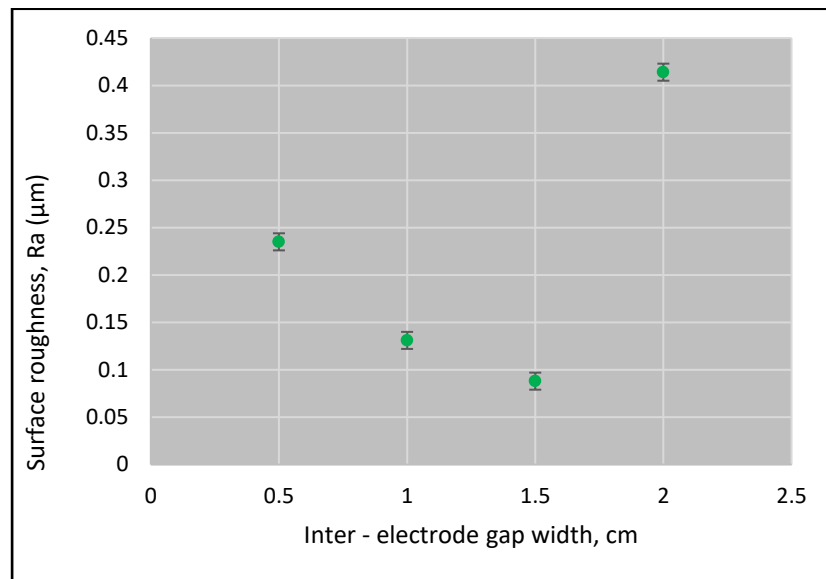
Figure 5.2 Surface roughness results for various inter-electrode gaps.

6 Influence of Bath Ageing on Polishing Quality

In the preceding chapter, the operating conditions like the voltage, polishing duration and the inter-electrode gap for stainless steel workpieces under test are determined. Following on from this, this phase of research is focused on the systematic study of the influence of the ageing of the phosphoric - sulfuric polishing baths on stainless steel polishing qualities. These tests identify the variations seen in the amount of dissolved metal ions, bath properties and composition with the passage of a specific amount of polishing charge each time at fixed intervals spanning the course of bath ageing. The polishing efficiencies at each of these instances are evaluated through standard electropolishing tests. The polishing bath's gradual ageing is determined and then supplemented with fresh bath to retrieve the polishing qualities.

6.1 Materials and Methods

6.1.1 Materials

The electropolishing cell with the electrolyte solution and the electrodes is the essential component for performing the electropolishing experiments. Table 6.1 lists the electropolishing cell and the electrodes used for the main experiments. All the workpieces used for the standard electropolishing tests are cleaned well before and after performing the experiments.

Table 6.1 Apparatus and electrodes used for main experiments.

electropolishing cell	Experiments	Working electrode	Counter-electrode	Pseudo-reference electrode
5 litre glass vessel	Simulated bath ageing	Square bar, (75 x 75 x 6) mm	Stainless steel sheet	Not used
	Standard electropolishing tests	Rectangular pieces, (45 x 10 x 1) mm	Stainless steel sheet	Stainless steel wire

6.1.2 Simulated bath ageing

The bath ageing is simulated in the lab by accelerated systematic electropolishing of 316L-grade stainless steel bar of dimension (75 x 75 x 6) mm in the phosphoric - sulfuric solution at a constant polishing current of 1 ampere per litre. A stainless-steel sheet is used as a counter-electrode for the bath ageing. The ageing process is stopped after polishing with every ampere-hour per litre, and the polishing bath is permitted to cool down to room temperature. 15 mL solution is removed from the polishing bath after every hour of simulated bath ageing for bath characterization and standard electropolishing tests. The bath properties are recorded, the bath composition is approximated, and the bath's elemental analysis is performed as part of bath characterization. The simulated bath ageing procedure is repeated until the bath shows signs of contamination and produces poor polishing results. Table 6.2 tabulates the details of the polishing currents used for the simulated bath ageing.

Table 6.2 Simulated bath ageing at 1 ampere per litre for 1 hour.

Bath volume (mL)	Ageing Current (A)	Bath volume (mL)	Ageing Current (A)
1000	1.000	850	0.850
985	0.985	835	0.835
970	0.970	820	0.820
955	0.955	805	0.805
940	0.940	790	0.790
925	0.925	775	0.775
910	0.910	760	0.760
895	0.895	745	0.745
880	0.880	730	0.730
865	0.865	715	0.715

6.1.3 Bath properties

The properties of the bath; conductivity, specific gravity and viscosity is measured for the fresh bath and is estimated throughout the bath ageing at the specified intervals:

i.   Measuring conductivity

The electrolyte bath conductivity is measured using the Thermo Scientific conductivity meter at room temperature at the end of each ageing cycle. The probe is placed into the bath to record the conductivity reading. The average of 3 readings is considered for the conductivity value.

ii.   Measuring specific gravity

An empty beaker with known mass is washed and dried well. A sample of 15mL of the electrolyte bath is transferred to this beaker, and the mass is determined. The density of the 15mL of the electrolyte solution is calculated, and the value of specific gravity is computed accordingly.

iii.   Measuring viscosity

The 15 mL solution used for measuring specific gravity is re-used to measure the viscosity using the Ubbelohde viscometer. The electrolyte is poured with a pipette through the tube into the reservoir. The efflux time is measured, and the viscosity is calculated by multiplying the efflux time with the viscometer constant. The sample is then stored in 15mL clear glass bottles for further classification by inductively coupled plasma-mass spectrometry (ICP-MS).

6.1.4 Bath composition

The composition of the fresh electropolishing solution is known from the titration results. The different bath composition is calculated every hour by approximating the phosphoric - sulfuric acid ratio in the ageing bath using the acid-base titration-end point detection method that uses methyl orange and phenolphthalein indicators, as stated in the appendix.

6.1.5 Elemental analysis

The bath samples stored in the glass bottles are further analyzed using Agilent-7500ce inductively coupled plasma mass spectrometer.

6.1.6 Standard electropolishing test

316L-grade stainless steel pieces of dimension (45 x 10 x 1) mm is polished every hour at a constant voltage of 5 volts for 10 min in the ageing bath. The polishing results are evaluated by measuring the roughness and inspecting the gloss. These polishing parameters were experimentally determined from the preliminary experiments on similar trial workpieces. The best results in terms of surface roughness and gloss were obtained at 5 volts for 10 min. A stainless steel sheet is used as a counter-electrode and a stainless steel wire as the pseudo-reference electrode placed at a fixed distance of 15 mm from the workpiece. Table 6.3 lists the details of operating parameters for the electropolishing tests.

Table 6.3 Polishing parameters for standard electropolishing tests.

Operating voltage (volts)	Polishing time (minutes)	Inter-electrode gap (mm)
5	10	15

6.1.7 Surface roughness evaluation

The sample surface roughness (measured in micrometre) of the samples is recorded before and after the standard electropolishing tests using the portable Mitutoyo Surftest SJ-210 series profilometer. The standard electropolishing tests are conducted on row samples cut out from the same piece of a 316-grade stainless steel sheet, characterized by the initial average surface roughness of Ra = 0.823µm (standard deviation = 0.0007µm). The average of 3 consecutive readings is considered for the surface roughness measurements. The readings are taken at the edges and the centre at equal distances.

