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Research Article

Performance evaluation of a simple electrochemical treatment model for saline wastewaters: Part A

Justinah Solayide AMOKO[1], Ezekiel Oluwaseun FEHINTOLA[1], Enoch Adedayo ADEKUNBI[1], Lasisi GBADAMOSI[1], Babatunde Moses OJO[1], Abidemi Iyewumi DEMEHIN[1], John Olugbemiga AWOTUNDE[1], Isaiah Adesola OKE[*2]

[1]Department of Chemistry, Adeyemi Federal University of Education, Ondo, Nigeria
[2]Department of Civil Engineering, Obafemi Awolowo University, Osun, Nigeria

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ABSTRACT

This paper examined the efficacies of the electrochemical treatment (E_{tt}) technique in the reduction of chloride ion (Cl^-) from saline (salty) wastewaters (brine). Saline wastewaters (Sw) concentrations between 10 g/l and 40 g/l of Cl^- were prepared and subjected to E_{tt} utilising a locally developed composite carbon–resin (as the anode) and aluminium (as the cathode) electrodes. E_{tt} of the simulated brine was conducted on a laboratory scale. The influence of selected factors on the efficacy of the E_{tt} process was monitored utilising fractional factorial experiments. These selected factors were optimized using steepest descent technique (between the minimum and maximum concentrations) and rate change of Cl^- removal efficacy through Microsoft Excel Solver. The optimum values of these selected factors were used to purify typical raw saline water. Efficacies of the E_{tt} process in removing Cl^- from the typical raw saline water was utilised to predict efficacy of the system using typical Cl^- concentration in seawater based on literature, previous and published studies. The study revealed the relationship between chloride removal efficacy (%), initial concentration of chloride, current through the wastewater and separation distance between the electrodes were best in the form of exponentials with coefficient of determination of 0.979, 0.920 and 0.977, respectively. The optimum values of these selected factors such as current, pH, treatment period and separation distance between the electrode (centre to centre of the electrode) were 10.5 A equivalent to 0.795 A cm-2, 6.7, 2.75 hr and 42 mm, respectively. It was concluded that E_{tt} with composite carbon-resin electrodes is among effective tools for removing Cl^- from saline wastewater during E_{tt}. The performance of the treatment technique was between 68.52 and 94.82 %.

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INTRODUCTION

Overall water available on the Earth as a planet has been estimated to be equivalent to 1400×10^6 km^3 [1]. This amount of water on the planet comprises 97 percent of salty water which is filled with a high concentration of salt and other minerals. This indicates that 97 percent of the earth's water is not potable. Out of the total remaining volume of water, 2 percent of the earth's water is glacier ice at the North and South Poles, which are not accessible and usable [1]. It has been reported that fewer than 1 percent of Earth's water is freshwater, which is accessible for human uses (drinking, transportation, heating and cooling, industry, and many other purposes) [2]. With a critical knowledge that water

***Corresponding author.**
*E-mail address: okeia@hotmail.com

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is among the primary life force which sustain all the living animals and plants [3], it is important to protect the quality of water. It is well established that sources of typical water (ground and surface) are facing critical deterioration in qualities due to various activities of man such as industrialization, agricultural practices, urbanization, and the relentless expansion of population [3]. This critical deterioration in qualities is aggravated by environmental adjustments and geological moves. Documents and researches have been revealed that aquatic environments are daily threatened by releasing large amounts of synthetic pollutants and industrial chemicals such as arsenic compounds [4], ionizable aromatic pollutants [5], arsenic and chloride contained materials [6, 7], zinc oxide nanocomposites [8], cationic and anionic dyes [9], ciprofloxacin antibiotic [10], tannery industry, and pharmaceuticals such as cefazolin antibiotic and personal care products [11], Bisphenol A, nonylphenols, benzophenones, and benzotriazoles [12]. Among the mentioned pollutants, Cl^-, which is widely utilised as a preservative and stabilizer or antioxidant for many types of plastics (polyvinyl chloride), must be removed from the environment such as water to make it potable [13]. Brine and saline water can be toxic and harmful to the aquatic animals and environment due to the presence of high salinity and other chemical substances [14], which indicates that these type of water and wastewater must be treated. Saline water or brine treatments using adsorption, electrochemical, membrane and electrodialysis are most promising alternatives to seawater treatments and brine disposal. These treatments techniques give an output that reduce the environmental pollution materials and environmental friendly, production of freshwater with extraordinary recovery and minimization of solid or liquid wastes volume [14].

In summary, electrochemical, ion-exchange, reverse osmosis membrane, distillation, adsorption and electrodialysis processes have been identified to be effective for the reduction of Cl^-, but some of these processes such as reverse osmosis membrane, distillation and ion-exchange are not cost-effective treatment processes and produce secondary wastes [4–9]. Some of these conventional treatment processes for the reduction of Cl^- from water and industrial wastewaters have other critical disadvantages [8–11]. Application of the adsorption process only transfers the target pollutant from the liquid phase to the solid phase such as nanoclay [15]; pretreated dried activated sludge [16] and other adsorbents [17]. Over the past few decades, electrochemical treatment technology has attracted great attention among many researchers as an advanced and emerging treatment technology for water and wastewater treatment [18]. Figure 1 presents publications on electrochemical treatment techniques in selected countries between 1977 and 2022. Electrochemical treatment techniques are electrical and voltage-driven technologies that have been utilised successful in saline water and brine desalination [19–167]. The treatment technique is based on the selective transportation of ions in aqueous solutions or electrolyte and utilises an applied electrical voltage gradient, difference, or slope

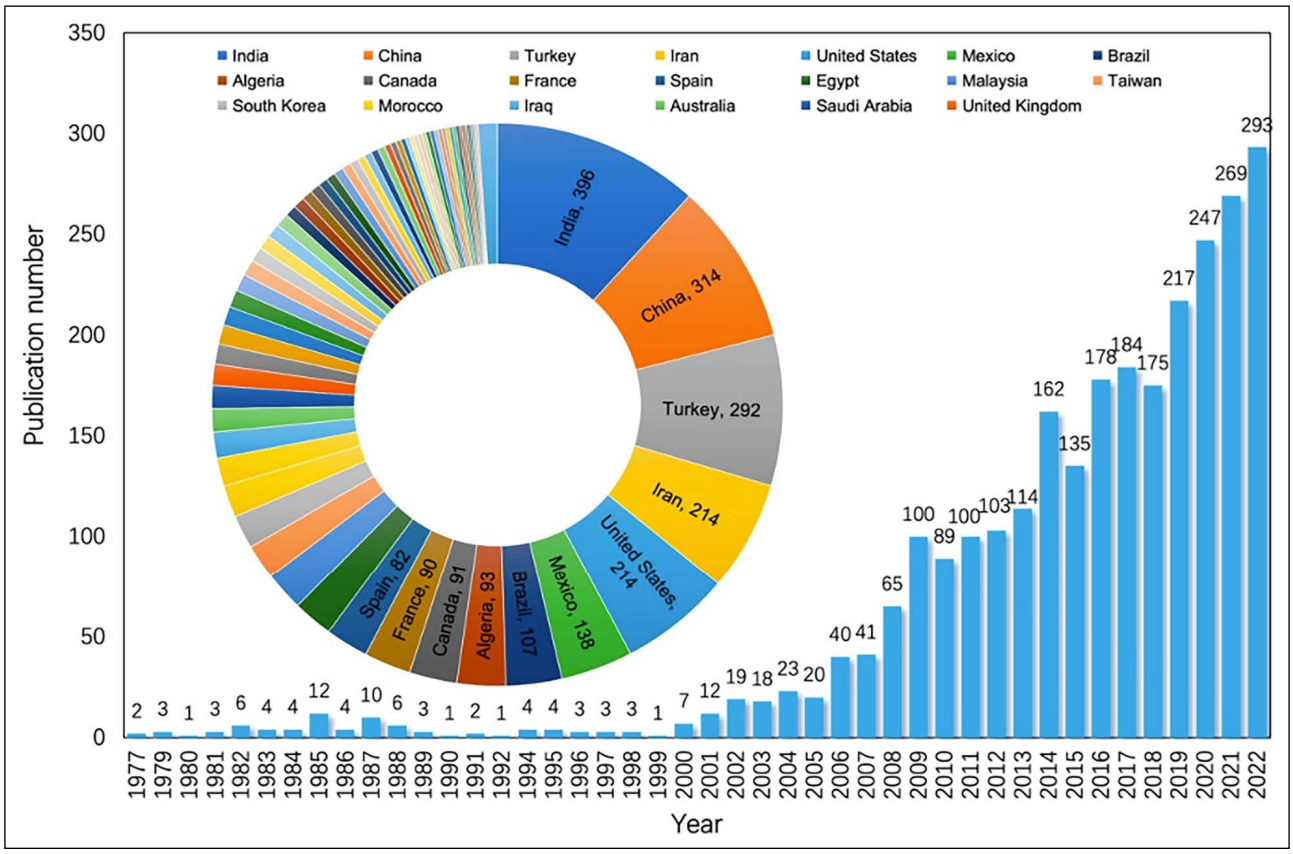

Figure 1. Publications on electrochemical treatment technique from selected countries between 1977 and 2022 (Source: Luciano et al. [131]).

