Electro-coagulation of Bio-treated Pharmaceutical Wastewater for RO Pretreatment

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Authors' contributions

This work was carried out in collaboration between both authors. Author AGM designed the study and edited the manuscript. Author JKSP analyzed the data and wrote the original draft of the manuscript. Both authors read and approved the final manuscript.

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ABSTRACT

\textbf{Background:} The advanced wastewater and water treatment by Reverse Osmosis (RO) system have almost become a common treatment option in industries. However, achieving a consistent RO feed water quality and the rigor of RO pre-treatment pose a big challenge for water treatment specialists. Due to the RO critical limiting feed parameters (Silica, Turbidity, BOD, and Total hardness) and the inadequate consideration of the limiting feed parameters in the recycling plant design, the Reverse Plant likely fails due to scaling of membrane and poor productivity. This calls for judicious consideration of an appropriate pre-treatment technology in line with the feed water quality.

\textbf{Objective:} The objective of the work was to study the electro-coagulation treatment of pharmaceutical wastewater with reference to critical RO feed parameters.

\textbf{Materials and Methods:} In this paper, the Electro-coagulation (EC) treatment of Bio-treated pharmaceutical wastewater was explored as a Pre-treatment for the RO system. In the EC reactor of 1m3 working volume, bipolar sacrificial Iron electrodes were used, and RO Critical parameters were examined post electro-coagulation treatment.

\textbf{Results:} Among the 14 RO critical parameters that was investigated, five parameters namely Aluminium as Al, Iron as Fe, Turbidity, Zinc as Zn, and Silica as SiO\textsubscript{2} have registered a reduction range of 80 to 96 \%, in the RO feed water after electro-coagulation. Four other parameters like Manganese as Mn, BOD, Phosphate as P, and Magnesium as Mg have shown a reduction range of 50 to 80\%.

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This enables the plant to be operated at higher efficiency with increased RO recovery. The test parameters before and after the study were subjected to regression analysis and were found to have a statistical significance of one and \( P<0.01 \).

**Conclusion:** EC pre-treatment is applicable for all types of RO (Disc & plate, conventional wound) membranes and enhances the life of the membrane by reducing membrane fouling, maintenance, chemical cleaning, and overall treatment cost.

**Keywords:** Bio-treated pharma effluent; electro-coagulation; iron electrodes; RO critical parameters; RO pre-treatment; silica removal.

1. **INTRODUCTION**

The treatment of high-strength wastewater in the pharma industry is a big challenge. Owing to its high pollution load due to recalcitrant pollutants like [1] organic and inorganic solvents and chemicals [2], salts, oil emulsions [3] and suspended solids [4], pharmaceutical wastewater [5] requires a comprehensive effluent treatment plant to treat and reclaim wastewater. To suit the requirement of wastewater recycling and comply with stringent pollution control standards, Zero Liquid Discharge Facility (ZLDF) has come into place. In a typical pharmaceutical industry Effluent Treatment Plant (ETP), conventional treatment methodologies like physicochemical and biological processes are followed [6-8]. An advanced ZLDF consists of primary, secondary, tertiary, and quaternary/advanced treatment systems processes. Secondary treated or biologically treated water is subjected to tertiary filtration systems followed by advanced treatment units like Reverse Osmosis (RO) and Multiple Effect Evaporator (MEE) in a typical ZLDF. Source segregation of streams facilitates separation of streams based on their characteristics and accordingly the stream is taken for appropriate treatment units in the ZLDF, including the Electrochemical treatment [2].

Of late, RO has become the main treatment system for reclaiming wastewater in most of the industries of various sectors. RO is increasingly used for water and wastewater treatment plants as small, medium, and large scale applications [9].

1.1 **RO Critical Feed Parameters**

In general Silica is observed naturally in the raw water depending on the water source [10] and it exists in reactive silica and colloidal silica. All forms of silica must be removed before treatment and reuse. Some of the familiar methods for silica removal from a waste stream include lime softening, ion exchange and reverse osmosis techniques [11].

Application of Reverse Osmosis technology for the removal of silica is a challenge, as it can potentially damage the RO membrane on account of its abrasive property [12]. This can result in a significant decrease in the treatment efficacy of RO membrane, justifying the need for a pre-treatment regimen to get rid of the constituents that foul membranes [13]. An efficient pre-treatment before RO membrane treatment, helps improve the RO recovery and optimize RO membrane life without expensive replacement.