6.1.8 Surface morphology

The surface morphology of electropolished samples is characterized using a Hitachi S-3400N scanning electron microscope.

6.2 Results and Discussions

6.2.1 Elemental analysis

Figure 6.1 shows the elemental analysis results for iron, chromium, nickel and manganese in the electrolyte bath obtained from ICP-MS. Metal ion concentrations are recorded throughout the bath ageing process versus the polishing current used per unit volume. The first measures of contamination of the fresh bath are minor. A near-linear rise in bath contamination is observed with the ageing of the electrolyte bath.
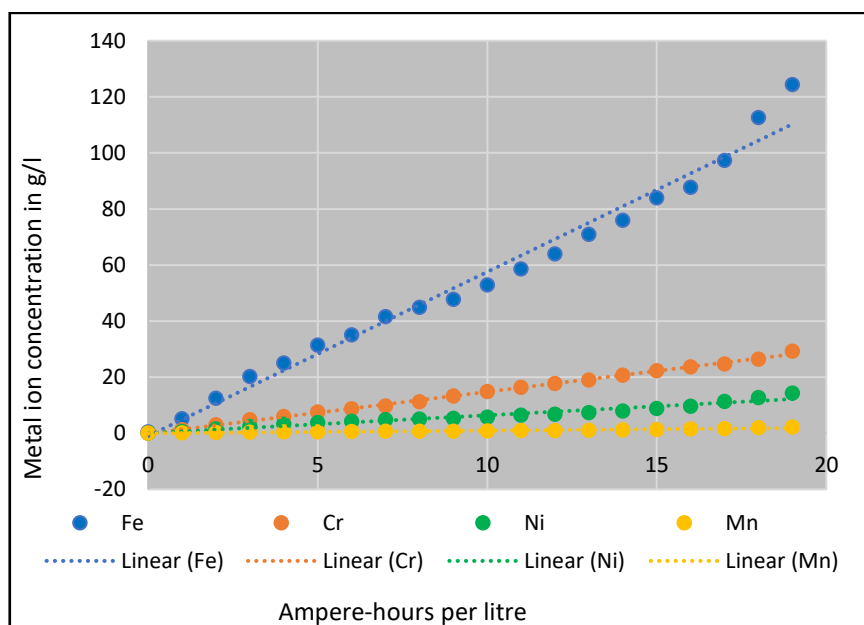
Figure 6.1 Dissolution of different metal ions in the bath versus the polishing charge used.

Note: This plot is only a representation of the metal dissolution during the electropolishing process. The ICP-MS results could not be validated due to the existing pandemic restrictions.

The different metal ions exhibit unequal rates of removal during the electropolishing process. Table 6.4 lists the dissolution rates calculated by linear regression for all these metal ions, based on Figure 6.1. Iron ions are dissolved more rapidly than the other constituents of stainless steel, chromium, nickel and manganese.

Table 6.4 Differential rates of metal dissolution with use.

Metal ions	Rate of dissolution (g per A-h per L)
Iron	5.9
Chromium	1.5
Nickel	0.6
Manganese	0.1

The fresh electropolishing solution is colorless. The color gradually changes to pale yellow and exact yellow green as the bath ages. The color darkens and gets dark green lately as the bath ages further. Figure 6.2 shows the changes seen in the color of the electropolishing bath throughout the ageing test. This color variation of the polishing bath is due to the dissolution of the metal ions with the extended operations.

Figure 6.2 Change in colour of the bath with use.

6.2.2 Bath composition

The acid composition changed from the early ratio of 50:35 (phosphoric acid: sulfuric acid) to 31:22 for the most aged bath. This change in bath composition is due to the formation of the complex-ions by the reaction of the dissolved metal ions and the sulphate/ phosphate ions from the acids. Figure 6.3 displays the alteration of the acid constitution with the bath ageing.
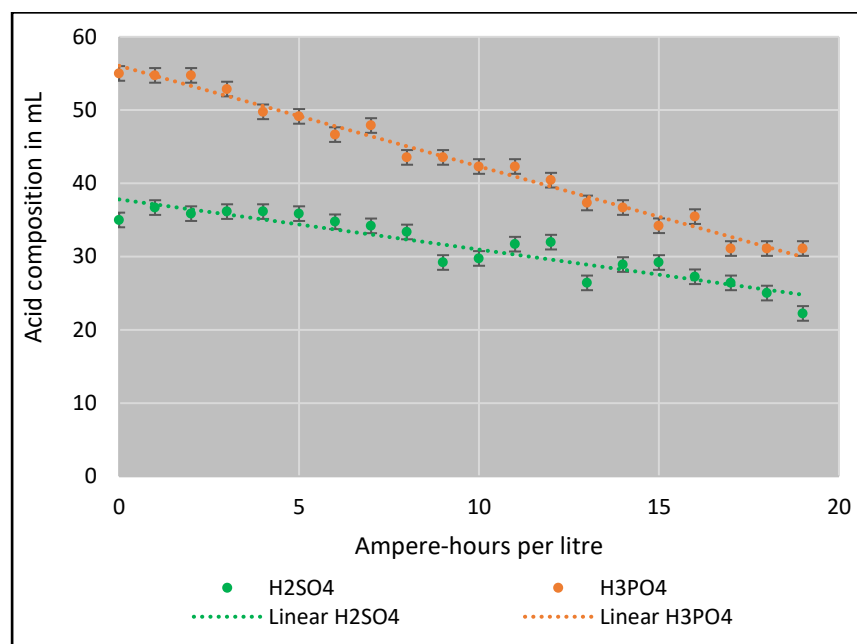
Figure 6.3 Variation in the acid composition of the bath versus the polishing charge used.

6.2.3 Bath properties

Bath properties such as electrical conductivity, specific gravity and viscosity are monitored over the extended bath ageing process. All the measured quantities evolve linearly with the polishing current per unit volume of the electrolyte bath, as shown in Figure 6.4:

- The electrical conductivity increased with the extended bath operations and attained twice the value measured for the fresh bath.

- The specific gravity went up proportionally with the continuation of the process.

- The viscosity expanded linearly as the tests advanced.