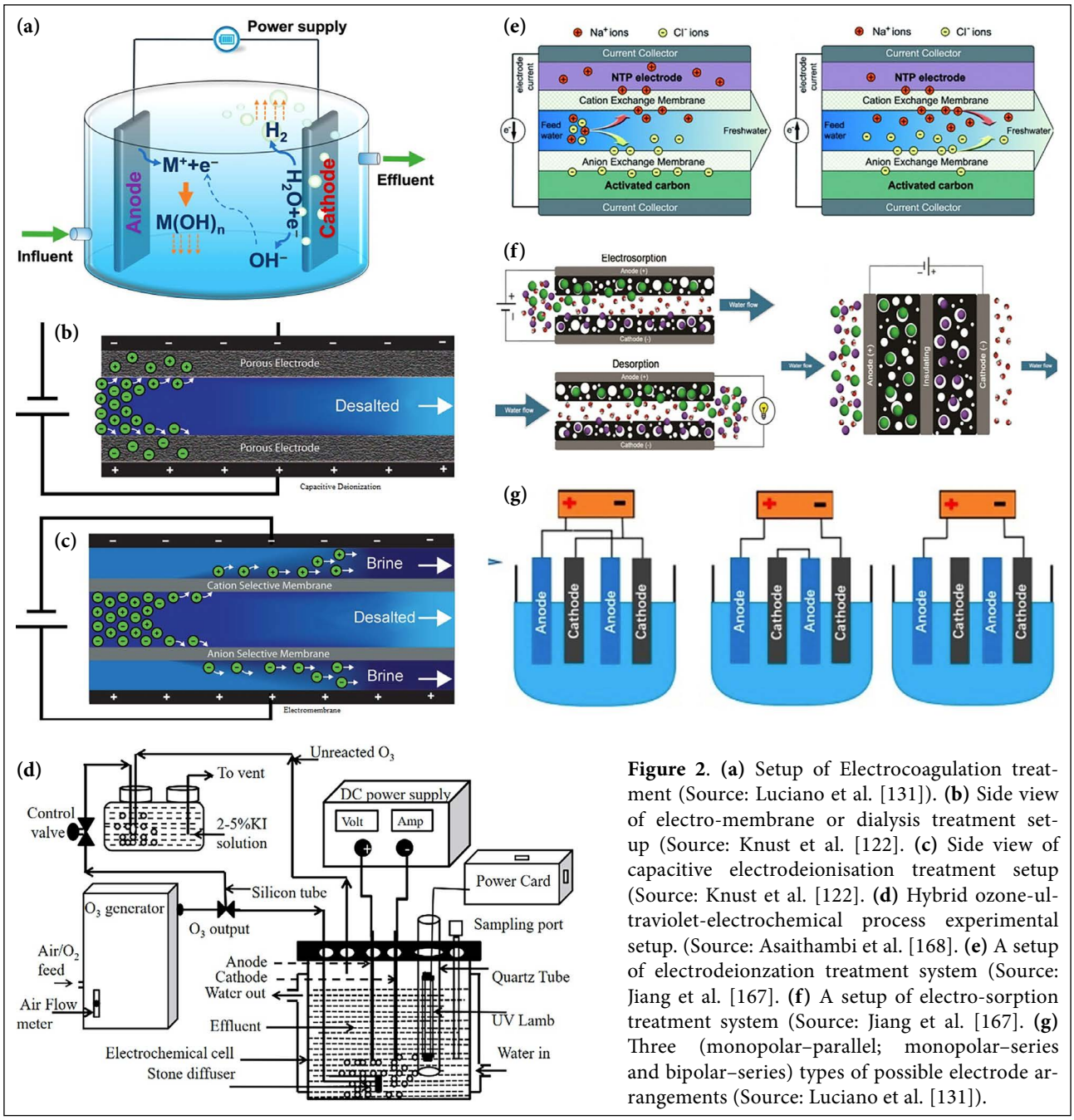

Figure 2. **(a)** Setup of Electrocoagulation treatment (Source: Luciano et al. [131]). **(b)** Side view of electro-membrane or dialysis treatment setup (Source: Knust et al. [122]. **(c)** Side view of capacitive electrodeionisation treatment setup (Source: Knust et al. [122]. **(d)** Hybrid ozone-ultraviolet-electrochemical process experimental setup. (Source: Asaithambi et al. [168]. **(e)** A setup of electrodeionzation treatment system (Source: Jiang et al. [167]. **(f)** A setup of electro-sorption treatment system (Source: Jiang et al. [167]. **(g)** Three (monopolar–parallel; monopolar–series and bipolar–series) types of possible electrode arrangements (Source: Luciano et al. [131]).

to drive anions and cations in opposite directions to the electrode. E_{tt} uses electric current and electrodes to neutralize and aggregate pollutants and contaminants in water and wastewaters [18–21]. Although, Advanced Oxidation Processes (AOPs) are also highly effective for degrading recalcitrant organic pollutants in water and wastewater treatment, E_{tt} processes are adaptable and can be tailored to various types of water and wastewater, addressing specific treatment needs to meet regulatory requirements [21–41, 112]. E_{tt} often complement traditional treatment methods, enhancing overall system performance [41–62]. E_{tt} is relatively inexpensive due to its lower equipment and maintenance costs and because no additional chemicals are required [131].The category and treatment of water and wastewater using E_{tt}, are controlled by several factors, which include nature, and size of reactive species to be generated in E_{tt} processes the type of the treatment technique, electrode or electro catalyst materials, water or wastewater composition, water or wastewater pH settings, and operational constraints [19–170]. E_{tt} can be inform of any of these treatment techniques [19–167]:

i. **Electrocoagulation:** This process uses electric current to dissolve metal electrodes, which produces coagulants in situ that neutralizes and aggregates the contaminants. Wide range of pollutants can be reduced and removed from wastewater using this technique. These pollutants are usually negatively charged such as microorganisms, inorganic colloidal particles, cyanobacteria, organic bacteria and clay [36–58]. Figure 2a presents a typical setup for electrocoagulation.

ii. **Electrooxidation:** The process allows the passage of electric current and a chemical reaction in which an atom or a molecule losses electron or electrons. At the anode (made of the catalytic material needed for conversion) the movement of electrons or molecules allows for oxidation of the pollutants. These oxidation processes can be anodic oxidation where pollutants are oxidized directly on the electrode or indirect oxidation by generation of oxidizing species or agents. The principle of the process can be in the form of [39–71]:

   a. **Anodic Oxidation:** It is possible at low potential differences. The main set back of the process is that the process allows deposition of polymeric layer on the surface of anode, which reduces electrical conductivity.

   b. **Indirect Oxidation:** In this process there is no direct electrons transfer between the anode and the organic matter, which prevents the fouling of anode due to organic particulate.

The process is based on the principle that oxidization of pollutants is conducted in the aqueous solution through oxidizing agents [39–71].

iii. **Electro-flotation:** The process uses electrolytically generated gas bubbles, which are typically hydrogen and oxygen to float and separate suspended solids or particles. It is a gravity separation process. The process is cost effective process for the separation of many inorganic and organic pollutants. The process removes hydrophobic ions from aqueous solutions [79–88].

iv. **Electrodialysis:** This technique utilises ion exchange membrane for the separation of pollutants and electrolytes from the wastewater and water. The process uses an electric field to drive ions through selective membranes, thus separate the pollutants from wastewater and water. It is based on the principle of potential gradient technique or method. It helps to select the ions to pass through the membranes. The main requirement for the process is direct current and ion exchange membranes (anion exchange membrane and the other is cation exchange membrane). The selection of the membrane is based on the function and the purpose of usage [104–145]. Figure 2b shows an arrangement of electrodialysis treatment process.

v. **Electrochemical Advanced Oxidation Processes:** Electrochemical Advanced Oxidation Processes is a combination of electrochemical methods and advanced oxidation processes to generate highly reactive species that degrade pollutants [46–51].

vi. **Electrochemical Reduction:** The process involves reduction reactions at the cathode to remove pollutants or convert pollutants into less harmful substances. [29–35]. In this process one or more electron of an atom or molecule is deposited on the surface of the cathode due to passage of electric current in the electrochemical system. Electrochemical reduction can be used for removal of organic and heavy metals such as Pb, Hg, and similar metals. The system is cost effective, but the process efficiency is very sensitive to wastewater composition or ingredients.

vii. **Electrochemical Desalination or Capacitive Deionization:** The process uses electrochemical techniques or methods to remove salts from water, either through capacitive deionization or through other electrochemical means. It uses direct current power source. In the process current passes through saline water. The ions in the solution are absorbed at cathode and anode. Finally, the ions are de-absorbed form electrodes. This technique is use for the purification of saline water and brackish desalination [24–29]. Figure 2c presents typical arrangement of capacitive deionization systems.

viii. **Electrochemical Peroxidation:** This process is combination of electrochemical oxidation and hydrogen peroxide generation in the process to enhance treatment efficacy [31–35].

ix. **Electrochemical Disinfection:** The process utilises electrochemical techniques to incapacitate microorganisms in wastewater and water. The process is more efficient method than the conventional chemical disinfection techniques or method. The technique works on the principle of the anodic generation of strong oxidizing agents such as O_2, O_3, and hypochlorite during water electrolysis [56]. Categories of electro-disinfection are as follows:

   a. **Electro-disinfection using oxygen gas:** The technique involves formation of anodic oxygen that has capacity of killing germs to some extent. It is usually recommended for the removal odour of water.

   b. **Electro disinfection using chlorine gas and hypochlorite ions:** The process involves activated chlorine for killing the bacteria, fungi, and spores.

   c. **Electro disinfection using O_3:** The technique has high oxidation potential and diffusion through the cell walls of microorganisms [20–35].

x. **Photoelectrochemical Treatment:** This technique combines photocatalysis and electrochemistry for pollutant degradation using light and electrochemical reactions [24–35]. Figure 2d shows the arrangement of photoelectrochemical treatment system.

xi. **Electrochemical Membrane or Electro-Filtration Processes:** This process integrates electrochemical methods with membrane filtration to enhance separation and degradation of contaminants. It is used for the removal of solid suspended particles. This is upgraded by using an electrical field across it for removal of dissolved organic carbon [16–30].

xii. **Electrodeionzation:** This method mainly utilises semipermeable membranes and ion exchange method for wastewater and water purification. The technique has specific semipermeable membranes that allow electrically charged ions to pass through. It is used for high purity of water [130–131]. Figure 2e show a setup of electrodeionzation treatment system.

xiii. **Electro Floto coagulation:** This technique is combination of electrical charges, gas flotations and coagulation process. It is especially deals with the particle size [69–71].

xiv. **Photo Electro Catalysis:** It is a process in which catalyst and light are utilized for the acceleration of the chemical reaction. Catalyst activities are accelerated by utilising light irradiation or solar. The technique efficiently treats wastewater and water containing inorganic ions, organic compounds reduction and for disinfection. The process is based on the principle of photoexcitation. Degradations of organic compounds by this technique are due to simultaneous actions of light and potential difference between the electrodes during the treatment time [130–131].

xv. **Son electro Catalysis:** In this, techniques sound waves having frequency 20kHz to 10^6kHz utilised for treatment of wastewater and water through the series of compression and rarefaction cycles, causing the pressure zone in the medium. One of the key set back of this technique is the polarization and passivation of electrodes due to the reduced mass transfer. In the process gas accumulate at electrode, which resulted in depletion of pollutants to the surface of electrodes boundary layer (Due to polarization). Accumulation of reactants at electrodes critically result in poor efficiency (Passivation) [134–145].

xvi. **Electro-Fenton Process:** The process involves electrochemistry and Fenton reaction. It is an advance oxidation process, which is based on radical reactions. The process has been used for the removal of organic pollutants such as pesticides, pharmaceuticals, phenol, dyes, and phenolic compounds. Electro-Fenton process can be carried out in the cells that can be divided by cation exchange membrane or by not dividing the cell with membrane [51].

xvii. **Electro-sorption:** The process involves combination of electrochemical and adsorption processes. In the process, the electrodes are passive in nature and particles from the electrodes or electrode's surface act as an adsorbent to adsorb the adsorbates which are the pollutants. [150–167]. Figure 2f show a setup of electro-sorption treatment system.

