

Research Article

# Production of Sodium Hypochlorite by Electrochemical Methods: Development of New Generation Electrodes

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## Abstract

*In the denim sector, the difficulty in the supply of sodium hypochlorite used in the washing processes where bleaching and bleaching processes are carried out and the hydrogen peroxide chemicals required for neutralization have become an important problem in the global market and their costs have increased. In addition, green chemistry and sustainable synthesis reactions are attracting attention in today's world where environmental concerns have reached the highest level. Electrochemical techniques, one of them, are generally used in treatment and disinfectant production. Industrially, the synthesis of sodium hypochlorite is carried out with chemicals and processes that are harmful to the environment. In this study, the synthesis of sodium hypochlorite, which is a bleaching and bleaching chemical used in various fields in denim production lines, as a cost-effective, environmentally friendly and sustainable green chemistry was carried out using electrochemical techniques with brine. Thanks to the new generation electrode and electrochemical cell design prepared using Mn (III) imprinted 402 grade steel, sodium hypochlorite production efficiency was improved by 40%. The bleaching and effecting results were compared with the conventional ones and found to be more effective.*

**Keywords:** Sodium hypochlorite, Electrochemistry, Green chemistry, Sustainability

## 1. Introduction

Globally, the sodium hypochlorite market grew by 12.50 million tones in 2020 and is estimated to reach a healthy CAGR of 5.15% by 2030 [1]. Sodium hypochlorite ( $\text{NaClO}$ ), commonly known as liquid bleach, is composed of sodium cation and hypochlorite anion [2]. It is a highly reactive, volatile and pale greenish-yellow aqueous solution traditionally used as a household hygiene chemical [3]. Sodium Hypochlorite is widely known as an excellent sterilizer, oxidizer, bleach, germicide and the most effective disinfecting agent [4]. Sodium Hypochlorite is produced on a large scale by combining chlorine gas and caustic soda [5]. Due to the strong disinfectant properties of sodium hypochlorite, it is largely used as an active ingredient in water treatment and cleaning solutions, helping to prevent harmful microorganisms from harming health [6]. Sodium Hypochlorite acts as a chlorinating agent that keeps swimming pools and drinking water safe and serves as an important ingredient in the formulation of cleaning solutions for various classes including veterinary, food processing, deodorization and others [7]. Sodium hypochlorite has versatile bleaching properties and is therefore used as a bleaching agent in the textile industry [8]. In recent years, its effectiveness in the disinfection of viruses, bacteria, fungi, mycobacteria and other microorganisms has led to an increasing market for sodium hypochlorite [9]. Based on type, the Sodium Hypochlorite market is segmented into two segments, food grade and industrial grade. Among these, the food grade segment holds the largest share in the market as Sodium Hypochlorite is widely used as biocide and pulp digestion chemical. On the basis of end-use industries, the Hypochlorite market is segmented into wastewater treatment, agriculture, chemical, textile, medical and others. The wastewater chemical treatment industry has been the major driver of the Sodium Hypochlorite market, mainly due to rapid urbanization and industrialization in developing economies. The exponentially increasing demand for bleach by the textile industry is expected to further boost the worldwide Sodium Hypochlorite market in the coming years. However, the hazardous nature of Sodium Hypochlorite due to its strong oxidizing properties may hamper the growth of the market [10]. A wide range of literature studies have been carried out for the production of high concentration sodium hypochlorite for use in enterprises. In one study, sodium hypochlorite ( $\text{NaOCl}$ ) production from salty wastewater was carried out using an electrochemical cell. For this purpose, a porous graphite two-electrode laboratory type reactor was used and factors such as anodic current density, salinity, inert electrode spacing and inlet feed flow rate affecting  $\text{NaOCl}$  concentration and energy consumption were investigated [11]. It should not be forgotten that the most important component in the electrochemical cell is the electrode. In general, it is important to select materials that increase the surface area for sodium hypochlorite production [12-14]. It is concluded that the most suitable and cost-effective method can be obtained from brine by using electrochemical technique. When

the reviewed literatures are examined, almost all of them are sodium hypochlorite with an effective content not exceeding 7% and produced for use as a disinfectant [15-17].