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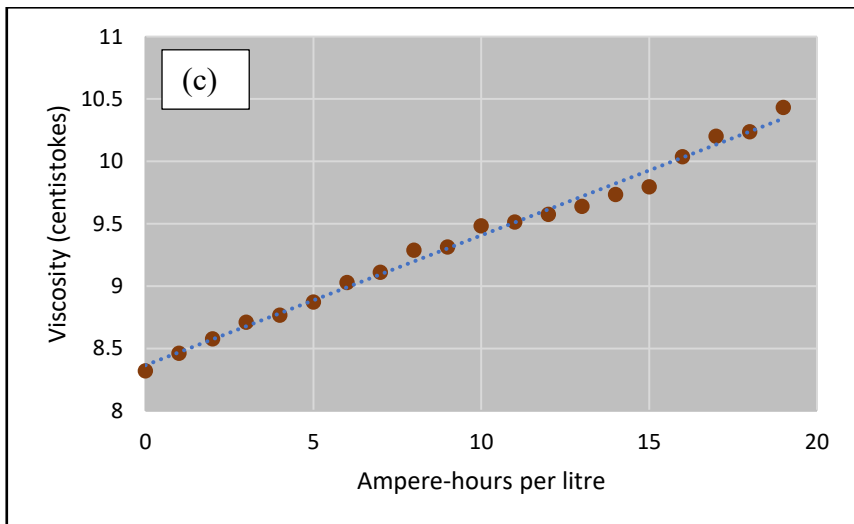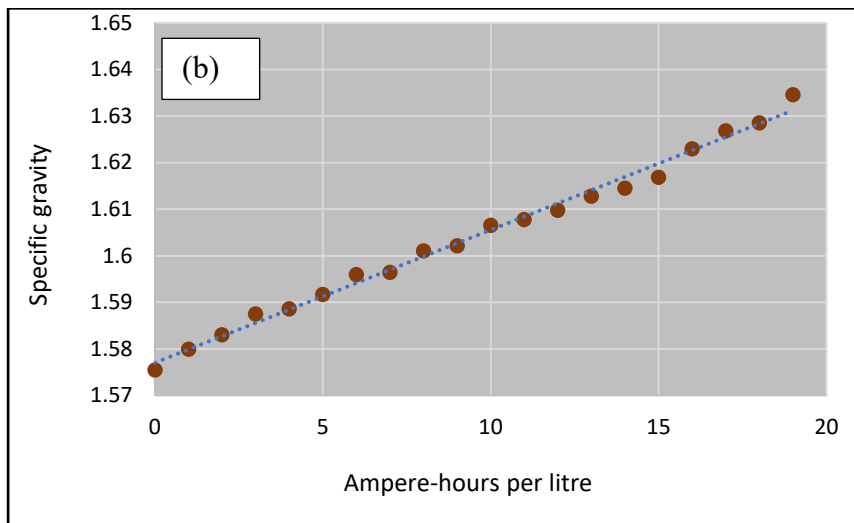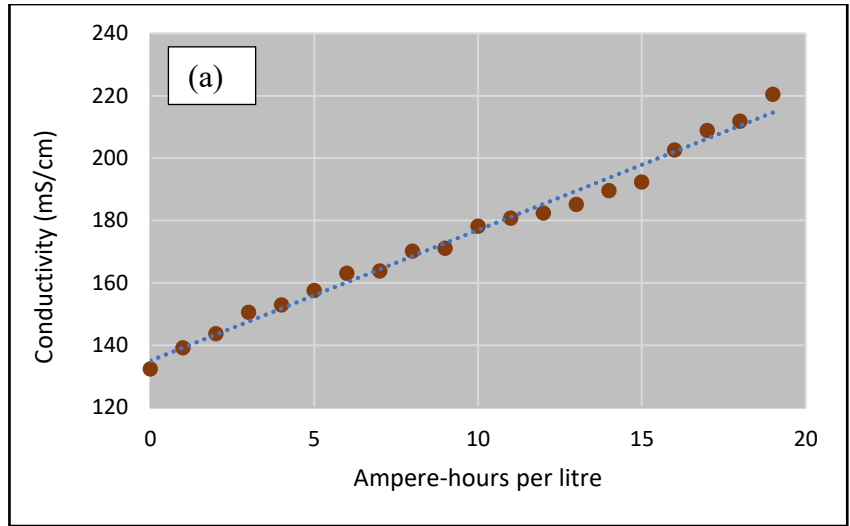
Figure 6.4 Variations in the bath properties (a) conductivity; (b) specific gravity; and (c) viscosity versus the polishing charge used.

6.2.4 Surface morphology

Figure 6.5 demonstrates the SEM micrographs of the surfaces polished under standard operating conditions at various bath ages. The workpiece polished in the fresh electrolyte bath has a highly smooth and clean surface. The parts polished in the close to the fresh bath are also smooth but disclose surface defects. More non-uniform surface states containing micrometre sized valleys and hills emerge as the polishing bath ages. A rough and uneven surface gradually evolves with deep valleys and peaks, with additional defects appearing due to an increase in the dissolved bath impurities over the intensive operation.
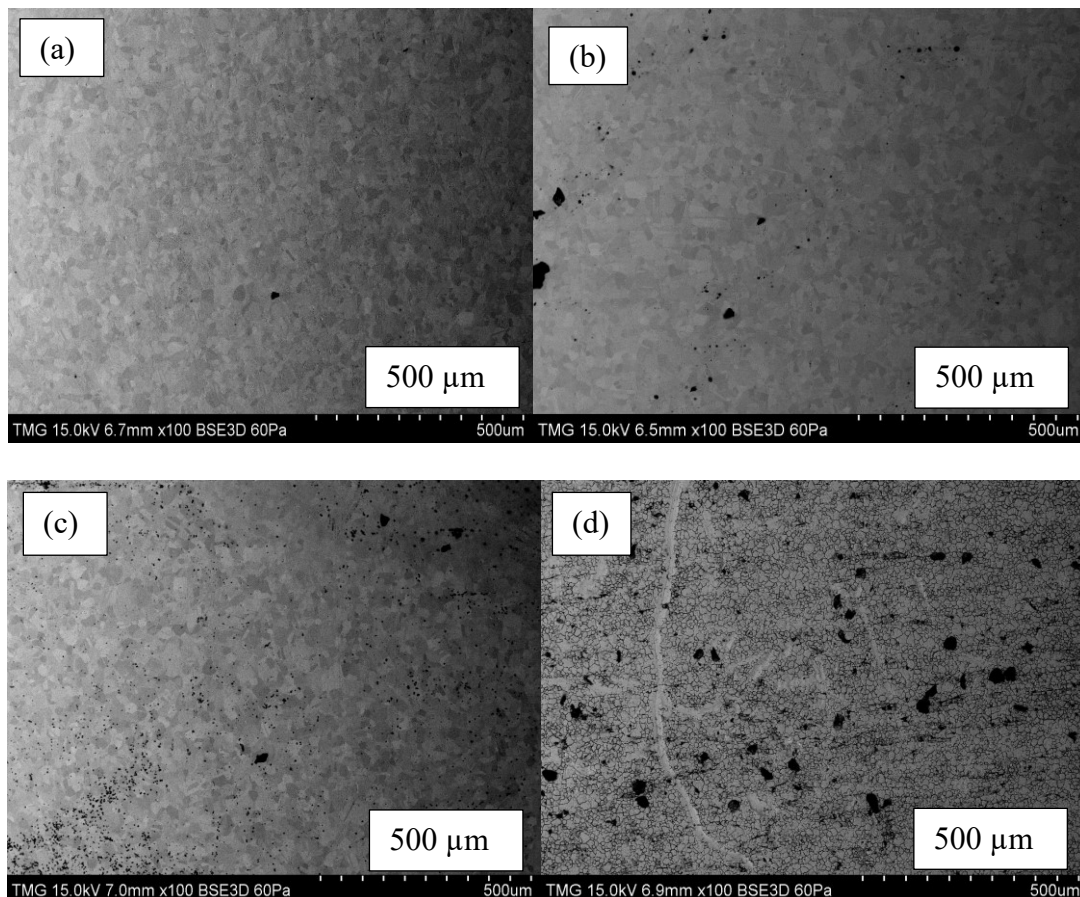
Figure 6.5 SEM images of samples polished in (a) fresh bath; (b) bath aged with 5Ah/l of polishing charge; (c) bath aged with 10Ah/l of polishing charge; and (d) bath aged with 20Ah/l of polishing charge.