In electrochemical treatment of water and wastewater, electrodes play a critical role in driving electrochemical reactions and end-products. Selection of electrode significantly influences the performance and efficiency, operational cost, longevity and durability of the treatment process [102–170]. Literature listed some of the main categories of electrodes (passive and active or sacrificial) in use as follows: graphite; titanium; titanium coated with mixed metal oxides; Boron-Doped Diamond; stainless steel; Platinum-Coated; Iron and Aluminum Electrodes; Carbon Felt and Carbon Cloth Electrodes; Lead Dioxide (PbO_2) Electrodes, Nickel and Nickel-Based, Zinc and Zinc-Based, and Polymer Composite Electrodes. There are three types of electrode arrangements (Fig. 2g) for electrochemical cells: monopolar–parallel, monopolar–series, and bipolar–series [1–95, 131].

Criteria and factors for the selection of any electrode during the treatment processes are as follows [1–170]:

a) Electrode Material: Must be conductive and compatible with the specific treatment process.

b) Durability, effectiveness and Corrosion Resistance: Important for longevity and cost-effectiveness.

c) Initial and operational Costs: Balance between performance and budget.

d) Electrocatalytic Activity: Determines efficiency in generating desired radicals or intermediates

e) Environmental Impact: Toxicity and disposal considerations.

With reference to the urgent needs for sustainable development goals, based on relationship between economy, environment, society and poverty eradication [171], sustainable water and wastewater management, the importance and performance of E_{tt} techniques in removing pollutants from aqueous solutions, there is a critical need to further evaluate the efficacy of E_{tt} in reducing Cl^- from salty water, which is common as sea water. The main objectives of the current study are to evaluate the efficacy of E_{tt} process (utilising carbon– resin and aluminium electrodes) in removing Cl^- from salty (saline) water, optimise selected operational factors, utilising the optimum values of the selected operational factors for the treatment typical raw saline wastewaters with critical focus on Cl^- removal and simulate the treatment performance.

MATERIALS AND METHODS

All chemicals and reagents used in this research study had a chemical purity of 95% or above. Distilled water was used in the preparations of primary and secondary standard solutions. All equipment used in the experiments were calibrated and the coefficient of determinations of these calibrations (relationship between expected and obtained values) were 96 % or above. This section is breakdown as follows:

a. **Materials:** Development and properties of fabricated composite Carbon (graphite) - Resin electrodes. Carbon (graphite) - resin electrodes were prepared, developed and established from wasted dry cells (dry cells were used based on availability as household solid waste at no additional cost). The discarded dry cells (D R_{20} UM_{-1}) were collected from different dumpsite locations in Nigeria. These collected cells were segmented and carbon (graphite) were removed from these cells, crushed and powdered. Powdered carbon was separated into different particle sizes using British Standard particle sizes. A fixed amount by weight of the powdered carbon was mixed with resin (organic binder), and moulded into 25- millimetre diameter, 100-millimetre long electrode using a fabricated extruder and plunger, and a compaction machine. Microstructures

and Energy Dispersive Spectroscopy of the developed Carbon-resin electrode were monitored to ascertain the composition of the electrode using a scanning electron microscope (Carl Zeiss Smart Evo 10 of secondary electron imaging detector, system vacuum of 89e06Torr and WD of 9.14mm at different magnification). Details of the preparation, development, physical and chemical properties of the electrodes were documented in previous studies such as Oke [172, 173]; Oke et al. [174–176]; Oke et al. [177]; Oke et al. [178]; Oke [179], Oke et al. [180]; Oke and Ogedengbe [181]; Olayanju et al. [182] and Oke et al. [183].

b. **Design and Development of Electrochemical Facility (Electrolysing Equipment):** Electrolysing equipment was designed and developed from local materials to convert alternating current to direct current [184]. The design, development, fabrication procedure, performance and properties of the device are as presented in previous publications such as Oke [172] and Oke and Ogedengbe [185].

c. **Preparation of Synthetic Saline Wastewater:** Analytical Sodium Chloride (60.0 grams) was dissolved in 1000 ml of distilled water as a stock solution and working salty wastewaters were prepared from the stock. The synthesised chloride wastewaters (between 10 g/l and 40 g/l) were prepared utilising procedures and methods specified in the Standard Methods for Water and Wastewater Examination such as APHA [186] and Van Loosdrecht et al. [187].

d. **Laboratory Setup and Electrochemical Treatment of synthesised chloride wastewaters (Desalination Experiments):** Salty wastewaters were subjected to E_{tt} utilising developed carbon–resin (anode) and aluminium (cathode) electrodes in a 2000 ml reactor. electro-coagulation and electro-oxidation based on two types of electrodes (aluminum and graphite) The choice of electrode impacts the effectiveness of water and wastewater treatment systems, influencing operational costs, treatment efficiency, and system durability. Fehintola et al. [188] presents the laboratory setup of the E_{tt} of the simulated wastewaters.

e. **Experimental Study of Operational Factors that affects the performance of Electrochemical:** The influence of selected factors (separation distance between the electrodes, volume of the wastewater used, applied current, flow rate, pH, depth of the electrode, initial concentration of the Cl^- and contact surface area of the electrode used) on the efficacy of E_{tt} process were monitored utilising fractional factorial experiment and optimised utilising combination of steepest and Microsoft Excel Solver techniques. Fehintola et al. [188] presents the standard fractional factorial experiments and the factors. The selection of the Microsoft Excel Solver was based on the availability of the software at no additional cost (available in all Microsoft Excel packages). Solver is an Add-in for the Microsoft Excel packages which are typically not enabled during the initial installation of Microsoft Office (Excel). The procedures required in using Microsoft Excel Solver can be summarized as indicated in Fehintola et al. [188]. The choice of these factors to be studied was based on the theoretical data about several factors that determine the performance of an electrochemical treatment process and the knowledge concerning carbon-resin and aluminium electrodes [102–170].

f. **Analysis of Chloride concentrations and Computation:** Chloride determinations in both raw and treated brine were conducted utilising the argenotometric method specified in APHA [186]. Chloride concentration was calculated using equation (1) as follows:

$$CI^-(mg/l)=35450\left(\frac{(A-B)N_0P_1}{V_S}\right)C_f \quad (1)$$

Where; N_0 stands for normality of Silver Nitrate used, P1 stands for dilution factor; Vs stands for volume of sample used (ml), A stands for volume of the titrate used for the sample (ml), Cf stands for calibration factor and B stands for volume of the titrate used for the blank (ml). Efficiencies of the process were based mainly on pollutant (chloride) removal (Y,%), which was computed using equation (2). The choice of the argenotometric and instrumentation methods was based on accuracy, type of wastewater (clear aqueous solution) and availability of required reagents.

$$Y=100\left(\frac{(C_0-C_t)}{C_0}\right) \quad (2)$$

Where: C_o stands for initial chloride concentration of the synthetic wastewater (mg/l). Ct stands for final chloride concentration of the synthetic wastewater (mg/l) and Y stands for chloride removed (%) at optimum values of the selected operational factors. These selected operational factors were optimised using steepest descent and rate change in the efficacy of the technique. Optimum values of the selected operational factors were utilised to purify typical raw saline water. The efficacies of the system with typical raw saline water were utilised to simulate efficacy and performance in typical seawater with chloride concentration of 31000 mg/l with reference to Akindahunsi et al. [189]; 35.3779 g/l of chloride ion based on Thabit et al. [190]; 41.80 g/l based on Mehan-Martes and Mertel et al. [191] and 43.6995 g/l of chloride ions based on Lior and Kim [192]. Figure 3 presents the flow chart of the procedures used in the utilization of Microsoft Excel Solver.

RESULTS AND DISCUSSION

Results from this study are presented as follows:

a) Development, Properties, and Stability of the electrodes

The study established that electrical resistance per unit length, density and stability of composite carbon-resin electrode are functions of the following factors particle size, compressive pressure and percentage composition of the binder. Density of the electrode increased from 1.26 to

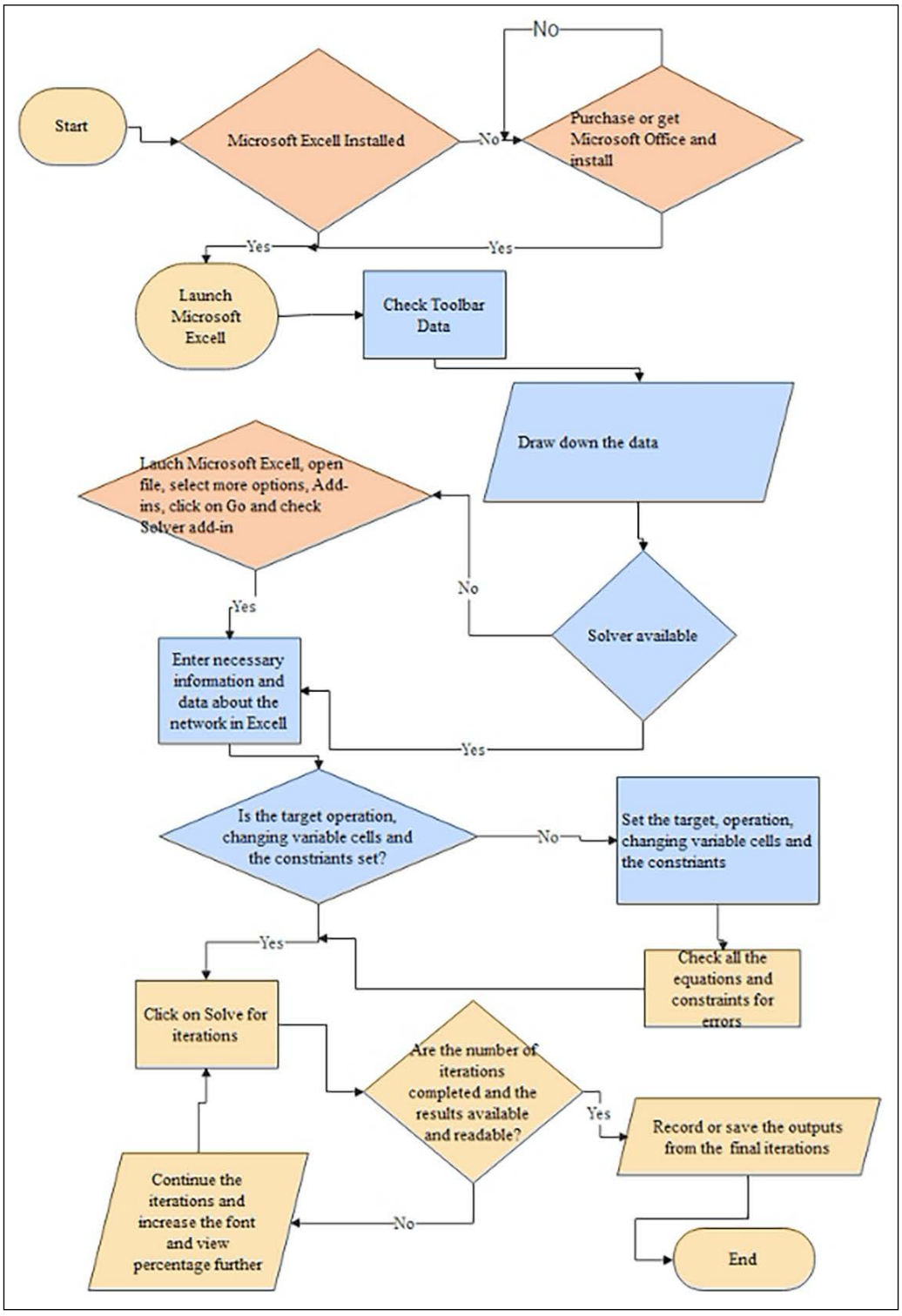

Figure 3. Flow chart of the step required in utilization of Microsoft Excel Solver.

