INVESTIGATION AND EXPULSION OF MICRO-PLASTIC BY ELECTROCOAGULATION FROM DYE-FINISHED TANNERY WASTEWATER

Siddhartha Sardar, Santanu Sarker and Md. Elias Uddin*

Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna9203, Bangladesh, eliasuddin@le.kuet.ac.bd

***Corresponding Author**

ABSTRACT

Removal of micro-plastic from tannery wastewater is significant to prevent potential harm caused by micro-plastic to marine life. The aim of this study is to remove micro-plastic from tannery wastewater stream by using Aluminum anode electro-coagulation cell as floc. In this study wastewater from dyeing and finishing section of tannery was used. This wastewater of 40ml was treated with Fenton Reagent of three different concentration to separate the microplastic from organic and inorganic compounds. The characteristics of microplastic (charge, size, pH, NaCl concentration) was determined by using FTIR spectroscopy and SEM. Removal efficiency of micro-plastic using Aluminum anode electrolytic cell was 75% over a pH value of 5-7.5. Most valued efficiency was found at 94.67% at pH 7.3. An economic evaluation of the reactor operating costs revealed that the optimum NaCl concentration in the reactor, mainly due to the reduced energy requirements linked to higher water conductivity. In regard to this, electrocoagulation process can be used to effectively remove microplastic from tannery wastewater stream in ETP plants in Bangladesh with a weight of 20-30 %.

Keywords: *Electro-coagulation, Flocculation, Micro-plastic, Sustainable, Wastewater*

1. INTRODUCTION

In recent years, the escalating global concern surrounding plastic pollution has shed light on the pervasive and detrimental effects of microplastics in aquatic environments. As a by-product of variousindustrial processes and everyday consumer activities, microplastics, defined as plastic particles less than 5 millimeters in size, have become ubiquitous in water bodies worldwide. Among the myriad sources contributing to this environmental challenge, the discharge of microplastics from industrial wastewater, particularly that generated by the finishing industries, poses a significant threat to aquatic ecosystems. (Abdul Mannan Zafar a b, 13 December 2023)The finishing industry, encompassing sectors such as textile, metal, and plasticproduction, utilizes a multitude of materials that contribute to the release of microplastics during the manufacturing and processing stages.

As a result, the need for effective and sustainable strategies to mitigate microplastic contamination in wastewater has become increasingly imperative. t is also widely known that microplastics can be primary, contributed directly by products or materials containing plastics of microscale such as microbeads, microfibers and plastic pellets, or secondary, produced from the breakdown of larger plastic items. Primary microplastics come from personal care and cosmetic products such as facial scrubs, exfoliants and toothpaste, as well as from synthetic textiles. Secondary microplastics originate from plastic wastes and mismanaged plastics entering the environment. (Chunjiang An a b, Emerging usage of electrocoagulation technology for oil removal from wastewater: A review, 1 February 2017) These plastic wastes are generated by multiple sectors particularly the packaging sector, and the building and construction sector. Mismanagement of plastics is a concern, largely in developing countries with China reportedto have the largest proportion of mismanaged plastics entering the environment, followed by Indonesia and the Philippines One promising technique gaining attention for its potential in treating wastewater laden with microplastics is electrocoagulation. (Azthena, 10 September 2020)

