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Electrochemical Treatment of Membrane Cleaning Wastewater in Desalination and Drinking Water Treatment Plants: A Study on Free Chlorine Removal

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ABSTRACT: Chemical cleaning of membranes in desalination and drinking water treatment plants generates wastewater characterized by high concentrations of free chlorine and elevated pH values. This study investigates the potential of electrocoagulation (EC) for the treatment of such effluents, with particular emphasis on the removal of free chlorine and its conversion to chloride ions. Experiments were conducted using synthetic wastewater representative of typical membrane cleaning solutions, employing iron and aluminium electrodes under varying current intensities (5, 10, and 15 A), treatment durations (up to 60 min), and pH conditions. The results demonstrate that EC effectively removes free chlorine, achieving up to 100% removal efficiency, particularly under neutral pH conditions. The conversion of free chlorine to chloride was confirmed by a corresponding increase in Cl^- concentrations. These findings highlight electrocoagulation as a promising and efficient method for the treatment of chlorine-rich membrane cleaning wastewater prior to discharge.

1 INTRODUCTION

The increasing global demand for clean and safe freshwater has led to the widespread adoption of membrane-based technologies in modern water and wastewater treatment facilities. Processes such as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are now essential components of both desalination and drinking water treatment plants. These technologies are highly effective in removing salts, organic pollutants, and microbial contaminants (Anwar et al., 2020). However, membrane systems are particularly vulnerable to fouling caused by organic matter, microbial growth, and inorganic scaling, which significantly reduces membrane permeability and overall operational efficiency (Maeda, 2024; Mahmoud et al., 2023).

To maintain membrane performance and extend service life, frequent cleaning-in-place (CIP) procedures are required. These procedures typically employ chemical cleaning agents such as sodium hypochlorite (NaOCl) for biofouling control and sodium hydroxide (NaOH) for the removal of organic deposits (Ang et al., 2011; Wang et al., 2011). As a result, CIP operations generate large volumes of chemically reactive wastewater characterized by high concentrations of free chlorine, elevated pH values, and strong oxidizing conditions (Saleh et al., 2016). If discharged without appropriate treatment, such effluents may pose serious environmental risks. Free chlorine and its transformation products, including chlorate and chlorite, are toxic to aquatic organisms and can cause persistent ecological damage in receiving water bodies (Deborde et al., 2008; Richardson et al., 2007).

Conventional treatment methods for CIP wastewater include chemical neutralization using reducing agents (e.g., sodium thiosulfate), pH adjustment, and dilution or mixing with municipal wastewater. Although these approaches can be effective, they are often associated with secondary pollution, increased sludge generation, and higher operational costs (Madaeni et al., 2007). Consequently, there is a growing need for alternative treatment strategies that are both efficient and environmentally sustainable.

Electrocoagulation (EC) has emerged as a promising alternative technology for wastewater treatment. This process involves the application of an electric current to sacrificial metal electrodes, typically composed of iron or aluminium. The dissolution of the electrodes releases metal ions, which subsequently hydrolyse in water to form amorphous hydroxide flocs. These flocs remove contaminants through adsorption, destabilisation, complexation, and sweep flocculation mechanisms (Mollah et al., 2004). In addition, electrochemical reactions occurring at the anode and cathode can transform reactive chemical species, including free chlorine, into less harmful forms (Hakizimana et al., 2017; Ammar et al., 2023).

Numerous studies have demonstrated the effectiveness of EC in treating a wide range of wastewaters, including those containing heavy metals, suspended solids, organic pollutants, and disinfection by-products (Chen, 2004; Emamjomeh et al., 2009; Sahu et al., 2014; Tang, 2024). Electrocoagulation has also been applied in membrane-related systems, particularly for pretreatment and fouling control. For instance, in the food industry, the integration of EC with membrane filtration has achieved high removal efficiencies of chemical oxygen demand (COD) and proteins from detergent-rich CIP effluents (Ates et al., 2017). Despite these advances, research focusing specifically on the treatment of chlorine-rich CIP wastewater from drinking water and desalination plants using EC remains limited.

This study investigates the application of electrocoagulation for the treatment of synthetic membrane cleaning wastewater. The model wastewater simulates CIP effluents from a real water treatment plant, with NaOCl concentrations ranging from 0.05% to 0.25%. The primary objective is to evaluate the effectiveness of EC in removing free chlorine from this chemically aggressive wastewater. The influence of key operational parameters—namely current intensity, treatment duration, initial pH, and electrode material—on chlorine removal and overall treatment performance is also examined. In addition, the transformation of free chlorine into chloride ions is assessed. Ultimately, the study aims to determine whether electrocoagulation can serve as a practical and sustainable solution for managing membrane cleaning wastewaters in desalination and drinking water treatment facilities.