1.65 gcm^{-3} when carbon particle size ranged from 245 to 45×10^{-6}m at 60 MNm^{-2} applied compressive pressure and declines from 1.86 to 1.65 gcm^{-3} with a range of applied compressive pressure from 100 to 60 MNm^{-2}. Electrical resistance per unit length was established to increase with cumulative portion of binder and declines with increasing in applied compressive pressure. The stability of the composite electrode was of increasing order with cumulative applied compressive pressure and declines with increase in current density and carbon particle size [175]. Estimated costs revealed that cost of producing composite carbon-resin electrode was cheaper ($13.25 m^{-1}) than that of heat-treated electrodes ($33.33 m^{-1}) [179].

More on the properties of this composite carbon-resin electrode can be established in literature such as Oke [172; 173]; Oke et al. [174, 176]; Oke et al. [177]; Oke et al. [178]; Oke et al. [180]; Oke and Ogedengbe [181]; Olayanju et al. [182] and Oke et al. [183].

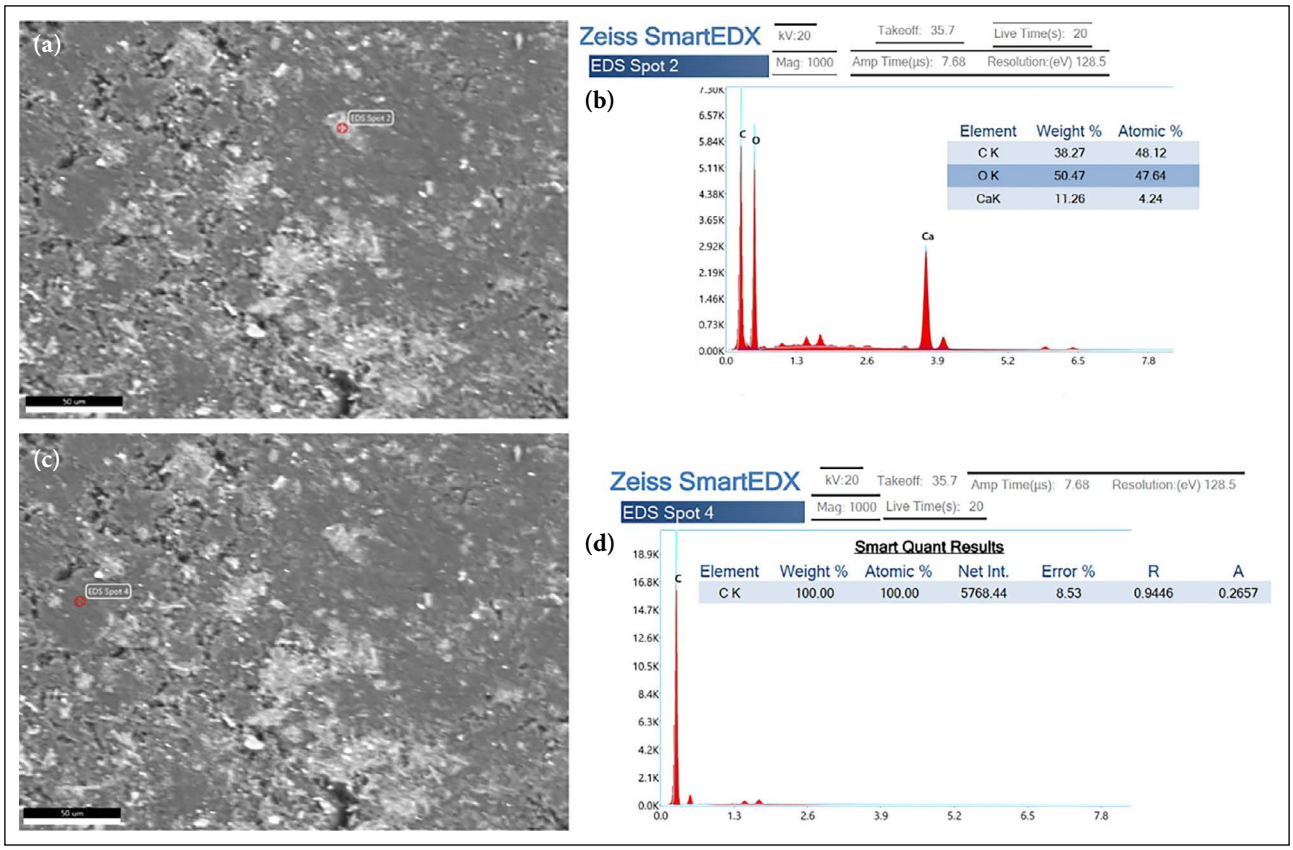

Figure 4. **(a)** The major constituents of the graphite resin electrode at spot 2. **(b)** The Result of zeiss smart EDX for spot 2. **(c)** The major constituents of the graphite resin electrode at spot 4. **(d)** The result of zeiss smart EDX for spot 2.

b) Scanned Electro Magnetic and Energy Dispersive Spectroscopy of the electrodes

Figure 4a-c and d provide the major and key configurations of the selected spots in graphite (carbon) resin electrode. The figure shown that the main components of the electrode are Carbon (between 38.27 % and 100 %) Oxygen (50.47 %) and Calcium (11.26%). The result specified the occurrence of Carbon and Oxygen at spots 2 and 4, as the highest composition of the developed carbon-resin electrode. The occurrence of these two components (carbon and oxygen) can be accredited to the organic binder used, powdered graphite used and likely trapped Oxygen during missing processes. This result of the composition revealed that removal of chloride may be attributed to adsorption by the pores and conversion of some of the components to calcium, carbon and oxygen end products such as $Ca(OCl)_2$ and $CaCl_2$. Figure 5a-c and d show and establish the Scanned Electro Magnetic (SEM) structures of the electrodes at various magnification of 100, 250, 500 and 750. From these figures, it is clearly showed that the powdered particles of the powdered carbon electrode were closely parked and porosity is very low. This lower porosity can be attributed to a lower concentration of binder, higher compressive pressure and nano-particle sizes utilised in the development of the carbon-resin electrode stated in Oke et al. [178]. The figures established that there are two categories of pore with reference to the nature of the pores (continuous and separated or standalone pores). The continuous pores have the tendency to accommodate more concentration of particles at the same time, while standalone adsorb different concentration of particles at different time.

c) Development and Performance of the electrolysing Equipment

The performance of the fabricated equipment converting (electrolysing equipment) alternating current to direct current was 95 % and above. The results of the performance were compared with similar imported equipment and analysed statistically using analysis of variance, total error, coefficient of determination, and model selection criterion. The results of total error, coefficient of determination and model selection criterion analysis were 22.8, 0.244, and 3.312 and 24.3, 0.243 and 3.066 for locally developed and imported electrolysing equipment respectively. The results analysis of variance indicates that there was no significant difference between the two equipment (locally developed and imported electrolysing equipment) at a 95 % confidence level. Detailed data are available in Literature such as Oke [172], Oke and Ogedengbe [185].

d) Desalination of Synthetic Salty Water and Effects of Selected Operational Factors on the Performance

The study established that the maximum values the performance of the system occurred with 94.82% removal of chloride concentration when the surface area of the composite carbon resin electrode was 19.64 cm^2, the flow of the wastewater was 2.0l/hr, the treatment time of 4.0 hr and the current flow through the wastewater was 10.0 A (higher factorial factor levels), which indicated that these mentioned factors

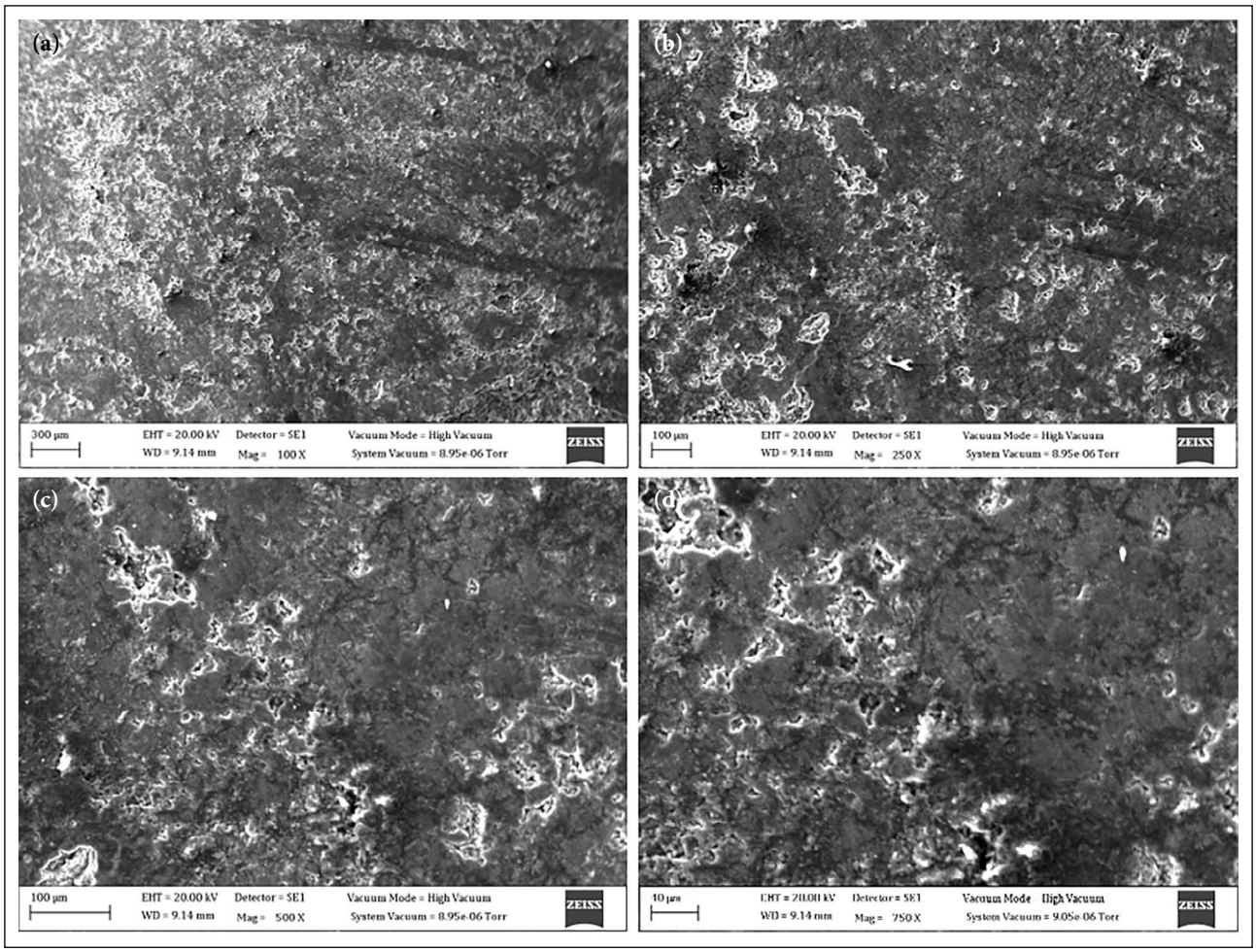

Figure 5. **(a)** Scanned electro magnetic (SEM) structures of the electrode at 300 µm. **(b)** Scanned electro magnetic (SEM) structures of the electrode at 100 µm. **(c)** Scanned electro magnetic (SEM) structures of the electrode at 100 µm. **(d)** Scanned electro magnetic (SEM) structures of the electrode at 40 µm.