The visual inspection results for the gloss also shows that the stainless-steel samples polished in the fresh bath possess a shiny, mirror-finish while the workpieces polished in the aged bath exhibits a dull, matt finish. Figure 6.6 represents the surface finish of the electropolished workpieces at various bath ages spanning the extended use.
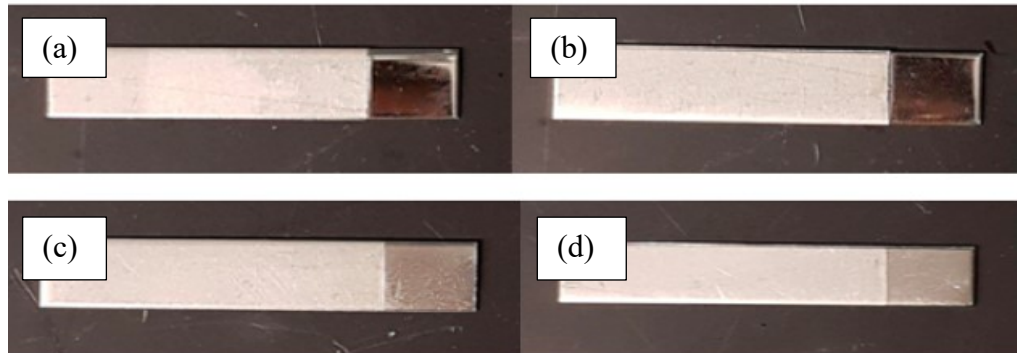
Figure 6.6 Gloss results for samples polished in (a) fresh bath; (b) bath aged with 5Ah/l of polishing charge; (c) bath aged with 10Ah/l of polishing charge; and (d) bath aged with 20Ah/l of polishing charge.

6.2.5 Surface roughness evaluation

Figure 6.7 shows the evolution of the surface roughness Ra of the polished workpieces as a function of the electropolishing current per unit volume of the polishing bath. The surface roughness of the sample electropolished in the most-aged bath is one order of magnitude greater than the part polished in the freshest bath.
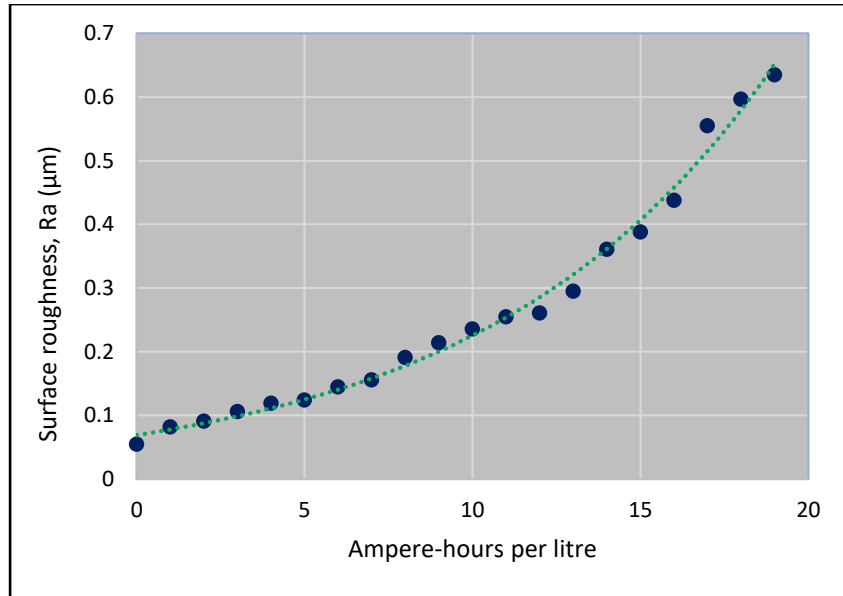
Figure 6.7 Variation of surface roughness results versus the polishing charge used.

6.2.6 Evolution of surface roughness with bath properties

All the measured bath properties and the surface roughness evolve linearly with the polishing current. Therefore, the surface roughness values are plotted as a function of the measured bath properties to analyse the evolution of the surface roughness versus the bath properties. All the three graphs in Figure 6.8 follow a quadratic trend.
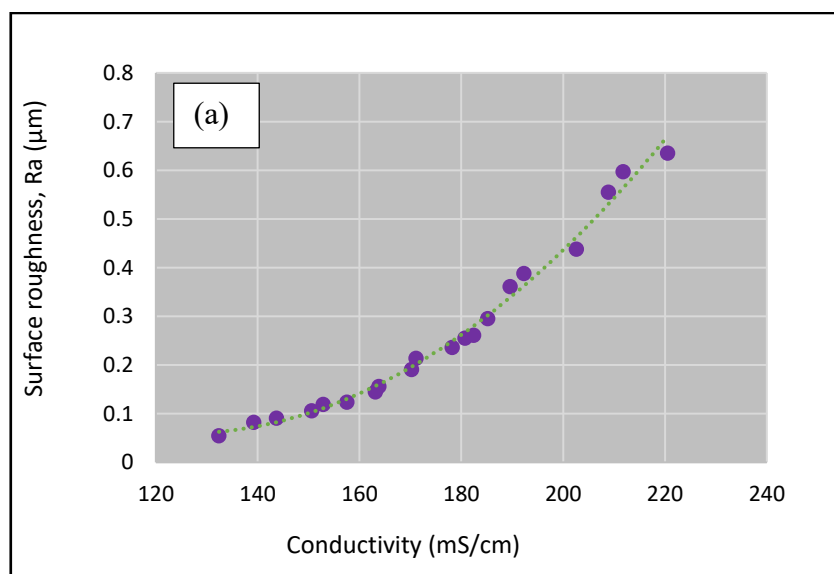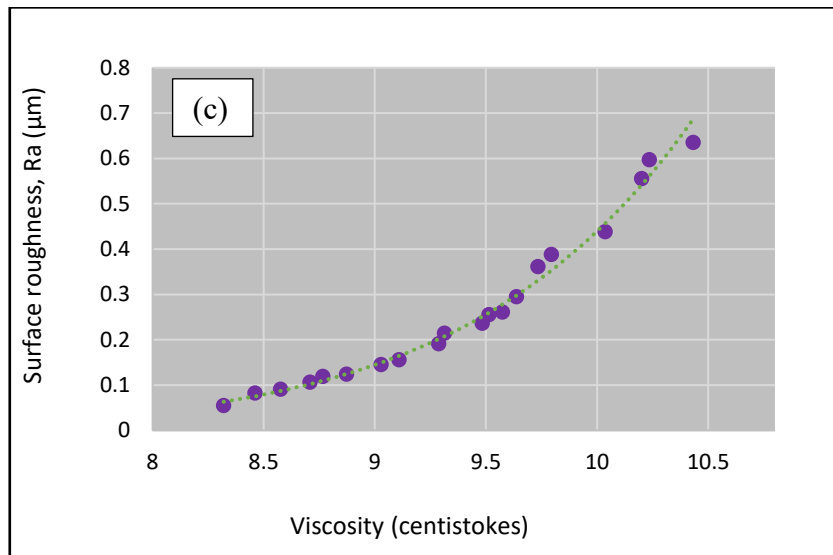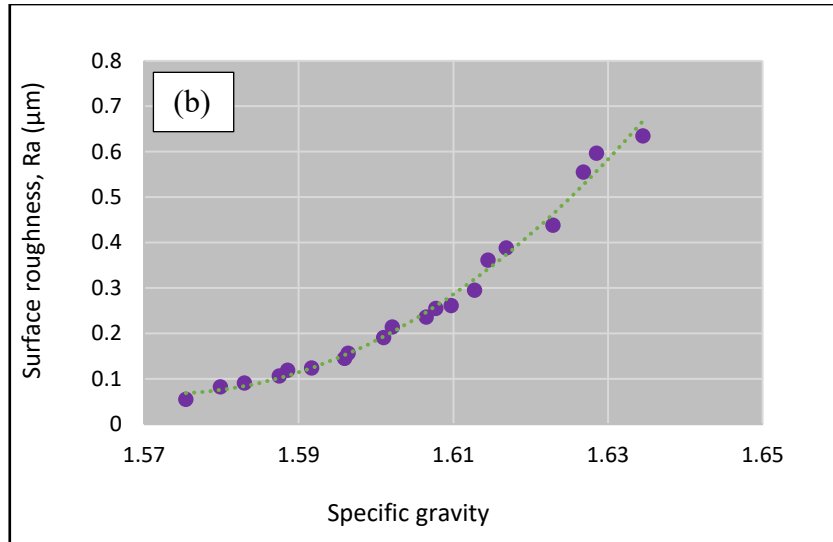
Figure 6.8 Evolution of the surface roughness as a function of the bath properties during bath ageing.