2 MATERIALS AND METHODS

2.1 *Experimental set-up*

This study was designed to evaluate the effectiveness of electrocoagulation (EC) in removing free chlorine from synthetic wastewater simulating membrane cleaning effluents generated in a drinking water treatment plant. All experiments were conducted in batch mode using a 10 L Plexiglas EC reactor (Fig. 1), equipped with six horizontally arranged iron (Fe) electrodes (three anodes and three cathodes) connected to a DC power supply. The inter-electrode distance was 1 cm, and the total surface area of each electrode was 9 cm^2. Continuous mixing was provided by an overhead mechanical stirrer to ensure solution homogeneity throughout each experimental run.

Two types of synthetic wastewater were prepared to represent typical membrane cleaning processes. The first solution, hereafter referred to as Solution A, consisted of 0.05% (w/v) NaOCl in tap water and simulated the daily backwashing of ultrafiltration membranes. The second solution, Solution B, contained 0.25% (w/v) NaOCl and 0.1% (w/v) NaOH, representing a more aggressive weekly chemical cleaning procedure. The initial physicochemical properties of the synthetic wastewaters are summarised in Table 1.

Table 1. Physicochemical characteristics of the simulated wastewaters

SOLUTION	pH	TDS, mg/L	Ƙ, µS/cm	Cl_2, mg/L	Cl^-, mg/L
A	8.25	976	1977	276	470
B	11.57	4230	6670	2400	1970

2.2 *EC treatment and analysis*

Electrocoagulation experiments were conducted under three direct current intensities: 5 A, 10 A, and 15 A, as summarised in Table 2. Samples were collected at 10-minute intervals over a total treatment duration of up to 60 minutes. In addition, secondary treatment of the effluent was performed after each experiment using aluminium (Al) electrodes for an additional 10 minutes to evaluate whether a sequential electrode configuration could enhance overall removal performance. In Experiment 7, the initial pH was adjusted to 7 to assess the influence of pH on electrochemical treatment efficiency.

Table 2. Experimental matrix

Run	Solution	Applied current
1	A	5 A
2	A	10 A
3	A	15 A
4	B	5 A
5	B	10 A
6	B	15 A
7	B, pH 7	15 A

The primary parameters monitored throughout the experiments were free chlorine (Cl_2) concentration, chloride (Cl^-) concentration, pH, temperature, electrical conductivity, and total dissolved solids (TDS). Free chlorine and chloride concentrations were determined using Nanocolor® colorimetric test kits in combination with a Nanocolor® 500D photometer. Physicochemical parameters were measured using a multiparameter probe (HI9829, Hanna Instruments).

All experiments were carried out under controlled laboratory conditions, following strict safety protocols, including the use of personal protective equipment and chemical fume extraction. Upon completion of each experiment, all treated solutions were neutralised with sodium thiosulfate ($Na_2S_2O_3$) prior to disposal.

The experimental data were used to calculate the percentage removal of free chlorine and the corresponding increase in chloride concentration as an indicator of chemical conversion. All experiments were performed in triplicate, and mean values were used to determine treatment efficiencies.

3 RESULTS AND DISCUSSION

3.1 *Efficiency of EC treatment*

Electrocoagulation (EC) demonstrated a high capacity for the removal of free chlorine (Cl_2) from synthetic wastewater simulating membrane cleaning effluents. Process efficiency was influenced by current intensity, treatment duration, initial pH, and wastewater composition. The efficiency of each experimental run, expressed as the percentage of free chlorine removed, is summarised in Table 3.

Table 3. Experimental results

Run	Solution	Current density	Treatment time	Efficiency
1	A	18 A/dm^2	50 min	100 %
2	A	37 A/dm^2	30 min	100 %
3	A	55 A/dm^2	20 min	100 %
4	B	18 A/dm^2	60 min	37.6 %
5	B	37 A/dm^2	60 min	79.8 %
6	B	55 A/dm^2	60 min	92.7 %
7	B , pH 7	55 A/dm^2	50 min	99.9 %

In experiments using the low-strength NaOCl solution (Solution A, 0.05%), free chlorine removal was rapid and nearly complete across all current intensities tested. At 5 A, more than 99% of Cl_2 was removed within 60 minutes, with concentrations decreasing from 276 to 0 mg L^{-1}, accompanied by a corresponding increase in chloride (Cl^-) from 470 to 550 mg L^{-1}. This indicates that electrochemical reduction of Cl_2 to Cl^- was the dominant removal mechanism, likely occurring at the cathode via electron transfer reactions.