had positive influence on the performance of electrochemical treatment of the wastewater. It was revealed that during the treatment process. The lowest value of the performance of the process occurred with 68. 52% removal of the chloride by the treatment process. This level of performance occurred when the initial concentrations of chloride was 40×10^3 mg /l, the separation distances between electrodes was 10.0 cm, the depth of the electrode was 1.0 cm and pH was 10.0 (higher factorial factor levels), which meant that these latter mentioned selected factors contributed negatively to the performance of the treatment process. The cations moved toward the negatively charged cathode, while anions moved toward the positively charged anode. The outcome is the separation of concentrated brine aqueous solutions and freshwater. The detailed efficacy of the E_{tt} process in the current study is presented in another paper specifically such as Oke [172]; Oke et al. [184] and Fehintola et al. [188]. The electrolysis chemistry of the reactions at the developed carbon-resin electrodes and solution are as follows [21, 112, 137]:

Anode: $2Cl^{-}\rightarrow Cl_2+2e^{-}$ (3)

Cathode: $2H_2O+2e^{-}\rightarrow H_2+2OH^{-}$ (4)

In solution: Cl_2+H_2OÄ $HOCl+Cl^{-}+H^{+}$ (5)

$HOCl$Ä $H^{+}+OCl^{-}$ (6)

Dissociation constants

$$K_3=\frac{[HOCl]\ [Cl^{-}]}{Cl_2}\approx2\times10^{-4} \quad (7)$$

$$K_4=\frac{[H^{+}]\ [OCl^{-}]}{[HOCl]}\approx2\times10^{-4}\ at\ 0°C \quad (8)$$

Loss reactions at:

Anode:

$$6OCl^{-}+3H_2O\rightarrow2Cl_3^{-}+4Cl^{-}+6H^{+}+\frac{3}{2}O_2+6e^{-} \quad (9)$$

Cathode:

$$2H_2O\rightarrow O_2 4H^{+}+4e^{-} \quad (10)$$

$$OCl^{-}+H_2O+2e^{-}\rightarrow Cl^{-}+2OH^{-} \quad (11)$$

Solution:

$$2HOCl+OCl^{-}\rightarrow ClO_3^{-}+2Cl^{-}2H^{+} \quad (12)$$

$$2ClO^{-}\rightarrow O_2+2Cl^{-} \quad (13)$$

$$H_2+OCl^{-}\rightarrow H_2O+Cl^{-} \quad (14)$$

Other likely reactions:

$$Mg^{2+}+2OH^{-}\rightarrow Mg[OH]_2 \quad (15)$$

$$Ca^{2+}+2OH^{-}\rightarrow Ca[OH]_2 \quad (16)$$

$$X^{n+}+nOH^{-}\rightarrow X[OH]_n \quad (17)$$

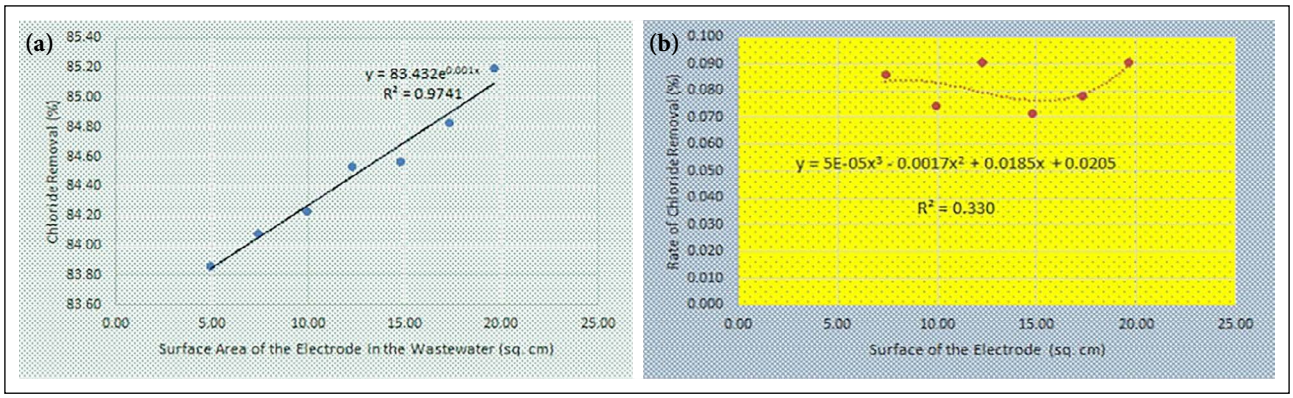

Figure 6. **(a)** Relationship between surface area of the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the surface area of the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique.

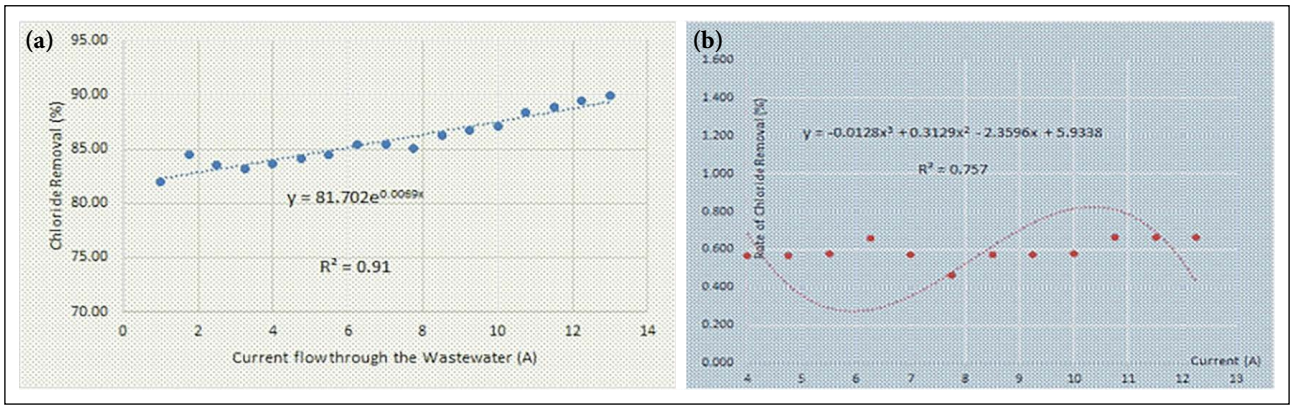

Figure 7. **(a)** Relationship between current flow through the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the current flow through the wastewater and performance of the electrochemical treatment process using steepest descent technique.

e) Optimisation of the Selected factors in the Desalination of Salty water and Simulated Performance

Figure 6a presents relationship between surface area of the developed carbon-resin electrodes in the wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is an exponential relationship, which is a positive indicating that surface area of the developed carbon-resin electrode increases the efficacy of E_{tt} process. The figure revealed that at higher surface area of the developed carbon-resin electrode in the wastewater efficacy of E_{tt} process improves greatly. Figure 6b provides information on the optimization and efficacy change in the process due to variation in the surface area of the developed carbon-resin electrode. The figure revealed that the optimum surface area of the developed carbon-resin electrode was 13.2 cm^2 of 2000 ml of the wastewater. The relationship between the surface area of the radius and the depth can be expressed as:

$$S_c=\Pi r_c^2+\Pi r_c d_e \quad (18)$$

Where; de stand for the depth of the electrode in the wastewater; rc represents the actual radius of the electrode and S_c stands for the contact surface area of the electrode. The rate change in the contact surface area can be expressed as follows:

$$\partial(S_c)=\frac{\partial}{\partial r_c}(\Pi r_c^2+\Pi r_c d_e)+\frac{\partial}{\partial r_c}(\Pi r_c^2+\Pi r_c d_e) \quad (19)$$

Mishra and Ram [193] stated that steepest descent technique is among the conventional, oldest, and well-establish explore techniques for decreasing multivariable unrestricted optimization challenges. This technique has performed a vital role in the advance of progressed optimization algorithms. The technique is a first-order derivative numerical and iterative optimization algorithm that convergence or divergence is linear for a situation of quadratic functions. More of steepest descent technique can be established in literature such as efficient numerical method in Wu et al. [194]; numerical technique for multicriteria optimization highlighted in Bento et al. [195]; numerical technique Variable Order Vector Optimization Problems documented in Wang et al. [196]; numerical technique for mining signal transduction network available in Bello et al. [197], numerical technique optimization of mechanical systems in Haug et al. [198] and numerical technique for multicriteria optimization Bento et al. [199]. The observation is similar to previous researches and studies such as Alam et al. [35] statement on treatment on saline wastewater, Korbahti [200] observation on optimization of E_{tt} of textile dye wastewater, Szpyrkowicz et al. [201] conclusions on E_{tt} of tannery wastewater and Deng et al. [202] on the efficacy of E_{tt} of nitrogen- containing organic wastewater by iron filings.