Electrocoagulation, a process rooted in electrochemistry, involves the application of an electric current to destabilize and aggregate suspended particles in water. (Dina T. Moussa, 15 January 2017)As long-term solutions to microplastics elimination from the environment have yet to be framed, water and sludge treatment provides an immediate and feasible means of microplastics removal. Water treatment plants (WTPs) usually also encompass wastewater treatment plants (WWTPs) though not all WTPs treat wastewater. Treatment plants for drinking water frequently draw water from different water sources including surface water, groundwater and seawater for treatment and these sources of water are subject to microplastic contamination WWTPs focus on treating waste streams generated from industrial, commercial or residential entities Water treatment yields wastes such as effluents and sludge which trap microplastics and the return of these wastes to the environment reintroduces microplastics to the environment A study compared the microplastics levels upstream and downstream of six WWTPs andfound elevated microplastics level downstream of the WWTPs. This was attributed to the discharge oftreated sewage effluents containing microplastics into the rivers. The study reported variations in the ratios of the microplastics levels upstream and downstream of the WWTPs which seemed to correlate with their population equivalents served Microplastics < 500 µm have been detected in the effluents of WWTPs in quantities up to 9000 per m^3 with polyethylene (PE) most frequently found Polyethylene terephthalate (PET) is relatively common in the effluents Synthetic fibers, mainlypolyester, amounting to 1000 m^{-3} have also been reported to be present in the discharges of WWTPs Besides, (Singh, Kalyanasundaram, & Diwan, October 29 2021) microplastics particularly PE were present in sewage sludge of WWTPs Microplastics were detected in various stages of sludge treatment in a WWTP in Iran at 129 to 238 microplastics/g of dry weight sludge, thus, raising the concern that wastewater sludge could be a significant source of microplastics water treatment can be conventional, consisting of primary and/or secondary treatment stages with microplastics removal efficiency as high as 99% while it also concentrates microplastics for discharge Pre-treatment may precede primary treatment and it usually consists of coarse screens, grit chambers and sedimentation tanks for removal of large particles such as sand, aggregates and wood. Suspended organic matters evading primary treatment will be captured by secondary treatment otherwise known as the activated sludge process comprising an aeration tank or membrane bioreactor (MBR) Secondary treatment is more common in WWTPs due to the larger amount of organic matters in wastewater. To achieve higher discharge quality, (Dounia Elkhatib a, 22 December 2021) a tertiary treatment may be attached to a WWTP for further removal of contaminants in secondary Tertiary treatment may employ chlorination, ozonation, UV irradiation, rapid sand filtration, granular activated carbon. Similarly for drinking water treatment, filtration and disinfection akin to tertiary treatment are employed in the final treatment stage (Kuok Ho Daniel Tang a, 1)

This method has demonstrated success in the removal of various, including heavy metals, organic pollutants, and now, microplastics. By harnessing the principles of electrocoagulation, it becomes possible to address the unique challenges associated with microplastic separation from finishing wastewater. This paper explores the burgeoning field of electrocoagulation as an innovative and environmentally conscious approach to tackle the intricate issue of microplastic contamination in industrial wastewater. Other than the above-mentioned processes, promising, (Maocai Shen, 1 October 2021) relatively new technologies that utilize the concepts of electrochemistry are also available such as electrocoagulation (EC), electrooxidation and electro-floatation. Although using electricity for water treatment applications goes back to the 19th century, when EC was used for the treatment of drinking water in the United States, they were found impractical due to the high capital and electricity cost required (Chen, 2004). During the past two decades, electrochemical wastewater treatment technologies started to regain importance as an environmentally friendly option that generates minimal sludge, requires no chemical additives and minimal footprint without compromising the quality of the treated water. This paper focuses on reviewing recent advances in electrocoagulation with the aim of identifying the current state of the technology and its potential as an effective water treatment method. (Mike Wenzel a b, 12 December 2022) Despite the considerable number of publications about electrocoagulation, they tend to focus on laboratory scale experiments that prove the effectiveness of the technology in the removal of specific pollutants. Few authors looked into the kinetics, modelling, cell design, cost analysis, integrating electrocoagulation with existing technologies, scale-up and industrial applications, which are key factors that represent major challenges to the success of electrocoagulation. This review attempts to point out specific gaps, where more research is needed to develop electrocoagulation as a reliable and cost-effective water treatment technology. We delve into the principles underpinning electrocoagulation, discussing its efficacy in destabilizing and aggregating microplastic particles. Furthermore, we examine the potential advantages and challenges associated with the application of electrocoagulation technology in the context of wastewater treatment within the finishing industry. (Nicolás Alejandro Sacco 1, 4 September 2023)

2.METHODOLOGY

2.1 Materials

Finishing wastewater including PU, Binders, resins, and ethanol were collected from SAF Leather Limited, Bangladesh. $FeSO_4.2H_2O_2$ Fenton Reagent was prepared in the lab for the identification of MPs. The commercially graded filter paper (Whatman™ 125mm) was used for filtration and for electrocoagulation-electro flocculation reactor was made by using Aluminum and copper metals as cathode & anode.