Increasing the applied current intensity to 10 A and 15 A resulted in significantly faster chlorine removal. Complete removal was achieved in less than 30 minutes at 10 A and in less than 20 minutes at 15 A (Fig. 2), consistent with enhanced anodic dissolution and increased generation of coagulant species at higher current densities.

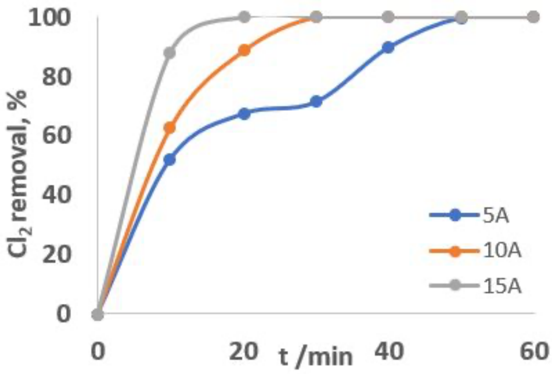

Figure 2. Efficiency of the EC process for experiments 1–3.

For the high-strength cleaning solution (Solution B, 0.25% NaOCl + 0.1% NaOH), initial free chlorine concentrations were substantially higher, reaching approximately 2400 mg L^{-1}. Under these conditions, chlorine removal was more challenging due to the strongly alkaline environment (pH > 11.5). In Experiment 6 (15 A, no pH adjustment), Cl_2 removal reached 92.7% after 60 minutes. However, when the initial pH was adjusted to neutral conditions, nearly complete chlorine removal was achieved within the same treatment duration (Fig. 3.).

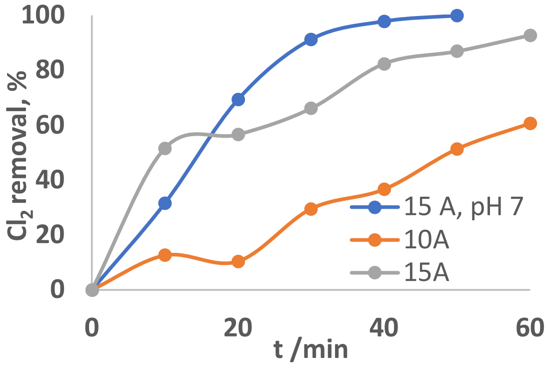

Figure 3. Efficiency of the EC process for experiments 5–7.

Under otherwise identical operating conditions (15 A, 10 L reactor volume, Fe electrodes), adjusting the initial pH to 7 resulted in a reduction of Cl_2 concentration from 2400 to 1.6 mg L^{-1}, corresponding to a removal efficiency of 99.93%. At neutral pH, metal hydroxide flocs exhibit enhanced destabilisation capacity, and electrochemical reduction reactions are thermodynamically more favourable. These findings are consistent with previous studies reporting improved EC performance under near-neutral pH conditions, owing to optimal coagulant speciation and surface charge characteristics (Mollah et al., 2004; Hakizimana et al., 2017).

3.2 *The mechanism of Cl_2 removal*

The removal of free chlorine during electrocoagulation (EC) is primarily governed by electrochemical reduction and associated chemical transformations occurring at the cathode surface. In aqueous solution, chlorine exists predominantly as hypochlorous acid (HOCl) and hypochlorite ions (ClO^-), with their relative proportions depending on the pH. Under near-neutral to alkaline conditions, ClO^- is the dominant species.

During EC, cathodic reactions facilitate the reduction of ClO^- to chloride ions (Cl^-). This reductive pathway is enhanced by increasing current density and extending reaction time, both of which increase the electron flux available at the cathode. In addition to electrochemical reduction, chlorine species may also be removed through adsorption onto in situ generated metal hydroxide flocs, such as $Fe(OH)_3$ or $Al(OH)_3$. This mechanism is particularly relevant under conditions that promote strong electrostatic interactions or sweep flocculation. Although adsorption is generally considered a secondary removal pathway, it may contribute significantly under specific conditions, such as elevated pH or excessive coagulant generation.

Importantly, the conversion of reactive and potentially hazardous chlorine species (e.g., Cl_2 and ClO^-) into chloride ions (Cl^-), which are considerably less toxic and more environmentally benign, highlights the suitability of EC for treating oxidative membrane cleaning wastewater. This reductive transformation is especially advantageous in preventing the formation of harmful disinfection by-products (DBPs) in downstream receiving waters.