The electrodes used during electrochemical production play a very important role. This new electrode system was prepared by 'molecular imprinting' technique [18]. It is a technique generally used for the preparation of polymers with selective recognition sites for analytes [19]. Carriers prepared by molecular imprinting are very important due to their high selectivity to the target molecule [20]. Molecular imprinting method was first described by Günter Wulff and his group in 1972 and was used to obtain highly selective binding sites by arranging the three-dimensional structures of functional groups in polymers [21]. Later studies have shown that 'artificial enzymes' can be obtained by using substrates and products of desired enzyme reactions as mold molecules [22]. The technique that transfers the recognition mechanism of biological systems such as antibody/antigen or enzyme/substrate to polymeric structures is called 'Molecular Imprinting' [23-24]. Molecularly imprinted polymers (MIP) are suitable for molecular recognition, inexpensive and easily prepared. In addition, molecularly imprinted polymers are highly durable due to their high mechanical properties, resistance to heat and pressure, physical robustness, high stability in media such as acids, bases, metal ions and organic solvents [25]. Molecular imprinting method follows the steps of pre-complexation, polymerization and removal of the analyte molecule.

## **2. Materials and Methods**

### **2.1. Physical and chemical properties**

In this study, the well water of BAYKAN Denim Plant was used. The analysis of the plant water was carried out in Kahramanmaraş Sütçü İmam University, ÜSKİM research center according to TS EN ISO/IEC standards. The results were interpreted and it was determined whether it was of suitable quality (soft water) for the sodium hypochlorite planned to be produced. Conductivity value was determined as 145 siemens and hardness as 20 F. Commercially available sodium chloride salt was selected as Merck brand, pH 6.7-7.3. The content analyses of the sample taken from the 500:1 solution prepared with both are summarized in Table 1.

Table 1. Physical and chemical characteristics of brine

Properties	Values
Conductivity, mS/cm	61.8
pH	6.7-9.1
Hardness as CaCO <sub>3</sub> , ppm	9132
Total alkalinity as CaCO <sub>3</sub> , ppm	121
Chloride as Cl <sup>-</sup> , ppm	25.12
Fluorine F <sup>-</sup> , ppm	13.4
Sulfate as SO <sub>4</sub> <sup>2-</sup> , ppm	1234
Phosphate PO <sub>4</sub> <sup>3-</sup> , ppm	176
Nitrate as NO <sub>3</sub> <sup>-</sup> , ppm	11.9
Nitrite as NO <sub>2</sub> <sup>-</sup> , ppm	9.87
Sodium as Na <sup>+</sup> , ppm	10.5
Salinity, (%)	45.1

In this table, pH value was measured using Mettler Toledo brand, Seven Excellence S400-Basic, pH/mV benchtop meter. For total dissolved solids, Mettler Toledo brand Halogen Moisture Analyzer HX204 was used. In order to calculate the concentrations of anions and cations in the brine, it was filtered through a 0.20 µm membrane filter and used in the Dionex ICS4000 HPIC Capillary System ion chromatography device of Thermo brand located in Kahramanmaraş Sütçü İmam University, ÜSKİM Laboratory. Standards and methods determined by TS EN ISO were used for the determination of ions [26].

## 2.2. Electrochemical Cell Design

Firstly, sodium hypochlorite was obtained from 3 M NaCl solution using galvanic cell and triple electrode system in the laboratory environment (Figure 1). For the electrolysis of the brine prepared for electrochemical studies, 5 ml of 0.1 M tetrabutyl-ammonium tetrafluoroborate (TBAP) solution was added to the solution as a support electrolyte. While the voltammograms of the prepared solutions were taken continuously, nitrogen gas with a constant flow rate was passed through the solution. Ag<sup>+</sup>- AgCl (BAS MF-2052) was used as reference electrode, platinum wire electrode (BAS MW-1032) as counter electrode and glassy carbon electrode (BAS MF-2012) as working electrode. Before electrolysis of saline solutions of different concentrations, the working electrodes were cleaned. For this purpose; Mettler Toledo, Cavitator Ultrasonic Cleaners were used. In an electrochemical reaction, the electrode surface must be clean. When this process is not performed, a decrease in peak current and shifts in peak potential occur. In order to activate the electrode surface, the surface of the working electrode was made shiny and smooth. P4000 Buehler cleaning paper was used for this purpose. The electrode is polished on the surface of this paper. Alumina powder of 1 µm was added to this paper

and the electrode was cleaned in a circular motion, then the cleaning process was repeated with alumina powders of 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$ , respectively.