2.2 Preparation of Fenton Reagent

Ferrous iron ($Fe^{2+)}$ and hydrogen peroxide (H_2O_2) were combined to create the Fenton reagent. Strong oxidizing agents called hydroxyl radicals (·OH) were produced when these two components react. The common procedure was mixing a hydrogen peroxide solution with a ferrous salt, usually ferrous sulphate ($FeSO_4$). The response can be shown as:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO^{\bullet}Fe^{3+} + H_2O_2 \rightarrow HOO^{\bullet} + Fe^{2+} + H^{+}$$

Considering that Fenton reagent produced hydroxyl radicals, which had the ability to oxidize a varietyof organic and inorganic materials, it was crucial to remember that this extremely reactive compound needs to be produced and handled carefully. Usually, the reaction occurs in an acidic environment (pHof around 3), because the presence of protons.

2.2 Electro-coagulation Cell:

An electrocoagulation cell is a water treatment technology that utilizes an electrolytic process to remove contaminants from water. In this system, copper is employed as the cathode (negative electrode), while aluminum serves as the anode (positive electrode).

2.2.1 Cathode:

During electrocoagulation, an electric current was applied to the cell, initiating electrochemicalreactions at the electrodes. At the aluminum anode, aluminum ions were released into the water, undergoing oxidation. These aluminum ions reacted with water molecules to form aluminum hydroxide flocs. Meanwhile, at the copper cathode, water was reduced to hydroxide ions and hydrogen gas.

2.2.2 Anode:

The aluminum hydroxide flocs generated during the process act as coagulants, attracting and neutralizing negatively charged particles, colloids, and other impurities present in the water. As a result, these impurities form larger, heavier particles that settle or could be easily removed through filtration. The electrocoagulation cell is effective in treating a variety of water contaminants, includingsuspended solids, organic matter, heavy metals, and some pathogens. This method offered advantages such as simplicity, minimal chemical usage, and the ability to handle a wide range of water qualities& 97.23% pure Aluminum (Al) was used to make the Aluminum electrode. It was important to note that the specific design and parameters of an electrocoagulation cell, such as voltage, current density, and electrolyte concentration, can be adjusted to optimize its performance for different water treatment applications. The ideal pH range for aluminum-based electrocoagulation is usually 5.5 to
8.5. Aluminum hydroxide becomes less soluble at lower pH levels, whereas insoluble flocs of aluminum hydroxide may form at higher pH levels. Potassium Chloride (KCL) of 0.1 N 2.34ml solution was used as Salt Bridge. PeakTech® P 6120» AC/DC Laboratory Power Supply 0 - 30 V/5 Awas used.2.34g Sodium chloride (NaCl) was used as conductance enhancer.98% Sulfuric Acid was used & 1.23L distilled water was used. 0.2N Sodium Hydroxide (NaOH) was used to optimize the pH. (Q. Li, 2009)

2.2 Separation of Microplastics:

2.3.1 Anodic Reaction (Aluminum Anode):

At the aluminum anode, oxidation occurs, resulting in the release of aluminum ions (Al^{3+}) into the water. The aluminum ions react with water to form aluminum hydroxide ($Al(OH)_3$) through the following reactions:

$$\mathbf{Al \rightarrow Al^{3+} + 3e^-}$$
$$\mathbf{Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+}$$

2.3.2. Cathodic Reaction (Copper Cathode):

At the copper cathode, reduction occurs, leading to the formation of hydroxide ions (OH^-) and hydrogen gas (H_2):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

2.3.3. Formation of Aluminum Hydroxide Flocs:

Aluminum hydroxide ($Al(OH)_3$) is formed as a result of the anodic reaction.
The aluminum hydroxide species undergo polymerization and precipitation, forming larger flocs.