There are various RO feed water pre-treatment schemes with the combination of Advanced Oxidation Process (AOPs) techniques and filtration methods like sand and activated carbon filtrations[14]. RO plants need high-quality feed water towards an efficient and consistent operation of the RO system [9], hence pre-treatment with electro-coagulation (EC) can be strongly considered as a supplementary pre-treatment technique. This could help especially where the RO feed water is expected to fluctuate for various reasons and seasons. Thereby the desired design productive levels can be achieved on a steady basis, with reduced maintenance and lifetime costs. Hence in this paper, EC treatment of Bio-treated Pharma wastewater and the extent of reduction of RO critical feed parameters were examined using sacrificial Iron electrodes.

2. **MATERIALS AND METHODS**

2.1 **Electro-coagulator Reactor**

The electrocoagulation reactor was made of Polypropylene material with a working volume of 1 m³ including the electrodes. The reactor features and test set up parameters are given in Table 1. Each electrode had a dimension of 600 mm length, 1200 mm breadth with a thickness of...
3mm, and a surface area of 0.72 square meters per plate. The electrodes were arranged in a bipolar model with a combined electrode surface area of 36 square meters. The scum and sludge removal mechanism were facilitated through high retention clarifier and the reactor was equipped with a Polarity change facility. The gap between anode and cathode was kept below 3 mm at a current density of 0.8 A/m².

The number of anodes and cathodes, its dimension, the material of construction, and the type of electrode are tabulated in Table 2.

2.2 Test Sample

Adequate quantity of Treated wastewater after the biological treatment system in a pharmaceutical unit was collected and pumped into the Electro-coagulation reactor for the pre-treatment study.

2.3 Test Condition

The bio-treated wastewater that is proposed for Reverse Osmosis treatment was taken in the reactor and the initial pH was observed to be 7.0. The pre-treatment study was conducted with the optimized current density of 0.8 A/m² at a contact time of 4.8 minutes. The test conditions were arrived based on previous trials.

Three tests were conducted based on the optimized Electro-chemical treatment test condition and the treated wastewater was analyzed for fourteen parameters critical to the RO system.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characteristics of Effluent and Treatment

Based on the aforesaid test conditions, the Electro-coagulation study was conducted with the Iron electrodes and the sample was analyzed for all the basic effluent test parameters in a competent laboratory. The physicochemical characteristics of the Pharma Bio-treated effluent before and after Electrochemical Treatment is shown in Table 3. This table tabulates 24 parameters analyzed before and after the electro-coagulation study period.

| Table 1. Features and test parameters of electro-coagulation reactor |
|---------------------------------------------------------------|
| **Electro coagulation reactor**                              |
| Size (L x W x H)                                              | 1 m³ including electrodes |
| MOC                                                          | PP                        |
| Contact Time                                                 | 5 to 6 minutes             |
| Electrode surface area                                        | 36 m²                     |
| Gap between anode & cathode                                  | < 3 mm                     |
| Scum & Sludge Removal Mechanism                              | HRS Clarifier              |
| Electrode arrangements                                       | Bi-Polar                   |
| Current density                                              | 0.8 A/m²                   |
| Polarity change frequency                                    | Yes                       |

| Table 2. Details of Iron Cathode and Anode used in the Electro-coagulation Reactor |
|-----------------------------------------------------------------------------------|
| **Test electrodes**                                                              |
| **Anode**                                                                        |
| Number of Electrodes                                                             | 25 numbers                |
| Size (L x W x Thick)                                                            | (600mm*1200mm*3mm)        |
| MOC of electrodes                                                               | Mild Steel                |
| Sacrificial/ Non-Sacrificial                                                    | Sacrificial               |
| **Cathode**                                                                     |
| Number of Electrodes                                                             | 25 numbers                |
| Size (L x W x Thick)                                                            | (600mm*1200mm*3mm)        |
| MOC of electrodes                                                               | Mild Steel                |
| Sacrificial / Non-Sacrificial                                                    | Sacrificial               |
Table 3. Characteristics of pharma bio-treated effluent before and after electrochemical treatment