Figure 1: Electrochemical cell and triple electrode system

As a result of the conversion of saline water to sodium hypochlorite by electrochemical method in the laboratory environment, cell and electrode design was carried out for plot production. Yihua 3005D 0-30V 5A adjustable DC power supply was used to create potential. Two separate electrodes; 302 quality stainless steel and 402 quality titanium coated plates were used as parallel plates by combining them. The potential of the cell was measured using a SDM3055 5 1/2-digit benchtop digital multimeter. A metering pump was used to supply the brine. It is a regulated and controlled pump capable of injecting the maximum flow rate into the cell with an upward flow through the system with a flow rate of 3.2 L/hour. Teflon bearings were screwed between the parallel plates forming the electrode and placed in an acrylic glass tube. While the solution is supplied to the system through the feed hole opened to the lower part, both the hydrogen gas formed and sodium hypochlorite are allowed to pass continuously through the hole opened to the upper part.

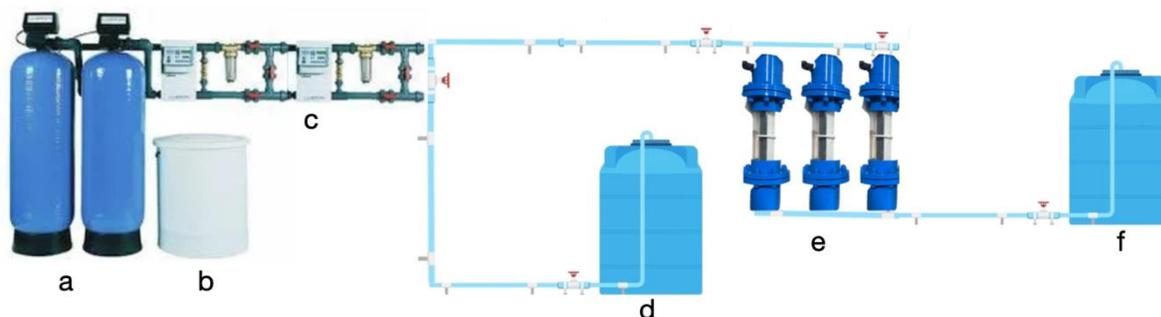


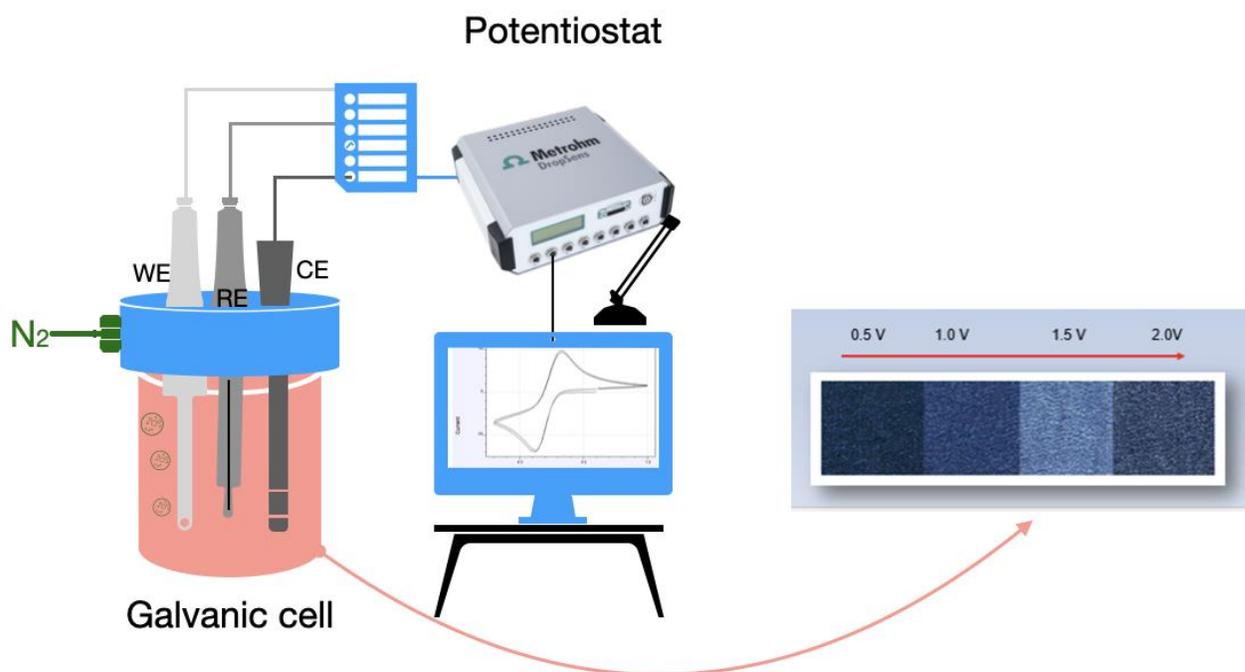
Figure 2: Electrochemical cell, a) Water softening unit, b) water tank, c) jet ejector system, d) brine tank, e) Electrodes, f) product tank