Figure 7a presents relationship between current flow through the wastewater and efficacy of the E_{tt} process util-

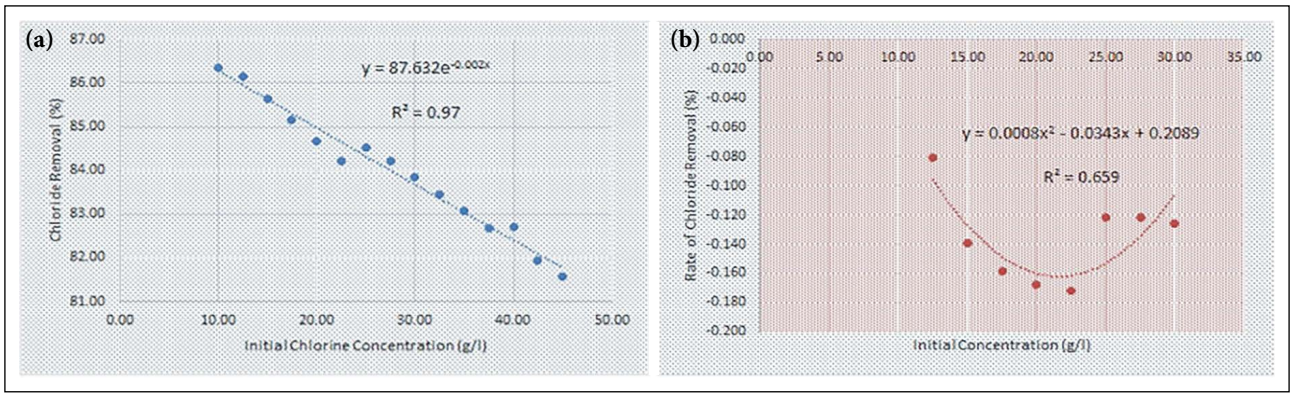

Figure 8. **(a)** Relationship between initial concentration of Chloride ion in the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the initial concentration of chloride ion in the wastewater and performance of the electrochemical treatment process using steepest descent technique.

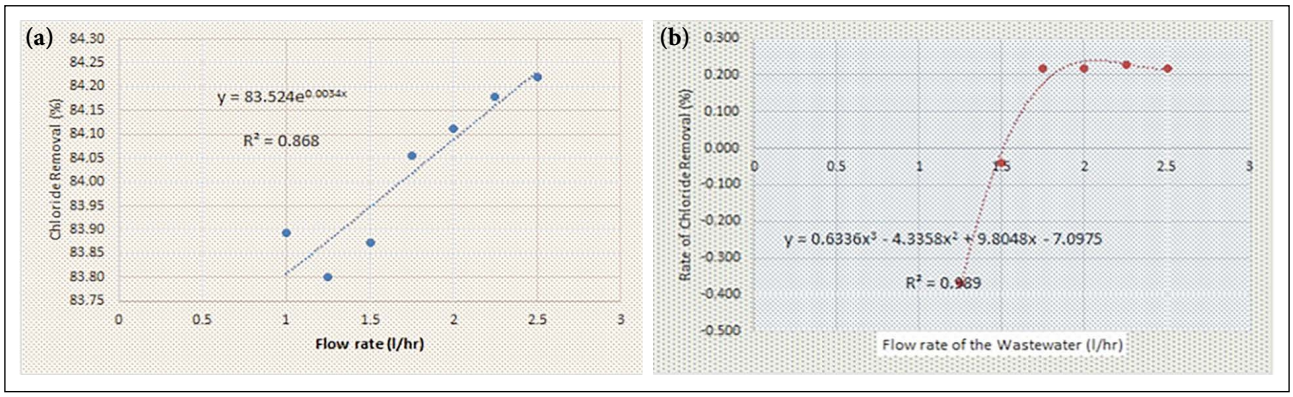

Figure 9. **(a)** Relationship between flow rate of the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the flow rate of the wastewater and performance of the electrochemical treatment process using steepest descent technique.

ising steepest descent technique. The figure establishes that there is a positive relationship, which is exponential form between the flow and efficacy of the process, which indicate that current flow through the wastewater increases the efficacy of E_{tt} process. This positive relationship can be attributed to further influx of chloride ion and flocs formation of the pollutant. The figure revealed that at higher current flow through the wastewater the efficacy of the system improves greatly. The observation is similar to previous researches and studies such as Alam et al.[35] statement on treatment on saline wastewater, Tulin and Serdar [203] observation on efficacy of electrooxidation- E_{tt} of container washing wastewater, Lyvia [204] conclusion on influence of current density of electro-bioreactor treatment on reduction of phosphorus and micropollutants, and reduction or elimination of fouling, Feng et al.[205] on efficacy of two new E_{tt} systems for wastewaters and Li and He [206] on optimizing the efficacy of a membrane bio- E_{tt}. Figure 7b provides information on the optimization and efficacy change in the process due to variation in the surface area of the developed carbon-resin electrode. The figure revealed that the optimum current flow through the wastewater was 10.5 A of 2.0×10^3 millilitres of the wastewater, which is equivalent to current volumetric of 5.25×10^{-3} A per ml and a current density of 0.795 A per cm^2, which is greater than 30 A per m^2 as minimum value stated in previous researches and studies such as Phalakornkule et al. [207], Acosta-Santoyo et al. [208] and Korbahti [200].

Figure 8a presents relationship between initial concentration of chloride ions in the saline wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is a negative exponential relationship, which indicates that initial concentration of Cl^- decline, increases the efficacy of E_{tt} process. This efficacy can be attributed to higher concentration load of chloride available at a given time than other times and lower contact area and current at present. The figure revealed that at higher initial concentration of Cl^- in the saline wastewater, efficacy of the E_{tt} system declines greatly. Figure 8b provides information on the optimization and efficacy change in the process due to variation in the initial concentration of chloride ions in the wastewater. The figure revealed that the optimum initial concentration of Cl^- in the saline wastewater was 27.5 g/l. This behaviour of Cl^- reduction is described by the complex composition of the initial concentration of Cl^- in the saline wastewater and the low contribution of both direct and indirect electro-oxidation and electro-adsorption mechanisms [208].

Figure 9a presents relationship between flow rate of the wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is an exponential relationship, which is positive indicating

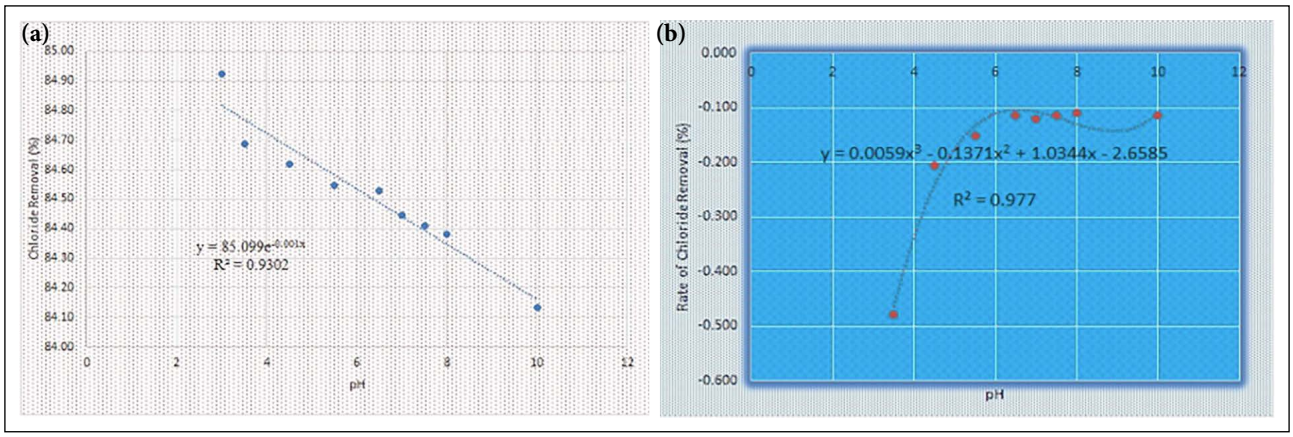

Figure 10. **(a)** Relationship between pH of the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the pH of the wastewater and performance of the electrochemical treatment process using steepest descent technique.

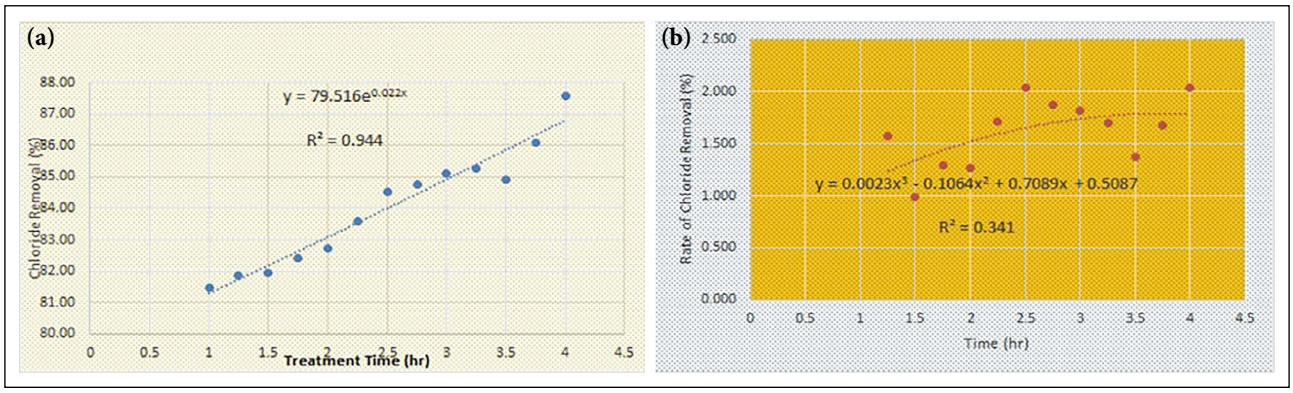

Figure 11. **(a)** Relationship between treatment time of the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the treatment time of the wastewater and performance of the electrochemical treatment process using steepest descent technique.

that flow rate of the wastewater increases the efficacy of E_{tt} process. The figure revealed that at higher flow rate of the wastewater, the efficacy of E_{tt} system improves greatly.

These results, finding and observation of optimum initial concentration is similar to 31000 mg/l based on Akindahunsi et al. [189]; 35.3779 g/l of chloride ion based on Thabit et al. [190]; 41.80 g/l based on Mehan-Martes and Mertel et al. [191] and 43.6995 g/l of chloride ions based on Lior and Kim [192]. These optimum concentrations of saline wastewater are functions of locations, nature of the process and other critical factors. In addition, the observation is similar to previous studies such as Alam et al.[35]; Korbahti [200]; Isaac et al.[209]; Garcia-Seura et al. [210]; Ensano et al. [211] and Meng et al. [212]. Figure 9b provides information on the optimization and efficacy change in the process due to variation in the flow rate of the wastewater. The figure revealed that the optimum flow rate of the wastewater was 1.89 l/hr of the wastewater. This behaviour of flow rate of the wastewater is explained by the complex flow rate of the wastewater, availability and accessibility of the initial concentration of Cl^- in the wastewater, mixing phenomenon and the contribution of both direct and indirect electro-oxidation, electrocoagulation and electro-adsorption mechanisms.