6.2.7 Bath regeneration

The polishing bath is contaminated after the simulated bath ageing, and the standard electropolishing tests produce poor results. Therefore, this study phase is carried out to simulate the bath recovery operations performed in the electropolishing industry.

i.   Method

A 10% volume of the aged bath is removed and replaced with a 10% fresh bath volume. The bath properties, conductivity, specific gravity and viscosity, are measured followed by a standard electropolishing test. This process is continued until the bath properties get close to the initial fresh bath's properties.

ii.   Verifying polishing performance

Standard electropolishing tests are performed after each step of bath recovery and bath characterization. The plots of the surface roughness versus the bath properties are enhanced with the new data set. The results are compared to the results of the standard electropolishing tests from the simulated bath ageing. Figure 6.9 shows the surface roughness values as a function of the bath properties. All three plots confirm that the surface roughness is a function of the current bath state regarding the bath properties.
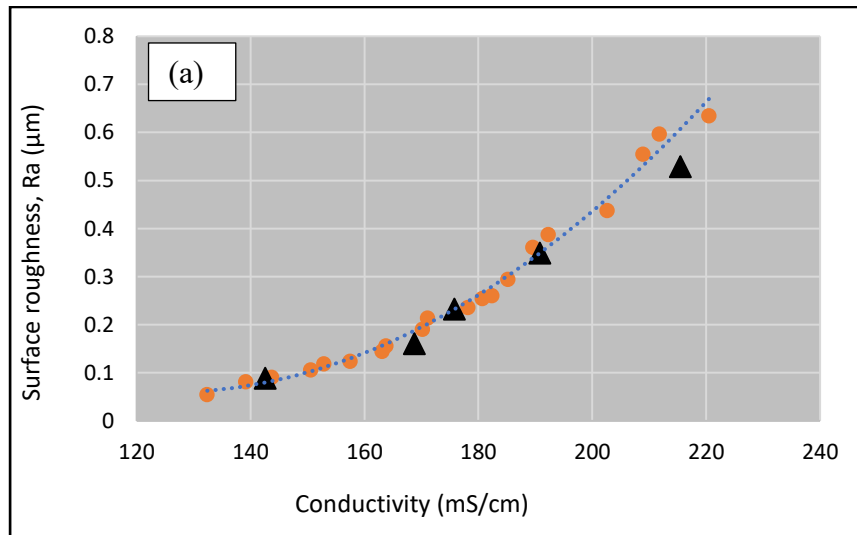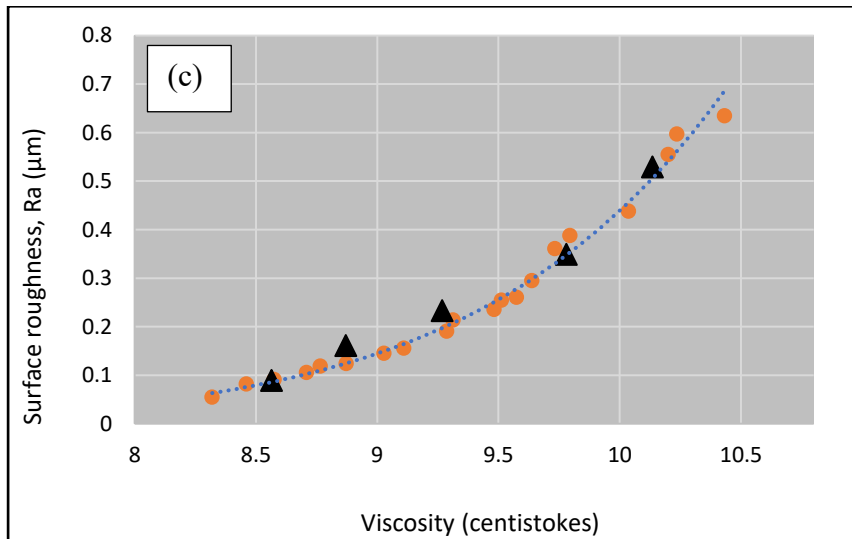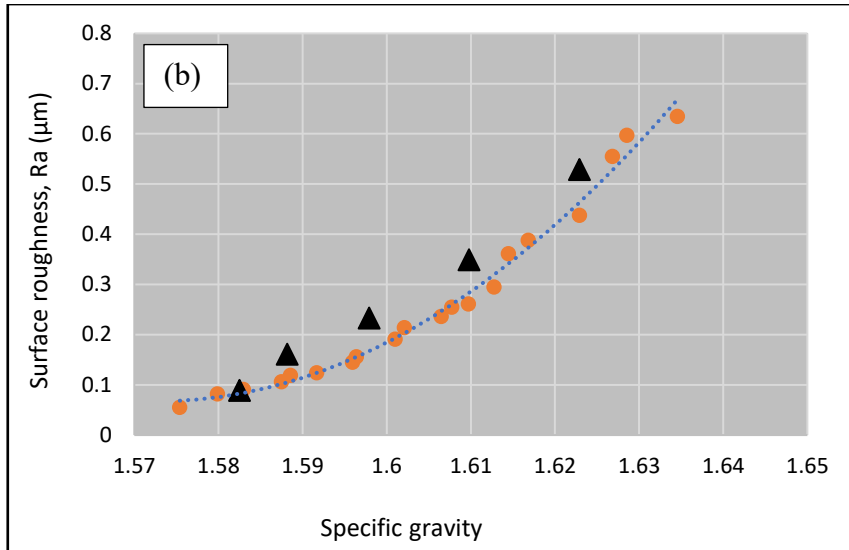
Figure 6.9 Surface roughness results evolving as a function of the bath properties during bath regeneration.