### 2.3. Preparation of electrodes

For the synthesis of Mn(III) imprinted microspheres; 0.15 g polyvinyl alcohol (PVA) was dissolved in 100 mL of ultrapure water to provide dispersion medium. To this solution, 12 mL/20 mL EGDMA/Toluene mixture, EGDMA-[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>] monomer complex dissolved in 100 mL ethyl alcohol and 0.093 g 2,2-Azobisisobutyronitrile (AIBN) as initiator were added. The polymerization process was completed at 55-60 °C for 12 hours and at 80 °C for 24 hours in a heater with magnetic stirrer. The resulting microspheres were washed continuously with ethanol and then with ultrapure water to remove unreacted monomers and other wastes. Removal of molded Mn(III) ions from the microspheres was carried out using 6M HNO<sub>3</sub> and 3M HCl solution (1:3). The Mn(III) ion suppressed microspheres were then filtered and washed with ultrapure water and left to dry at room temperature. Then, they were kept in the immersion pool at 80 °C for 1 hour to adhere on 402 grade stainless steel.

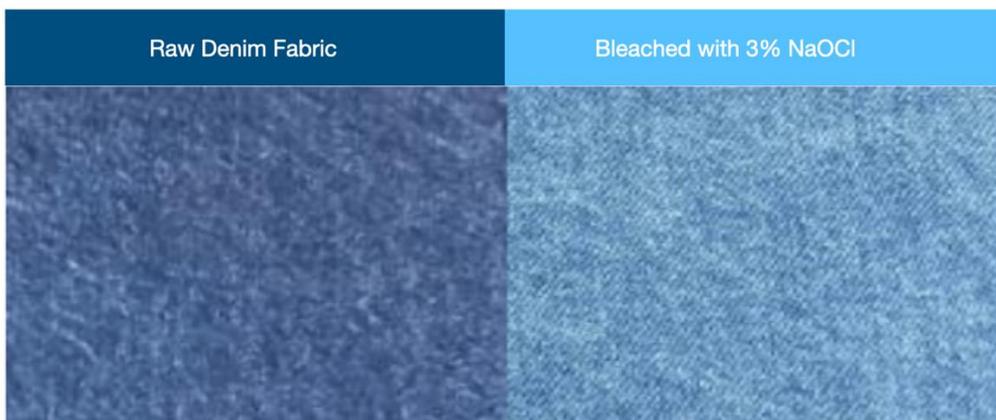
### 3. Results

In the R&D laboratories of Baykan denim enterprises, it was firstly investigated whether sodium hypochlorite production was realized by using galvanic cell and triple electrode system for sodium hypochlorite production. 3 M NaCl and water (Water:NaCl:TBAP, 1:500:0.5) placed in the galvanic cell was carried out by applying potentials of 2 mV continuously to the system prepared in nitrogen gas environment and by applying electrical potential. The effects of the obtained sodium hypochlorite on 1 cm denim fabric are shown in the figure (Figure 3).