Figure 10a presents relationship between pH the wastewater and efficacy of the E_{tt} process utilising steepest descent technique. The figure establishes that there is a negatively expressed exponential relationship, which indicates that an increase in the pH declines the efficacy of E_{tt} process. The figure revealed that at higher pH of the wastewater, the efficacy of E_{tt} declines or decreases greatly. Figure 10b provides information on the optimization and efficacy change in the process due to variation in the pH of the wastewater. The figure revealed that the optimum pH of the saline wastewater was 6.7. Tulin and Serdar. [203] reported that higher pH of wastewater required low retention time of operation and lower pH value required high detention time to perform the efficacy. Figure 11a presents relationship between treatment time of the wastewater and efficacy of the electrochemical treatment process utilising steepest descent technique. The figure establishes that there is a positive exponential relationship, which indicates that treatment time of increases the efficacy of electrochemical treatment process. This observation agrees with literature and previous studies [203]. Figure 11b provides information on the optimization and efficacy change in the process due to variation in the treatment period of the wastewater. The figure revealed that the optimum treatment time of

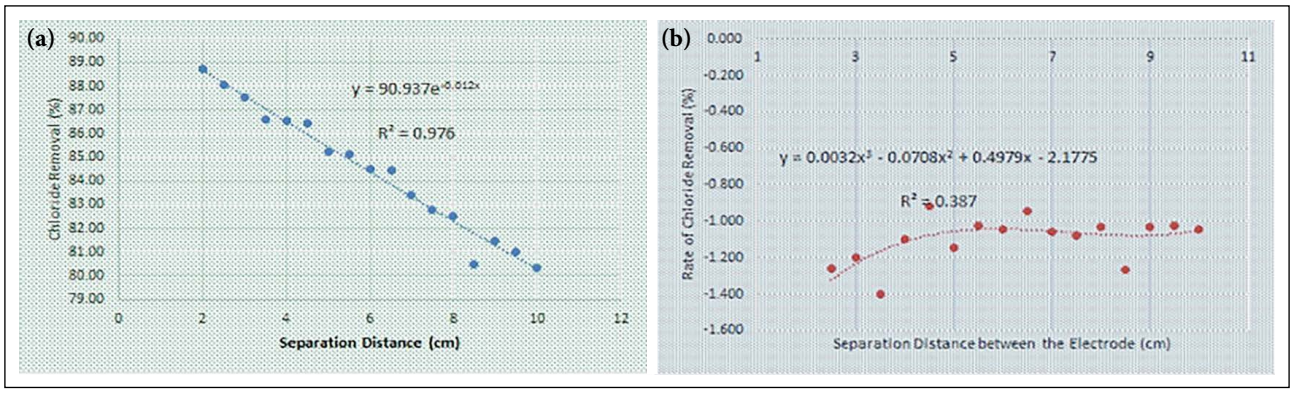

Figure 12. **(a)** Relationship between separation distance between the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique. **(b)** Relationship between change in the separation distance between the electrodes in the wastewater and performance of the electrochemical treatment process using steepest descent technique.

the wastewater was 2.75 hours. Tulin and Serdar [203] reported a treatment time of 300 minutes (5 hours) for container washing wastewater at pH of 3.0 and 120 minutes for the same wastewater at pH value of 5.0.

Figure 12a presents relationship between separation distance between the electrode in the wastewater and efficacy of the electrochemical treatment process utilising steepest descent technique. The figure establishes that there is a negatively response- exponential relationship, which indicates that separation distance between the electrode declines the efficacy of E_{tt} process. The figure revealed that at higher separation distance between the electrode in the wastewater, the efficacy of the system declines or decreases greatly. Figure 12b provides information on the optimization and efficacy change in the process due to variation in the separation distance between the electrode in the wastewater. The figure revealed that the optimum separation distance between the developed carbon-resin electrodes in the wastewater was 42 mm centre to centre of the aluminium cathode of 20 mm diameter and carbon-resin anode of 25 mm diameter. Phalakornkule et al. [207] obtained 8.0 mm as optimum distance between the electrodes, contact time of at least 5.0 minutes and current density of at least 30 A per m^2 for the treatment of reactive blue 140 utilising iron anode. Obijole et al. [213] obtained a mathematical representation that correlates resistance of an aqueous solution (Rc), the distance or separation space between the developed carbon-resin electrodes during electrochemical treatment of wastewater (X_c), and electrical conductivity of the aqueous solution (E_c) as follows:

$$R_c = \frac{R_c}{E_c} \ln\left(\frac{R_c + X_c}{R_c}\right) \quad (7)$$

Where; rc stands for the radius of the cylindrical electrode in the wastewater.

Although, optimization of E_{tt} salty is limited in literature, but the results were similar to optimization of electrochemical removal of cefazolin antibiotic from hospital wastewater [12], arsenate from aqueous solution by electro-coagulation [38], arsenic removal from groundwater samples utilising iron electrocoagulation treatment [39], optimization of arsenic removal from potable and drinking water by electrocoagulation treatment [49]; arsenic treatment utilising technology of electrocoagulation [58]; arsenite reduction from groundwater samples in a batch electrocoagulation treatment process [61] and optimization of the electrocoagulation treatment process for the reduction of lead from water samples [47]. It is like optimization of the adsorption of a textile dye onto nano-clay utilising a central composite design [15] and optimization of electrocoagulation treatment process for efficient reduction of ciprofloxacin antibiotic utilising iron electrode; kinetic and isotherm studies of adsorption [11]. In line with the efficacy, Feng et al. [202] reported that 4 m^3 per hour flow rate of E_{tt} system was established to reduce between 87% and 91% of Total-Phosphorous, between 74% and 96% of Total-Nitrogen, within 70 % and 94 % of NH4-N, between 88 % and 91 % of Total Organic Carbon and between 75 % and 87% of Chemical Oxygen Demand.

Similarly, for the same wastewater at a flow rate of 0.5 m^3 per hour, the system attained between 62 % and 90 % of Total-Phosphorous, within 83 % and 92 % of Total-Nitrogen, between 90 % and 100 % of NH4-N, and between 75 % and 83% of Total Organic Carbon, with between 80 % and 100 % of Chemical Oxygen Demand. Acosta-Santoyo et al. [207] documented that the efficiency of oxyfluorfen degradation by electro-oxidation treatment process increases with current density meanwhile the degradation of Total Organic Carbon follows an opposite trend. This behaviour or efficacy is explained by the complex composition of the initial sample and the contribution of both direct and indirect oxidation mechanisms. Alam et al. [35] documented that the effect of current density on efficacy of E_{tt} of wastewaters is considered a significant process constraint as it rules the coagulant dosage, which based or related to faradays first and second laws and hydrogen gas as an end product in the system. In addition, reduction of pollutants growths with the intensification of current density as it produces further flocs because of quicker anodic dissolution. Körbahti [200] reported that the optimized situations under specified cost driven constraints in the E_{tt} *of textile dye wastewater* were attained for the highest desirability at 6.7 mA cm^{-2}, 5.9 mA cm^{-2} and 5.4 mA cm^{-2}

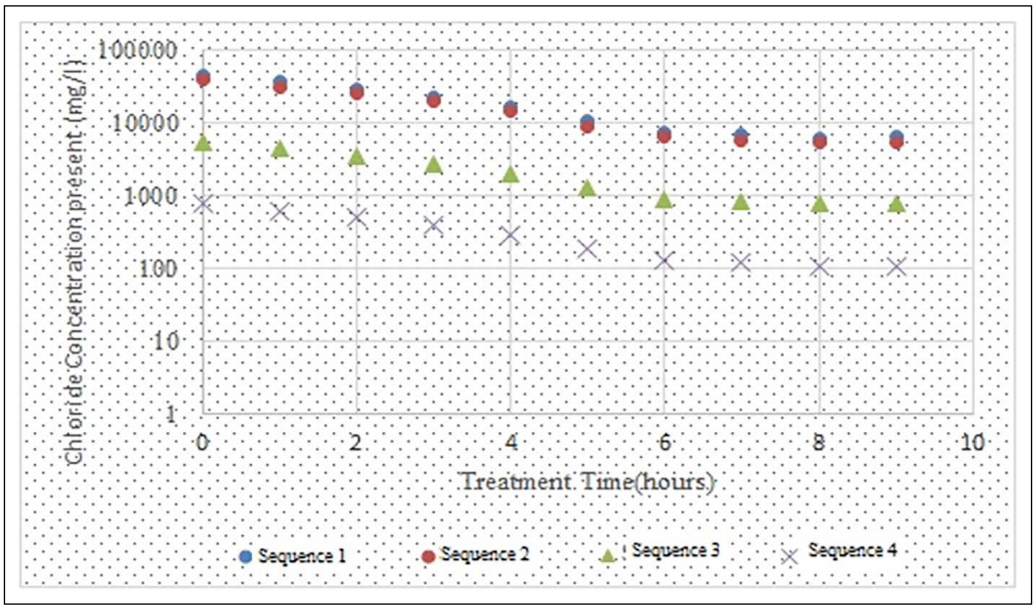

Figure 13. Treatment of typical raw saline wastewater utilising optimum values of operational factors.

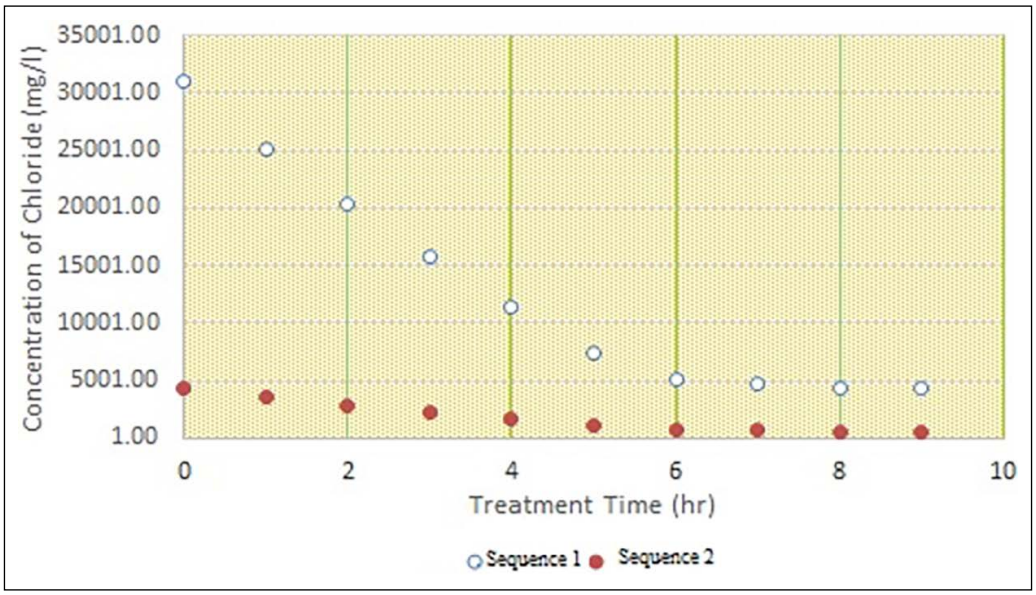

Figure 14. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Akindahunsi et al. [189].