| Sl. No. | Parameters* | Before EC | After EC |
|---------|-------------|-----------|----------|
| 1       | Aluminum as Al | 78.2      | 2.94     |
| 2       | BOD         | 700       | 300      |
| 3       | Calcium as Ca | 16        | 16       |
| 4       | Chloride as Cl | 4342    | 3837     |
| 5       | COD         | 2360      | 1560     |
| 6       | Electrical Conductivity | 21.07   | 21.03    |
| 7       | Iron as Fe  | 66        | 3.19     |
| 8       | Magnesium as Mg | 44       | 22       |
| 9       | Manganese as Mn | 0.89    | 0.21     |
| 10      | NH₃ – N     | 135       | 112      |
| 11      | Oil & Grease | 2         | 2        |
| 12      | Phosphate as P | 7.69    | 3.3      |
| 13      | Potassium as K | 1520   | 1510     |
| 14      | Silica as SiO₂ | 309     | 52       |
| 15      | Sodium as Na | 4930      | 4800     |
| 16      | Sulphate as SO₄ | 7902    | 7610     |
| 17      | TDIS        | 20060     | 20300    |
| 18      | TDS         | 20900     | 20880    |
| 19      | TKN         | 185       | 136      |
| 20      | TOC         | 852       | 608      |
| 21      | Total Alkalinity | 825     | 935      |
| 22      | Total Hardness | 220     | 120      |
| 23      | Turbidity   | 800       | 80       |
| 24      | Zinc as Zn  | 0.2       | 0.03     |

*All units are expressed in mg/l, except conductivity (µmho/cm) and Turbidity (NTU)

The percentage reduction of various physicochemical parameters in the bio-treated wastewater was arranged in descending order towards a better understanding, as manifested in Fig. 1. This figure shows the highest reduction of Aluminium as Al, Iron as Fe and Turbidity sequentially in descending order as 96, 95, and 90% respectively [3]. Further, the table indicates that there was not much impact on TDS, Conductivity, and Calcium. It also shows the negative reduction of Total Dissolved Inorganic Solids (TDIS) and Total Alkalinity, which present an increase of 1 and 13% respectively.

It is observed that three parameters namely Aluminium, Iron, and Turbidity registered more than 90% reduction, another three parameters Zinc, Silica and Manganese showed more than 75% reduction and yet another three parameters BOD, Phosphate, and magnesium showed a reduction of more than 50% after electro-coagulation treatment.

![Percentage Reduction in Descending order](image)

Fig. 1. Descending order of percentage removal of physicochemical parameters after Electrochemical treatment of Pharma bio-treated effluent
3.2 Statistical Significance

The data for the test parameters before and after Electrocoagulation was subjected to regression analysis, to check whether the data set has a statistical significance of one and the p-value of less than 0.01

3.3 RO Critical Parameters

The treated wastewater after three trials were analyzed for fourteen parameters critical to the RO system. The analysis test results of three samples post the electrochemical treatment is given as an average value and the standard deviation based on three trials are tabulated in Table 4.

The percentage reduction of 14 RO critical parameters is shown in the chart in descending order as shown in Fig. 2.

The importance of the RO critical 14 parameters are discussed hereunder.

Five parameters namely Aluminium as Al, Iron as Fe, Turbidity, Zinc as Zn, and Silica as SiO$_2$ have registered a reduction range of 80 to 96 %, in the RO feed water after electro-coagulation [3]. Four other parameters like Manganese as Mn, BOD, Phosphate as P, and Magnesium as Mg have shown a reduction range of 50 to 80%, whereas the reduction for Total Hardness, COD, TOC, and TKN were in the range of 25 to 50%.