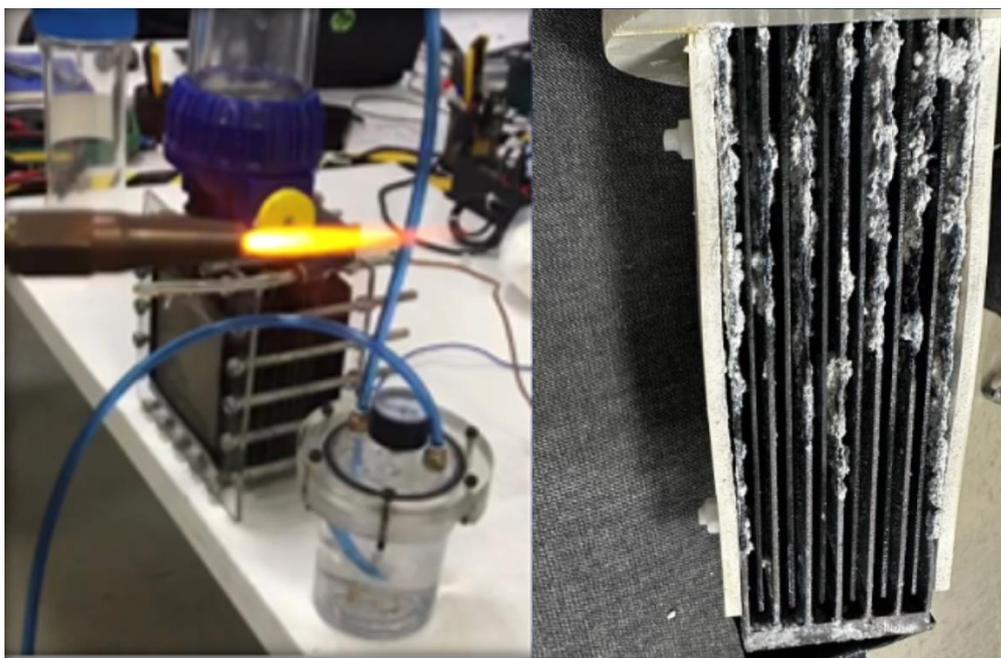
*Figure 3: Effect of potential on NaOCl concentration and bleaching on denim in sodium hypochlorite production*

Active chlorine was determined by taking a sample from the sample that started to turn yellow as a result of electrochemical reaction. For this purpose, 1 ml of the sample to be analyzed was taken into a 50 ml balloon jug and completed with water up to the meniscus line. 5 ml of water, 1 ml of concentrated acetic acid and 0.1g KI were added into a 50 ml flask and dissolved. To this, 5 ml of the prepared sample was added from the balloon jar and immediately titrated with 0.1 N sodium thiosulphate. Starch solution was used as an indicator. The disappearance of the blue color was determined as the turning point. The result was calculated as g/L active chlorine. The obtained 3% sodium hypochlorite was tested on denim fabric produced from 100% cotton indigo dyed fabric (Figure 4).



*Figure 4. Bleaching effect of the obtained NaOCl on denim fabric*

Then, pilot scale electrochemical cell design was started for multiple production. The brine used here was prepared as 145 grams of sodium chloride per 1 litre. 402 quality stainless steel plates were used as electrodes. These plates were obtained by joining them parallel to each other in 10cm<sup>2</sup> dimensions (Figure 5).



*Figure 5: Electrochemical cell design and electrode plates for pilot production*

The first results obtained are that hydrogen gas is released from the system but sodium hypochlorite is not formed in the remaining part of the cell. Since the hydrogen gas formed on the electrode surface does not leave the system quickly, it combines with the chlorine ion in the solution environment and produces hydrochloric acid. It was observed that the 302 quality steel used as a method did not work as an electrode. Abrasions and deposits were observed on the electrode plates as shown in Figure 4. For this purpose, titanium coated 402 quality steel plates were ordered and turned into parallel plate electrode. As a result of the experiments carried out with it, the presence of 14% sodium hypochlorite was found. In order to ensure that the hydrogen gas released as a result of the reaction on the electrode surface leaves the environment immediately, a hydrogen vacuum pump was included in the system and supported by vertical pipelines (Figure 6).