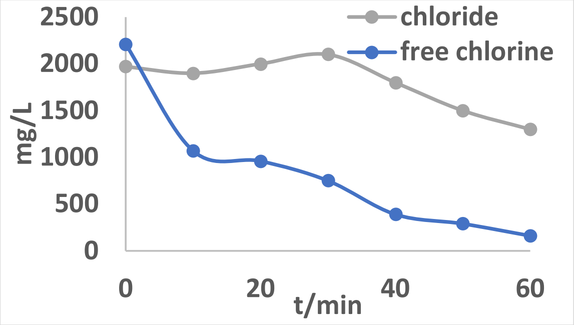

Figure 4. Changes in chloride and free chlorine concentrations during experiment 6

In all experiments, an increase in chloride ion concentration was observed, confirming the conversion of chlorine species to Cl^-. However, in some cases, as illustrated in Fig. 4, the chloride concentration began to decrease after reaching a maximum. This behaviour may be attributed to the entrapment or co-precipitation of Cl^- within the forming $Fe(OH)_3$ flocs.

This hypothesis is supported by previous studies reporting significant chloride removal during EC treatment of saline and industrial wastewaters. Wang et al. (2023) demonstrated that EC using aluminum electrodes can reduce chloride concentrations to below 250 ppm through mechanisms involving co-precipitation and electrostatic adsorption onto aluminum hydroxide flocs. They also reported that operational parameters, such as current density, electrode spacing, and the presence of competing ions, play a critical role in determining removal efficiency. Similarly, Al Raad et al. (2019) achieved up to 93% chloride removal from saline lake water using aluminum electrodes at a current density of 2 mA cm^{-2}, a reaction time of 80 minutes, and a pH of 8.

3.3 *Secondary treatment with Al electrodes*

After 60 minutes of primary electrocoagulation (EC) treatment using Fe electrodes, a secondary treatment step employing Al electrodes was performed to evaluate potential improvements in residual chlorine removal and overall water quality. The results indicate that post-treatment with Al electrodes did not result in a substantial additional removal of free chlorine, as chlorine concentrations were already close to or below the detection limit following Fe-based electrocoagulation.

Nevertheless, slight reductions in chloride concentrations were observed in some cases. This behaviour may indicate limited adsorption of chloride ions onto freshly formed $Al(OH)_3$ flocs or minor co-precipitation effects. In addition, the pH remained stable or exhibited a slight decrease during the aluminum treatment phase, likely due to the buffering effect associated with aluminum hydrolysis reactions.

Although no significant improvements in chlorine-related parameters were observed, aluminum post-treatment may offer benefits in practical applications involving real wastewaters, where additional removal of turbidity, residual organic matter, or colour is required. Further research is therefore needed to assess the full potential of sequential Fe–Al electrocoagulation in more complex matrices, particularly in wastewaters containing natural organic matter or disinfection by-products.

3.4 *Potential formation of disinfection by-products*

Although the present study focused on the removal of free chlorine, the potential formation of disinfection by-products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), chlorates, and chlorites, remains an important consideration when treating chlorinated effluents. DBPs are typically formed through reactions between chlorine and natural organic matter (NOM), bromide, or ammonia—constituents commonly present in natural waters and membrane backwash streams (Richardson et al., 2007).

In this study, however, synthetic wastewater composed of NaOCl solutions prepared in tap water was used, without the addition of organic or nitrogenous compounds. Consequently, DBP formation was neither expected nor observed, and DBP-specific analyses were not performed. This approach is consistent with the characteristics of the real wastewater represented in this case study, as chemical analyses of treated samples indicated negligible organic content.

Nevertheless, the application of electrocoagulation to real membrane cleaning effluents—particularly those derived from brackish or surface water sources with elevated NOM or bromide concentrations—may lead to DBP formation prior to or during treatment. Future studies should therefore include systematic monitoring of relevant DBPs to fully assess the environmental safety and regulatory compliance of treated effluents, as well as to evaluate the potential role of electrocoagulation in mitigating or removing such by-products.

4 CONCLUSIONS

The results of this study demonstrate that electrocoagulation is an effective technology for the removal of free chlorine from membrane cleaning wastewater, particularly when the solution pH is adjusted to near-neutral values and appropriate current densities are applied. The consistent increase in chloride concentrations provides direct evidence of redox transformation, confirming the conversion of toxic free chlorine into less harmful chloride ions and thereby reducing the potential for disinfection by-product formation.

These findings highlight electrocoagulation as a promising alternative to conventional chemical neutralization methods for managing oxidative residues in desalination and drinking water treatment facilities. Future work should focus on the application of this approach to real wastewater streams and on its integration with complementary treatment processes to ensure full compliance with discharge regulations and environmental protection requirements.

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