current density and 3.1 gL^{-1}, 2.5 g L^{-1} and 2.8 g L^{-1} supporting NaCl concentration. Szpyrkowicz et al. [201] showed that selectivity of the removal of deferent pollutants was affected by current density which direct anodic oxidation as an additional process for the destruction of the selected pollutants. The efficacy of the electrochemical of typical raw saline wastewater of 45000 mg/l ranges from 19% after 1.0 hour treatment to 85.9 % after 9 hours of treatment. Figure 13 present the efficacy of the system in respect of treatment time. Simulation with a sequence batch reactor revealed that first sequence ended at 6345 mg/l of NaCl at 9 hours, second sequence ended at 5450 mg/l of NaCl at 9 hours of treatment, third sequence ended at 768.5 mg/l of NaCl and fourth sequence ended at 108.4 mg/l of NaCl. Salt and high concentrations of dissolved solids in water in the leachate of urban sanitary landfill sites, surface runoff, contaminated groundwater, and the wastewaters subsequent from recycling units of gas, mining operations and oil industries [214]. Figures 14-17 present the efficacy of the system in respect to simulated process. These figures revealed that at least second batch sequence treatments are required for seawater. Figure 14 revealed the system require at least two sequences or two treatment systems in series for the seawater (Atlantic ocean) from Nigeria, with 4371.00 mg/l and 616.31 mg/l for first and second sequences, respectively. Figure 15 revealed the system require at least two sequences or two treatment systems in series for the seawater from Qatar, with 4988.28 mg/l and 703.35 mg/l for first and second sequences, respectively. Figure 16 revealed the system require at least two sequences or two treatment systems in series for the seawater from Spain, with 5893.80 mg/l and 831.03 mg/l for first and second sequences, respectively. Figure 17 revealed the system require

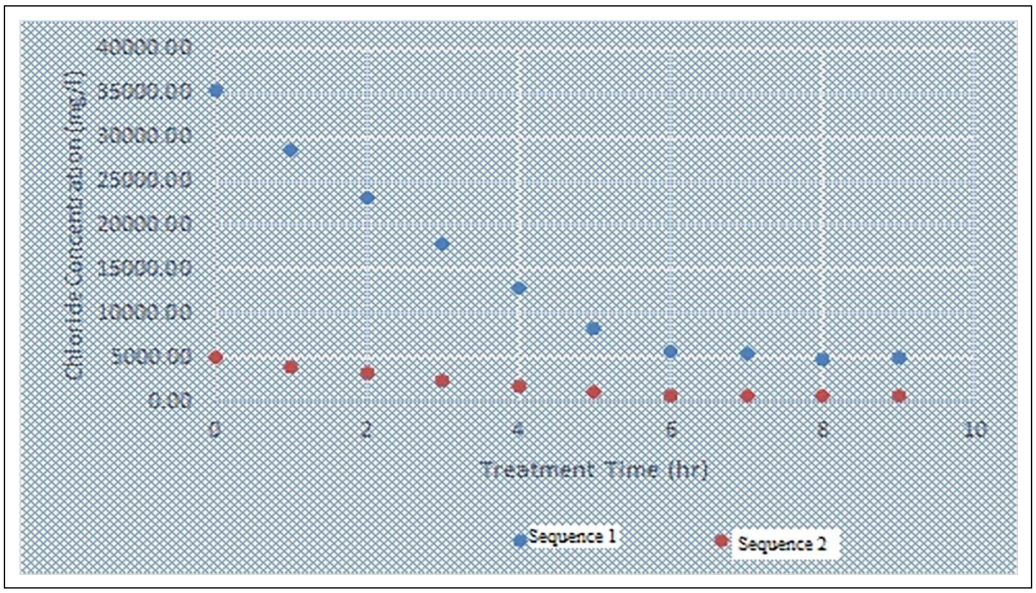

Figure 15. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Thabit et al. [190].

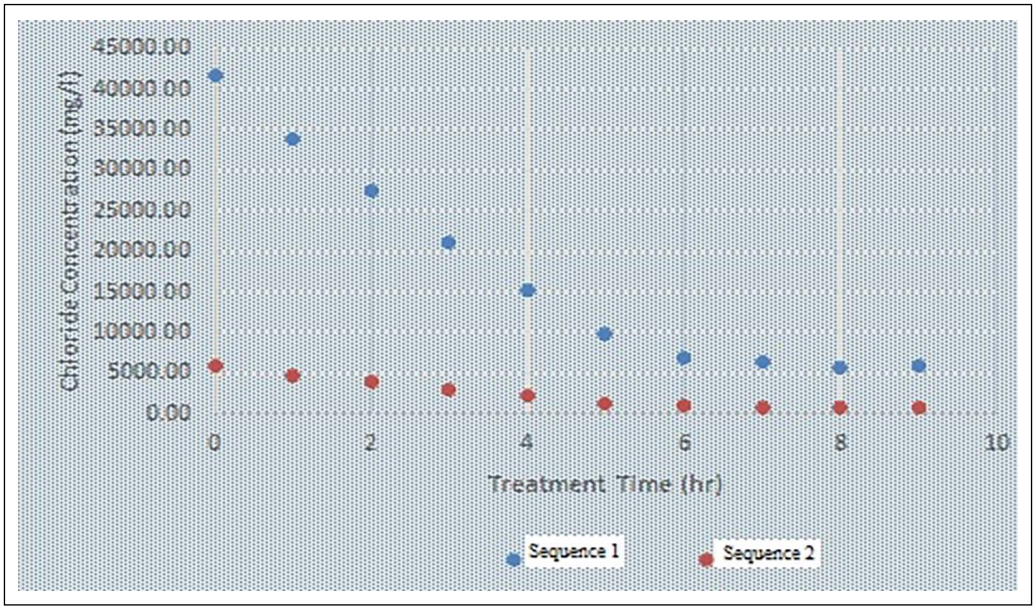

Figure 16. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Melian- Martel et al. [191].

at least two sequences or two treatment systems in series for the seawater, from United States of America with 6161.63 mg/l and 868.79 mg/l for first and second sequences, respectively. These sequence treatments are commonly experiences, which make electrochemical treatment applicable as an advance treatment or for polishing treated water [215–240]. Further information on electrochemical treatment toward perfecting water treated water can be established in literature such as Liu et al. [241], Xiao et al. [242]; Kakavandi and Ahmadi [243]; Jeddi et al. [244]; Zhang et al. [245]; Yun and Redzwan [246]; Jamal and Pugazhendi [247]; Shahata and Urase [248]; Lu et al. [249]; Ahmad et al. [250]; Eom et al. [251]; Huang et al [252]; Paredez et al. [253]; Jorfi et al. [254]; Maharaja et al. [255]; Formentini-Schmitt et al. [256]; Doltabadi et al. [257]; Ahmadi et al. [258] and Myint et al. [259].

CONCLUSION

It can be concluded based on the study that:

a. The electrochemical treatment with carbon-resin and aluminium electrodes is a direct electrolysis of saline or sea water, which reduce the concentration of chloride to an acceptable level with two or more sequence treatment,

b. The optimum values of these selected factors such as current, pH, treatment period and separation distance between the electrode (centre to centre of the electrode) were 10.5 A equivalent to 0.795 A cm^{-2}, 6.7, 2.75 hr and 42 mm (centre to centre of the developed carbon-resin electrodes equivalent to 19.5 mm space between the electrodes), respectively,

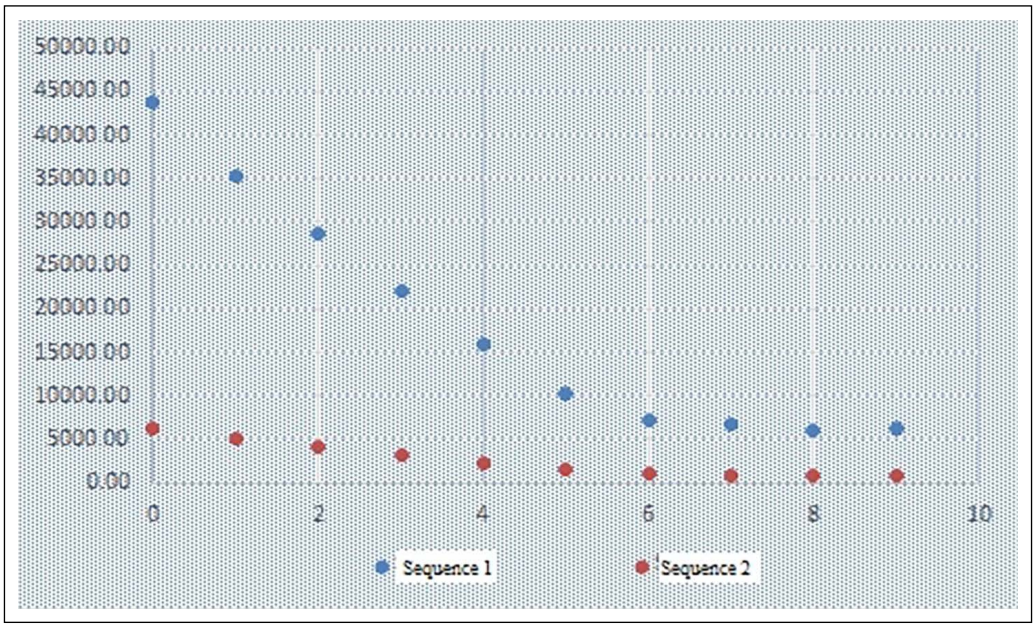

Figure 17. Simulation of typical raw saline wastewater utilising optimum values of operational factors based on Lior and Kim [192].

c. The process is limited to high concentration of salt such as chloride and dissolved solids, treated with graphite-resin and aluminium electrodes,

d. The challenges of the process include cathode passivation, periodic replacement of sacrificial anodes, the need for post-treatment due to high metal-ion concentrations, and high power-consumption costs in areas with limited access to electricity, optimization of operating conditions of electrochemical to achieve both low power consumption with adequate and high removal efficiency,

e. Future perspectives, utilisation of hypochlorite solutions by direct electrolysis of saline or sea water to decrease marine progress is significantly more suitable safer and appropriate exploring the techno-economic feasibility of electrochemical treatment with other treatment techniques,

f. The recommendations from this study include identification of energy pathways and energy application and management of hybrid electrochemical treatment systems; focus efforts on the effective removal of emerging pollutants from the environment utilising hybrid electrochemical treatment systems.

DATA AVAILABILITY STATEMENT

The authors confirm and establish that the data that supports and gives the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon sufficient request.

CONFLICT OF INTEREST

The authors of this article declared no potential or probable conflicts of interest with respect to the study, research, authorship, or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

The authors confirmed that Artificial Intelligence was not utilise in the computation, preparation, writing, editing or as a writing assistant in the development of the manuscript.

ETHICS

There are no ethical issues with the publication of this manuscript.

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