*Figure 6: Vertical Electrode design*

Mn(III) imprinted microspheres obtained by molecular imprinting technique, the synthesis stages of which are described in the materials and methods section, were applied on 402 grade steel. The work flow chart of the plates obtained accordingly is presented in Figure 7.

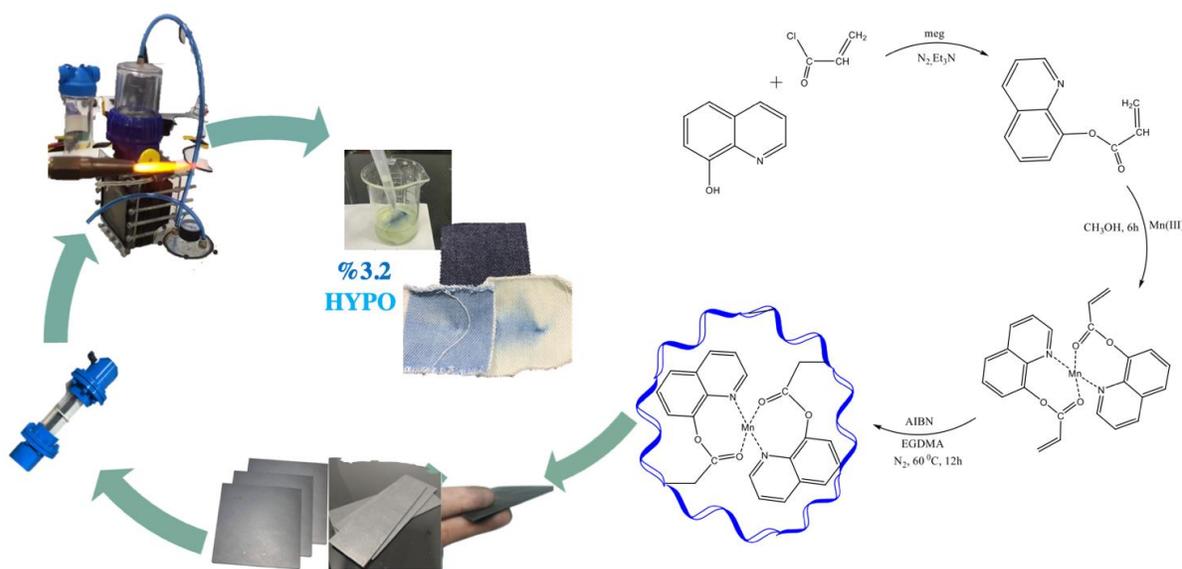


Figure 7: Electrode flow chart obtained by molecular imprinting technique

In this study, the electrochemical process to produce NaOCl from brine using an electrode consisting of porous and Mn(III) imprinted stainless steel plates was investigated by studying various materials and operating factors. These factors include the slab quality, design and inlet feed flow rate. Figure 6 shows the effect on the concentration of NaOCl produced from the electrochemical cell using porous Mn(III) printed electrode.

FT-IR spectra of the synthesised Mn(III) imprinted microspheres were taken using Perkin Elmer Spectrum Two, PIKE Gladi ATR Diamond technique. For this purpose, a small piece of the powdered material was taken, compressed in a diamond ATR, and infrared light was shone on it and analysed in the range of 400-4000  $\text{cm}^{-1}$ . The infrared spectrum of the compound is given in Figure 8.

When the spectrum was examined; the characteristic peaks of FT-IR analyses used for the characterisation of ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde monomer were determined. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1661.97  $\text{cm}^{-1}$  (aldehyde carbonyl peak), 1617.08  $\text{cm}^{-1}$  (C=C peak in vinyl group), around 3300  $\text{cm}^{-1}$  (O-H peak), 3049.25  $\text{cm}^{-1}$  (C-H peak in aromatic ring), 1150.88  $\text{cm}^{-1}$  (C-OH peak), 1596.10  $\text{cm}^{-1}$  (C=C peak in aromatic ring), around 1385  $\text{cm}^{-1}$  (N=N peak), around 1410  $\text{cm}^{-1}$  (C-N peak).