7 Data Analysis - Regression Model

7.1 Method

The plots of surface roughness versus the bath properties in Figure 6.8 from chapter six follow a quadratic trend. Based on this observation, a multiple-linear regression approach is used in analyzing the polishing results in terms of surface roughness at the various stages of bath ageing. The regression model facilitates the prediction of the response as a function of the quantitative independent variables. The linear model determines the interaction and significance of each parameter. The regression calculates the coefficients for each parameter to give a weight of importance to each parameter. The coefficients are based on the magnitude of change the parameter creates on the output [114]. For the simple linear regression model, $Y = \theta_0 + \theta_1 X$, the analysis process involves:

- Determining which dependent variable relates to the response;

- Choosing the form of relationship;

- Selecting the best fitting regression model;

- Estimating the parameters, θ_0 and θ_1 of the regression function;

- Testing the hypothesis of the estimated parameters of the regression function;

- Predicting Y at values of X_1, X_2,.., X_k to see if the same is observed;

- Establishing the correlation between X and the Y based on R-value and root mean square error (RMSE).

7.2 Multiple Linear Regression Model

The regression model is built from six attributes involving the vital bath properties and is used to anticipate the surface roughness Y at that instant state under the standard polishing

conditions, as denoted by equation 8. The table 7.1 presents the fitted parameters for these attributes obtained by solving the normal equations.

$$Y = \theta_0 + \theta_1 X_1 + \theta_2 X_2 + \theta_3 X_3 + \theta_4 X_4 + \theta_5 X_5 + \theta_6 X_6 \qquad (8)$$

Here, X_1 = conductivity, X_2 = (conductivity)², X_3 = specific gravity, X_4 = (specific gravity)², X_5 = viscosity and X_6 = (viscosity)²

Table 7.1 Regression coefficients of each parameter.

	Coefficients, θ_i
constant	-1198.35
conductivity	-0.02
conductivity²	6.0
specific gravity	1531.84
specific gravity²	-475.72
viscosity	-7.12
viscosity²	0.38

7.3 Fitting the Regression Model to Experimental Data Set

The surface roughness values are computed from the regression model using the bath properties measured during simulated bath ageing. The calculated surface roughness values are then plotted versus the bath properties. Figure 7.1 displays the regression model fitted to the experimental data set and confirms the bath properties' influence on the surface roughness, and a good fit is observed. A good fit is seen, and all the three graphs are similar to the plots of the actual surface roughness versus the bath properties plots from Figure 6.8 in chapter six.
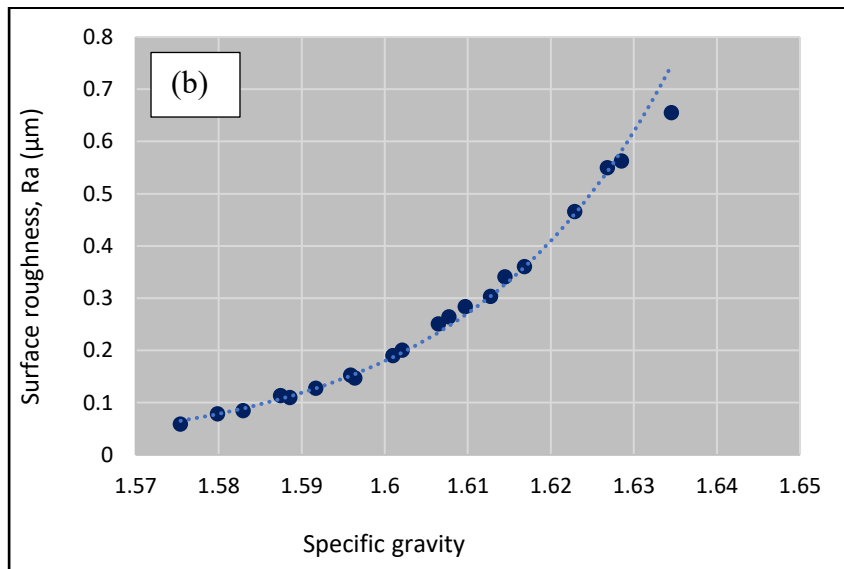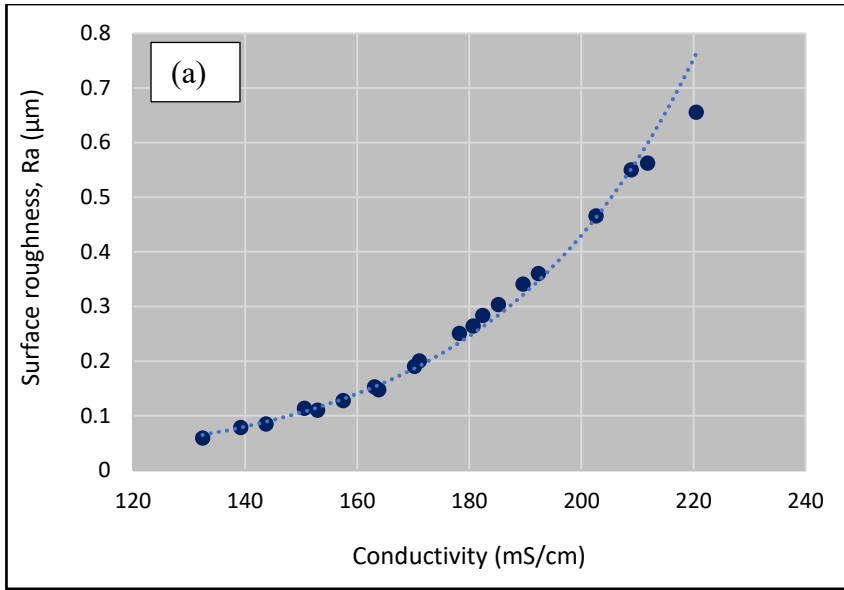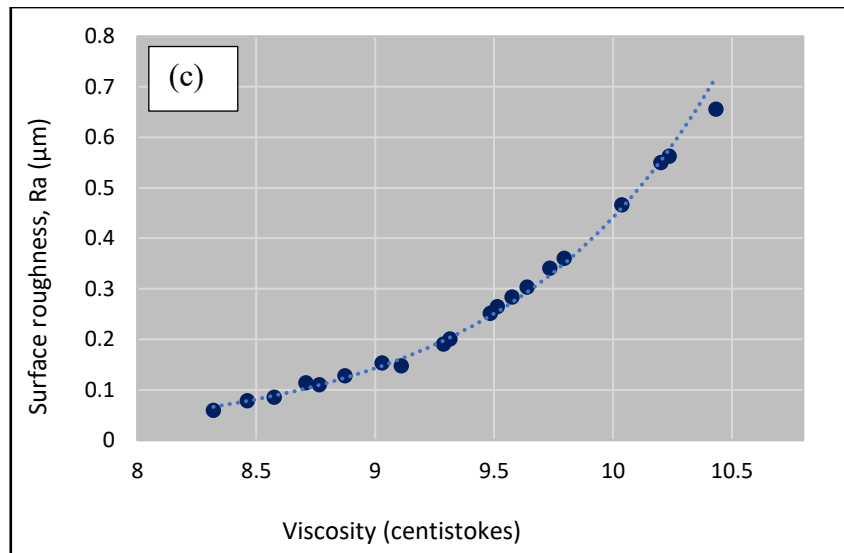
Figure 7.1 Fitted surface roughness values versus the bath properties.