Table 4. Table of selective RO Critical Parameters of Pharma bio-treated effluent before and after Electrochemical treatment

| Sl. No. | Parameters*       | Before EC | Average After EC | STD Deviation* |
|---------|-------------------|-----------|------------------|----------------|
| 1       | Aluminum as Al    | 78.2      | 3.3              | 0.57           |
| 2       | BOD               | 700       | 313.3            | 41.63          |
| 3       | COD               | 2360      | 1507             | 61.10          |
| 4       | Iron as Fe        | 66        | 3.1              | 0.21           |
| 5       | Magnesium as Mg   | 44        | 22.7             | 3.06           |
| 6       | Manganese as Mn   | 0.89      | 0.2              | 0.01           |
| 7       | NH$_3$ – N        | 135       | 113.3            | 6.11           |
| 8       | Phosphate as P    | 7.69      | 3.3              | 0.20           |
| 9       | Silica as SiO$_2$ | 309       | 52.0             | 8.00           |
| 10      | TKN               | 185       | 132.0            | 10.58          |
| 11      | TOC               | 852       | 599.3            | 16.77          |
| 12      | Total Hardness    | 220       | 115.3            | 5.03           |
| 13      | Turbidity         | 800       | 79.0             | 3.61           |
| 14      | Zinc as Zn        | 0.2       | 0.03             | 0.00           |

*All units are expressed in mg/l, except Turbidity (NTU); *Standard deviation based on three test results

![Fig. 2. Percentage Reduction of RO Critical Parameters](image)
There is a considerable removal of hardness together with chemical oxygen demand (COD) and turbidity through electro-coagulation which helps in reducing the potential for scaling and fouling of Reverse osmosis membranes and the same has been demonstrated by other researchers as well [15].

The frequency of different ranges of percentage reduction of the critical RO parameters is plotted as a Percentage reduction histogram, as shown in Fig. 3.

The actual value of the critical RO parameters before and after EC was sequentially plotted and is shown in Fig. 4.

To the extent COD, TOC, and BOD levels have reduced, the turbidity in the wastewater has also decreased significantly from 800 to 80 mg/l at a 90% reduction. A literature survey of the Electro-coagulation of oil-emulsions has shown the reduction of turbidity, color, and COD to the extent of 99.5, 96, and 92% respectively [3].

3.4 Silica Removal

Silica content is one of the most important limiting factors in Reverse Osmosis plant design and operation. Silica removal is very difficult in conventional pre-treatment and most of the cases, instead of treating silica with special costly treatment, the RO recovery is compromised based on the input silica level and its scaling potential. In this study, Silica removal was observed to be very much encouraging, reducing from 302 to 52 mg/l (as shown in Table 4) with 83% reduction through electro-coagulation. It was reported that the conventional chemical clarification for silica removal by lime, soda ash, alum and caustic soda [10] has not produced silica removal equivalent to that of the electro-coagulation method. The presence of a high
amount of silica in RO feed water will result in hard deposition of scales [13] which will impair the RO membranes and severely affect the productivity of the RO system [12].

Total Hardness reduction was found to be reduced from 220 to 120 mg/l at 45.45% reduction, which denotes that the scaling tendency of the temporary hardness contributing salts was removed considerably. Increased electrolysis time could still facilitate a further reduction of Total hardness [15].

Conventional filtration systems may not be better, compared to Electro-coagulation pre-treatment on account of the significant level of reduction observed for COD, TOC, Turbidity, and Total hardness observed in Electro-coagulation.

The color of the bio-treated water before EC treatment was brownish which had turned colorless after EC treatment which is attributed to the reduction of turbidity by 90%. The bio-treated water before and after EC treatment is shown in the beaker as Figs. 5 and 6.

Thus the electro-coagulation technique tends to offer a simple and cost efficient approach for the removal of silica, organic compounds and other contaminants from RO feed water to mitigate the fouling process [16]. Compared to the conventional chemical coagulation techniques, the overall expenditure in EC treatment is considerably low, though the major cost is due to electrical power consumption.

With the advent of solar photovoltaic systems, the high consumption of conventional electrical power can be compensated through the supply of renewable solar power to the Electrooxidation units, leading to an environmentally friendly solution.

4. CONCLUSION

The data for the test parameters before and after Electro coagulation was subjected to regression analysis and the data set was observed to be statistically significant (p< 0.01).

This study has demonstrated that electro-coagulation is efficient than conventional pre-treatment methods, with significant removal rates for RO critical physicochemical parameters.

EC pre-treatment is applicable for all types of RO membranes and enhances the life of the membrane by reducing membrane fouling, maintenance, chemical cleaning, and overall treatment cost.

Owing to its potential economic and environmental benefits, this could be a preferred choice for water and wastewater treatment applications in industrial, municipal, and commercial establishments.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.
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