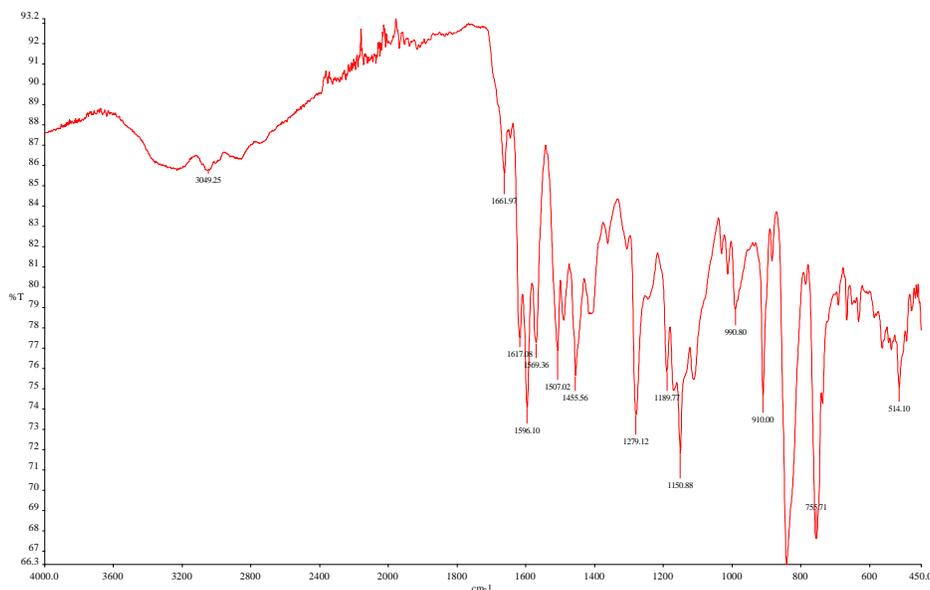


Figure 8: FTIR spectrum of Mn(III) microsphere printed plates

#### 4. Discussion and Conclusion

Denim garments have been popular for a long time. Its popularity is mainly due to the unique washing techniques in the production process of various styles. Washing techniques are techniques to obtain "worn" or "old" appearances on denim by removing dyes or surface fibers. In recent years, different washing techniques have been developed to create various denim garment designs. Among the various washing techniques, sodium hypochlorite bleaching, also called chlorine bleaching, has been applied for a long time and still plays a dominant role in industrial production due to its good performance. It has been shown that the chlorine bleaching effect depends mainly on the amount of sodium hypochlorite, temperature and processing time. In some studies, a quantitative mapping model has been established between the input variables and the washing effects. This shows that the trial and error method is still extensively carried out in the chlorine bleaching process for denim garment production and causes a large waste of waste material. Sodium hypochlorite production methods used in traditional methods are generally the combination of caustic and chlorine gas. However, when looking at the literature review, HYPO production from water generally remains at the disinfectant level. In light of this information, a process has been developed to obtain sodium hypochlorite from salt water in high concentrations by electrochemical methods. The most important component of electrochemical processes, the selection and production of electrodes, is directly proportional to product quality. For this purpose, porous structures on stainless steel were printed with Mn(III)-based polymeric microspheres using the molecular imprinting method and turned into plates. It was observed that the polymeric

spheres printed on 402 quality steel produced the best sodium hypochlorite. Another important point is the position of the electrodes in the electrochemical cell design. In the horizontal design, hydrogen gas accumulation on the plates was higher and this negatively affected the production. When the vertical design was switched to and the hydrogen vacuum pump was used, the production efficiency was increased by providing instant evacuation of the hydrogen gas formed. Moreover, it was concluded that the salt water was effective in the electrode feeding speed. During production, it was observed that the most effective efficiency was obtained when the current density was 1.86 mA/cm<sup>2</sup>, the salinity rate was 50,000 ppm, the inert electrode gap was 0.4 cm, and the electrolysis time was fixed as 15 minutes.

## 5. Acknowledge

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