7.4 Efficiency of the Proposed Regression Model

The computed surface roughness values are close to the actual surface roughness results. Figure 7.2 (a) shows the calculated surface roughness values plotted versus the actual surface roughness results. The fit gives an R-value of 0.9958, and this indicates that the proposed linear model shows a strong correlation between the variables. The residuals are analyzed in Figure 7.2 (b) to have a more quantitative description of the fit's validity. The random distribution of the residuals versus the computed surface roughness values confirms that the proposed multilinear model effectively describes the data set with a root mean square error of 0.01.
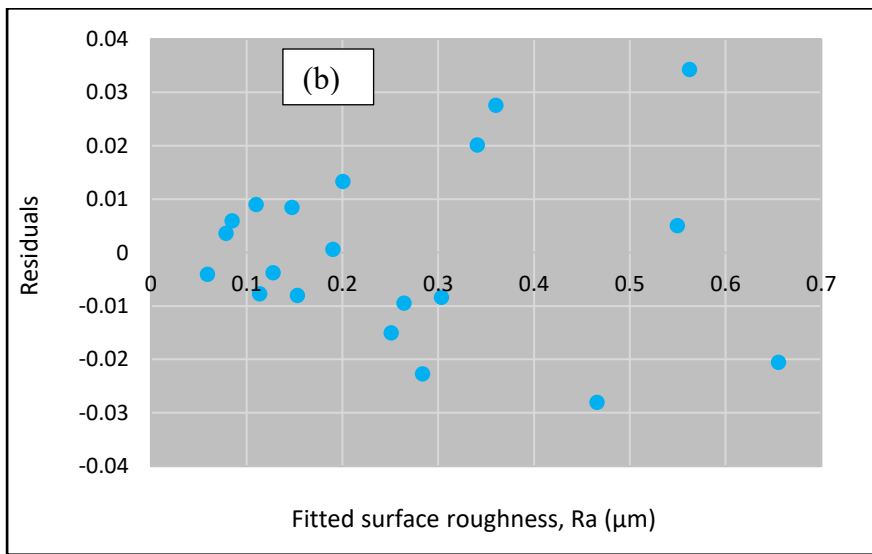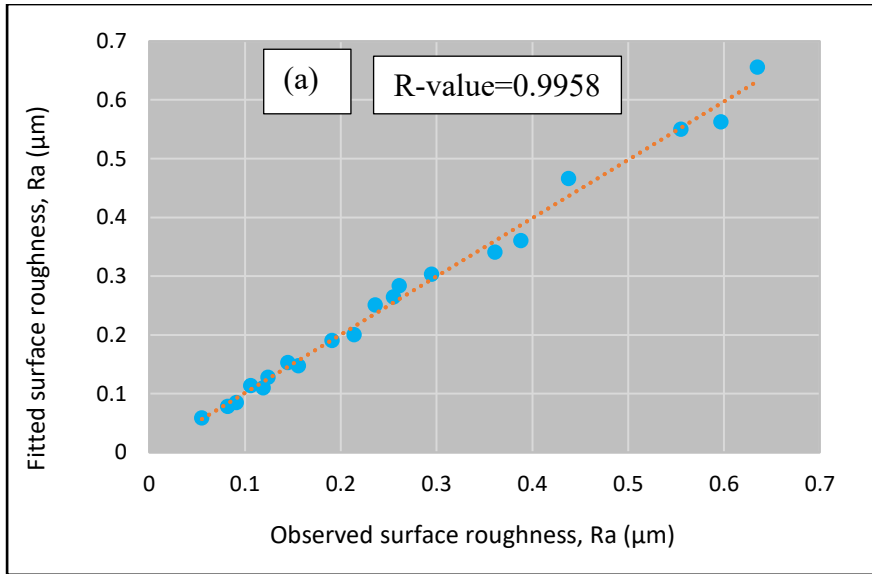
Figure 7.2 (a) Efficiency of the regression model with R-value = 0.9958 ; and (b) random distribution of residuals versus fitted surface roughness values with RMSE = 0.01.

7.5 Validity of the Proposed Model for the Regenerated Bath

The data recorded during the bath regeneration operation is used as a validation set for the proposed model. The surface roughness values are computed from the regression model using the bath properties measured during bath regeneration. The calculated surface roughness values are then plotted versus the actual surface roughness results recorded with the regenerated bath. The plot in Figure 7.3(a) has a good fit with an R-value of 0.9785. The residuals are analyzed in Figure 7.3 (b). The graph of the residuals versus the computed surface

roughness values shows that the proposed model remains valid for the new set of data with a root means square error of 0.06. This result confirms that the model can describe the instantaneous polishing capability in terms of surface roughness at any given state of the bath, considering the bath properties.
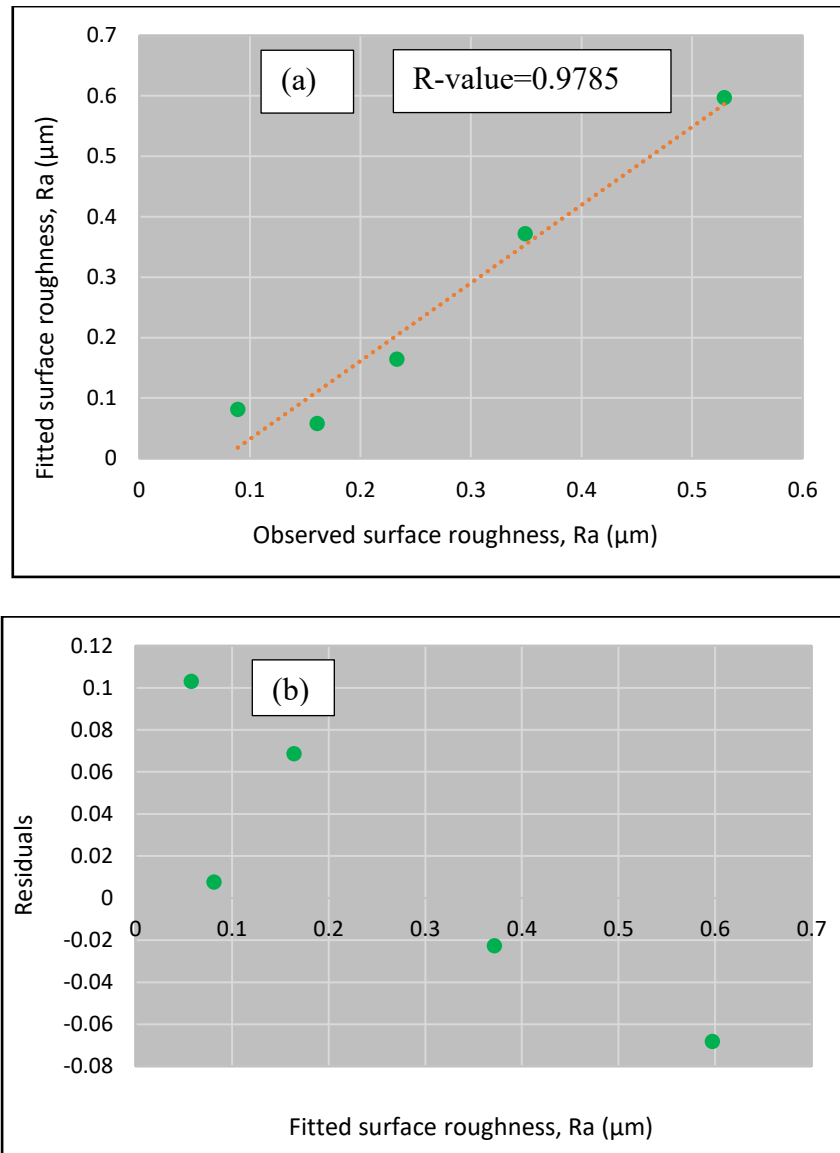
Figure 7.3 (a) Data recorded with the bath regeneration operation fitting the regression model with R-value = 0.9785; and (b) random distribution of residuals versus fitted surface roughness values with RMSE = 0.06.