2.3.4. Coagulation of Microplastics:

Microplastics present in the water are attracted to and enmeshed within the growingaluminum hydroxide flocs. Coagulation occurs as the microplastics become incorporated into the flocs, increasing their size and density.

2.3.5. Settling or Flotation:

The formed aluminum hydroxide flocs, now carrying the trapped microplastics, settle to thebottom of the electrocoagulation cell due to their increased size and weight.

Alternatively, flotation techniques can be employed to separate the flocs, carrying themicroplastics, to the water surface for removal.

2.3.6. Filtration and Separation:

The treated water is then subjected to filtration processes to remove the coagulated flocs,including the trapped microplastics.

Filtration methods may include sedimentation, centrifugation, or other physical separationtechniques.

2.3.7. Monitoring and Optimization:

The electrocoagulation process is monitored, and parameters such as voltage, current density, and electrolyte concentration may be adjusted to optimize microplastic removal efficiency.

2.3 Collection of Finishing wastewater:

Collected the waste water from SAF Leather Limited, Noapara, Jashore Bangladesh. Here we collected finishing wastewater as for the final coating on leather in finishing operation. The coated dyes and pigments contain microplastic.

2.4 Characterization of Finishing wastewater:

Experiment Name	**Our value**	**Standard value (ECR 2023)**
pH	7.3	6-9
TSS	82 mg/L	100 mg/L
Cl	1300 mg/L	2000 mg/L
S	.79 mg/L	1 mg/L
BOD5	19 mg/L	30 mg/L
COD	236 mg/L	250 mg/L

3. ILLUSTRATIONS:

3.1 FTIR Analysis:

MPs were observed in all examined individuals, with an average of 7.8 pieces per stomach. Most MPs were fragments (77%, n = 90) as opposed to fibers (23%, n = 27), with translucent/clear (46%) the most prevalent color. Fourier transform infrared (FTIR) spectroscopy revealed polyethylene terephthalate (65%) as the most predominant polymer in fibers, whereas polypropylene (31%) and acrylonitrile butadiene styrene (20%) were more frequently recorded as fragments. Mean fragment and fiber size was 584 μm and 1567 μm respectively. No correlation between total number of MPs and biological parameters (total body length, age, sexual maturity, axillary girth, or blubber thickness) was observed, with similar levels of MPs observed between each of the mass stranding events. Considering MPs are being increasingly linked to a wide. (Karen A. Stockin a, Fourier transform infrared (FTIR) analysis identifies microplastics in stranded common dolphins (Delphinus delphis) from New Zealand waters, December 2021)