8   Conclusions and Future Works

8.1 Conclusions

The results show that as the bath is operated, the metal concentration, conductivity, specific gravity and viscosity increase, and the bath composition changes. The polishing qualities diminish with the surge in the dissolved metal ions in the bath and with the change in the bath properties.

This research contributes to developing a multilinear regression model constructed with six attributes involving the vital bath properties. The model describes the polishing qualities in terms of surface roughness obtainable at any instant bath state under the standard polishing conditions. Once the bath properties are measured, the model can calculate the surface roughness available for that bath state.

This approach will assist the electropolishing shops by reducing the trial and error process they perform to figure out the operating parameters to compensate for the contaminated polishing baths. The bath is instantly available and will help them save the resources spent on the trial runs and getting bad results while polishing. The model built from the bath properties measured on the spot will help anticipate the polishing bath performance in terms of the polishing results.

This model based technique will also help them determine the state when the bath is no longer efficient, and thereby supplementing the aged bath with fresh solution. The study confirms that replacing a portion of the aged bath and adding it up with a fresh solution is the easiest method of maintaining the driving force for electropolishing and extending the overall bath life with less impact on operational cost. The regression model predicted the surface roughness accurately for the regenerated polishing baths too. Therefore, the multilinear model stays logical for any given bath state, fresh, aged or regenerated.

These findings are essential for the electropolishing industry as no systematic open-source data is available on the degrading of polishing performance with bath ageing. This model based technique would be beneficial in maintaining both efficiency and consistency during expedited polishing needs.

8.2 Future Works

The future extension of the current research includes:

- The connection between the instantaneous bath properties and the polishing qualities achieved under the standard conditions can be considered for additional studies to broaden the tactics to make polishing parameters flexible with a given bath state. The statistical model can be optimized to tune the bath parameters for the desired amount of surface roughness.

- Establishing a fundamental understanding of the role played by the conductivity, viscosity, and specific gravity on the electropolishing performance is a possible direct extension of this work. Proving the mathematical relationships between these parameters could lay the foundation for developing better capabilities for electropolishing systems.

- Studying the by-products produced during the electropolishing process, formed by the reactions of the dissolved transition ions and the anions provided by the bath acids, could explain the variations in acid composition as the bath ages.

- Extending the current study to other grades of stainless steel, namely, 400-series steels, duplex steels, different electrolyte solutions and for electroplating baths.

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Appendix

**Determining the acid composition in the electrolyte solution**

The phosphoric - sulfuric acid ratio in the electrolyte solution is measured by acid-base titration-end point detection method that uses methyl orange and phenolphthalein indicators, respectively, following the given procedure:

- Take 5 mL concentrated electrolyte solution in a beaker and dilute it to 500 mL by adding deionized (DI) water.

- Take 10 mL of the diluted solution in a conical flask and further dilute it by adding 150 mL DI water.

- Add four drops of methyl orange 0.1% indicator solution to this and the solution turns reddish pink.

- Titrate with 0.1 N sodium hydroxide solution until the color changes from reddish pink to light yellow.
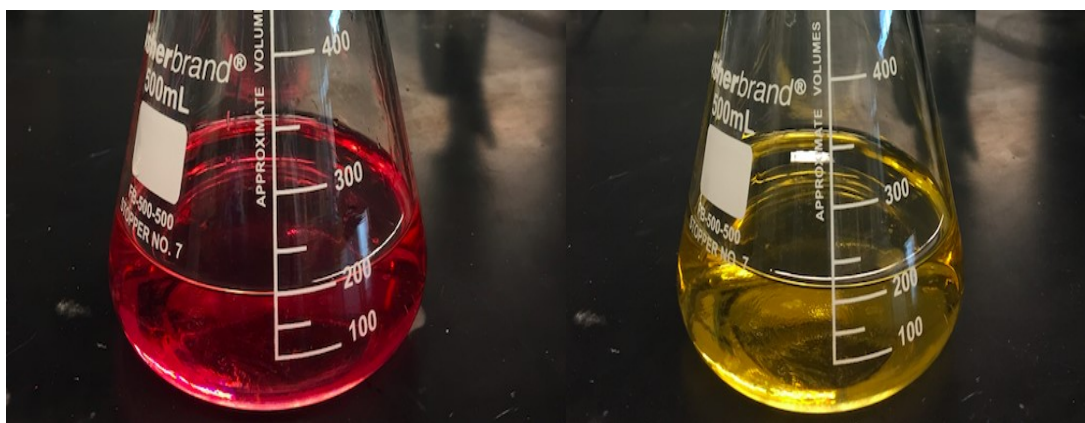
Figure 1 Color change of the electrolyte with the methyl orange indicator.

- Now, put four drops of phenolphthalein indicator to this solution.

- Titrate it with 0.1 N sodium hydroxide solution till the color changes from light yellow to pinkish orange.
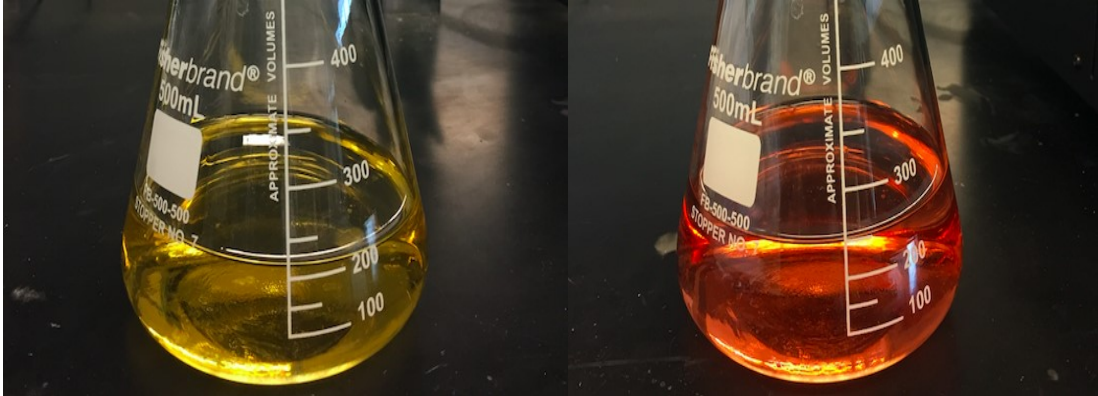
Figure 2 Color change of the electrolyte with the Phenolphthalein indicator.

If A is the volume of sodium hydroxide used for methyl orange color change and B is the volume of sodium hydroxide used for phenolphthalein color change, then:

➢ The volume percent of sulfuric acid = (2A-B) * 2.78

➢ The volume percent of phosphoric acid = (B-A) * 6.2

➢ The remaining volume percent is deionized water.