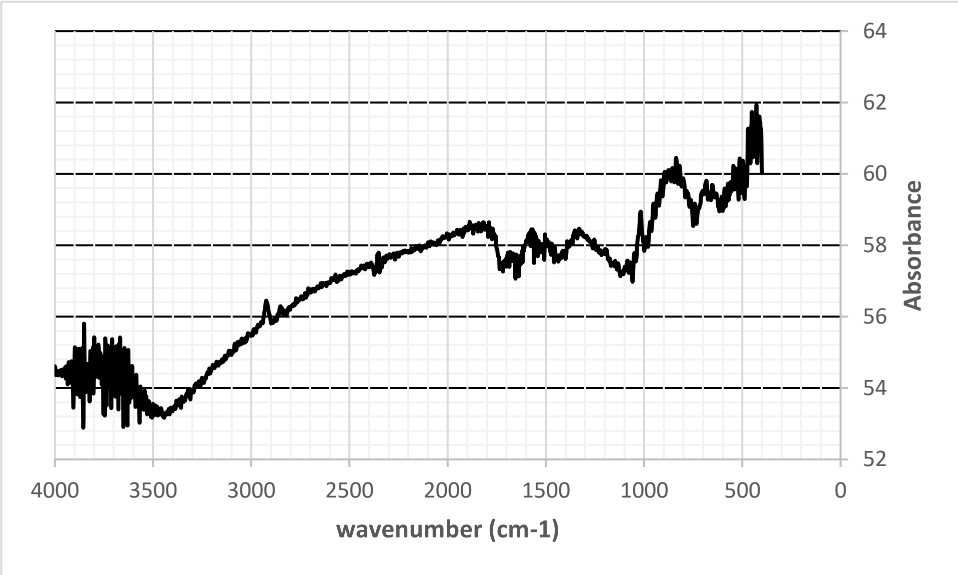
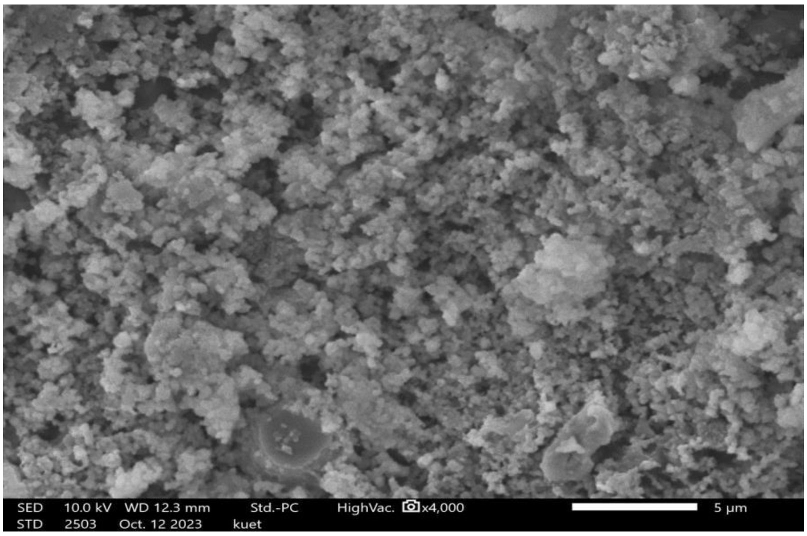


Figure 1: FTIR Analysis of Microplastics (MPs)

3.2 SEM Analysis:

Samples from SAF Leather Industry ltd. Finishing department were collected for an experiment aimed at showcasing the machine's capabilities. Before being put in the SEM, these samples were vacuum-filtered to remove any remaining water. Then, in just two hours and forty minutes, 435 fields measuring 2.75 mm2 each could be analysed using automated particle analysis and EDS to identify and analyse the individual particles. Following the initial analysis, 848 individual particles were found and detected. Each particle's chemistry and size (area and circumference) were then measured. he data below illustrates that most particles discovered had surface areas somewhere between 500 to 5000 μm^2, and the dominant type of plastics was Polyethylene terephthalate (PETE), frequently used in the production of plastic containers for liquids and foods as well as being a common material used in fibres for clothing. The other most-prevalent plastic found in the samples was Polylactic Acid (PLA), a popular bioplastic. Therefore, utilizing SEM incombination with EDS gives rise to an extremely effective tool when it comes to analysing various pollutants, particularly microplastics. Making practical use of automated feature analysis can lead to the development of straightforward and accurate techniques to usher in rapid analysis for the classification of microplastic particles in water samples. (Wei Gao a b, 12 December 2022)

Figure 2: SEM Analysis of Microplastics (MPs)



3.3 Electro-coagulation Separation:

3.3.1. Electrocoagulation treatment:

The microplastics were charged by the electric potential provided by the cathode and anode. The attraction force and repulsive force between the microplastic particles increased as they adjoined, creating floc that will rise to the surface. The negative charge of the microplastic sample is balanced by the positive charge of aluminum, which increases the microplastic particle's attraction and repulsive forces. Eventually, particles attach and the slow mixing caused by stirring results in the formation of floc. Aluminum is a recyclable material that is found in drink cans, scrap metal, and other materials. Following a 30-minute electrocoagulation treatment, the microplastic flocs separate and float on the sample's surface. The metal cations reacted with water and hydroxide ions to form metal hydroxide precipitates. These precipitates had coagulating properties, which means they destabilized particles in the water. (Zhila Honarmandrad, 21 September 2023) The metal hydroxide precipitates, along with the generated hydrogen bubbles, created conditions that lead to the coagulation of microplastic particles. The metal hydroxide precipitates were neutralized the charges on the surface of microplastics, promoting their aggregation into larger flocs. Once the microplastic particles have agglomerated into larger masses, they were more easily separated from the water. This separation occurred through settling, flotation, or filtration processes.The microplastic flocculated more when the pH rose to 7.8. DC power suppliesproduced flocs in two hours, and AC power supplies produced flocs in twenty-five minutes. Verylittle stirring was done in order to increase the floc formation change. Electrocoagulation has been explored as a potential method for removing microplastics from water due to its effectiveness in treating various types of contaminants. However, the efficiency of the process depended on factors such as the type of electrodes used, the initial concentration of microplastics, and the water matrix.

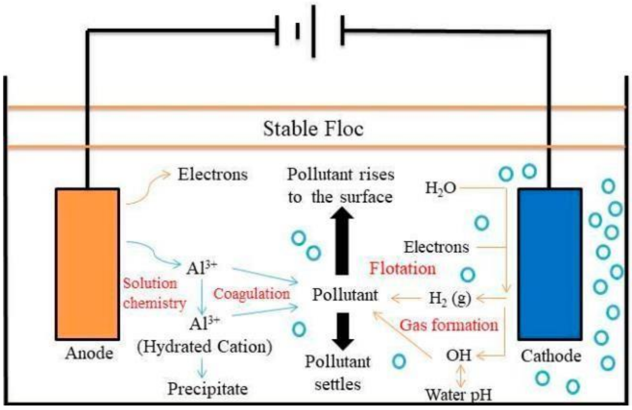


Figure 2: Electro-coagulation treatment

3.3.2. Filtration of Samples:

Filtration was performed with an inox filtration system connected to a vacuum pump, using glassfiber filters with a diameter of 125 µm (GF 6). The 1 L samples were divided into 100 ml, with the tensub-samples passing through individual filters i.e., each 100 ml was placed into the filtration system. Each filter was divided into quadrants and a needle was used to count.

4. CONCLUSIONS

An effective way to address environmental issues is to investigate and remove micro-plastics from wastewater that has been dyed and completed using electrocoagulation. Investigating the efficacy of electrocoagulation as a cutting-edge technique to eliminate microplastics from wastewater, the study produced positive outcomes. A significant environmental concern in the textile & leather industry wasaddressed by the electrocoagulation method, which showed great promise in getting rid of micro- plastics. We have characterized the finishing wastewater through BOD_5, pH, TSS, and other tests by following ECR 2023. The most valued efficiency was gained by 94.3% at pH 7.3. Electrocoagulation can be used for the effective removal of microplastic from the wastewater. During the test, we also annualized the sample through FTIR & SEM. We have got microplastics as Co-polymer and through SEM the EDS described all the characteristics of MPs. As a result, the results highlight the need of electrocoagulation in fostering environmental stewardship and highlighting its potential as a sustainable approach to address micro-plastic pollution in dye-finished effluent. Further tests and experiments can provide the exact result of the percentage of removal of Microplastics in the near future. So we added the process and application of Aluminum as metal which increases the efficiency of the removal of Microplastics.

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