



Operational Parameters, Kinetics and Energy Consumption of Chloride Removal by Graphene as a Capacitive Deionization Sorbent

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Received: 09.12.2024 Accepted: 05.03.2025 Published: 30.03.2025

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ABSTRACT

Capacitive deionization (CDI), a novel and emerging technology provides a solution to the conventional difficulties linked to desalination. The optimum benefits can be harnessed from the technology if a proper electrode material is chosen and its influential parameters are enhanced. The primary objective of the work is to enhance the maximum chloride removal efficiency of graphene employed in flow-by CDI cells by varying flow rate, voltage, pH, electrode spacing, and electrolyte concentration. The secondary objective is to assess the energy consumption and the rate-limiting period for optimal operational conditions. Results show that 95.8% of chloride can be effectively reduced by employing graphene as a CDI electrode. However, this removal efficiency was achieved by maintaining the applied voltage, flow rate, electrolytic concentration, pH, and electrode spacing at 2.36 V, 2 mg/L, 250 mg/L, 5.67, and 0.84 cm, respectively. Isotherm studies reveal that the electrosorption of chloride onto graphene follows the Freundlich isotherm. An increase in flow rate, voltage, duration, and electrode distance, proportionally increases the energy consumption, exclusive of an increase in electrolytic concentration.

Keywords: Capacitive Deionization; Graphene; Chloride removal; Operational Parameter; Kinetics; Energy consumption.

1. INTRODUCTION

Capacitive Deionization (CDI) is a growing desalination technology because of its energy efficiency, high-water recoveries, little contamination, and easy electrode regeneration by zero-voltage or cell polarity change (Sufiani *et al.* 2023). A CDI cell system compartmentalized by a dielectric material separator or open channel uses current collectors and porous (static or flow) electrodes as sorption media. A voltage across two electrodes creates an electric field due to the potential difference. The ions are transiently immobilized between the counter electrodes to produce fresh water and stored electrostatically in the electrical double layers (EDLs) formed at the electrode-water interface. The diffuse and stern layers make up EDLs. The diffuse layer is loosely linked to the first layer, but the former is tightly attached to the electrode. Electrostatic forces attract ions to the aft layer electrode. Ions that are not tightly bound to the surface but remain near the electrode due to coulombic interactions with the stern layer form the diffuse layer. Thus, the non-faradaic reaction governs the removal of ions from the feed water in traditional flow by CDI cell (Oladunni *et al.* 2018).

Capacitive deionization has its own challenges and it has numerous aspects that require further

development (Porada *et al.* 2013). One such issue is unintended reactions, such as Faradaic reactions, which can negatively impact performance, water quality, and system lifespan (Zhang *et al.* 2018). Various approaches have been suggested to mitigate Faradaic reactions, including optimizing cell architecture, regulating operating conditions, and utilizing electrolyte additives to alter the electrolyte's chemical and electrochemical properties. Another aspect is energy optimization, which is central to its success as a sustainable desalination technology. Many system characteristics impact the energy efficiency of the desalination, including electrode material, electrode spacing, applied voltage, flowrate, and the characteristics of the feedwater (salinity and temperature). These factors can affect the amount of energy required to remove ions from the water (Algurainy and Call, 2020).

This work makes an attempt to optimize operational parameters to improve traditional CDI electrode performance. High electronic conductivity, surface area, and hydrophilicity are considered while choosing CDI electrode materials (Shulga *et al.* 2021). Since graphene meets all the necessary requirements, this study has utilized graphene electrodes to build a CDI cell. The study analyzes the effect of electrolytic

concentration, flow rate, voltage, and electrode spacing on the CDI cell electrosorption capacity.

2 EXPERIMENTAL STUDIES

2.1. Electrode Fabrication and Reactor Set-up

The advantageous physicochemical and mechanical properties of graphene led to its selection as the active electrode material for the CDI process. Graphene was synthesized *via* electrochemical exfoliation of pencil graphite by employing a 0.1 M ferrous sulfate electrolytic solution. A 5 cm × 5 cm copper plate was coated with synthesized graphene (the active material) using a slurry composed of dimethyl acetamide and polyvinylidene fluoride (PVdF) as binder and solvent, respectively. The weight-based proportion of active material, binder, and solvent was 1:0.25:0.5 in the electrode slurry (Venkatesan and Pauline, 2022).



Fig. 1: Fabricated graphene electrode

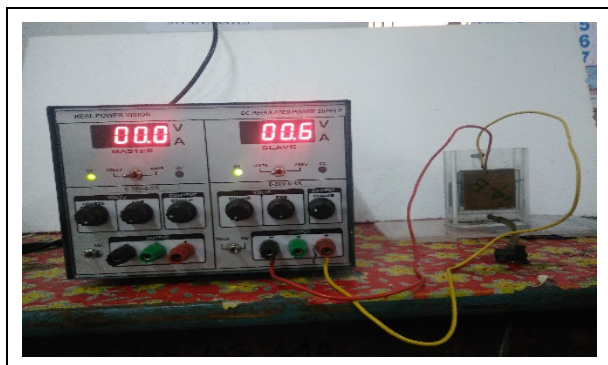


Fig. 2: Reactor set-up

The manufactured electrode (Fig. 1) was introduced into a reactor with the dimensions of 6 × 1.8 × 7 cm (Fig. 2). Acrylic was utilized to fabricate the reactor, which featured two sides with electrode insertion channels. Two holes with a diameter of 0.5 cm were created in the reactor. One hole was positioned 1 cm above the bottom to allow raw sample ingress. In contrast, the other was positioned 1 cm below the upper surface to extract the treated samples for subsequent

analysis. Table 1 lists the physical and chemical characteristics of the electrode material (Pauline and Venkatesan, 2019).

Table 1. Characteristics of Graphene

S. No.	Property	Unit	Value
1.	Average size of crystallite	nm	4.77
2.	Density	g/cm ³	0.945
3.	Specific surface area	m ² /g	1529.8
4.	Specific capacitance	F/g	974.45
5.	Electrosorptive capacity	mg/g	32.73

2.2 Optimization Studies

This study employed Taguchi analysis to determine the optimal value for each operational parameter and examined their impact (Salleh *et al.* 2023). Table 2 lists the fixed levels of each operational parameter based on the numerous studies conducted using the CDI process.

Table 2. Selected operational parameters and their levels

S. No.	Operational Parameter	Unit	Levels
1.	pH	No Unit	3, 5, 7, 9, 11
2.	Potential	V	0.2, 0.4, 0.6, 0.8, 1.0, 1.2
3.	Electrolytic concentration	mg/L	250, 500, 750, 1000, 1250
4.	Spacing between electrodes	cm	0.5, 1, 1.5, 2, 2.5
5.	Flow rate	mL/min	2, 4, 6, 8, 10

The necessary flow rate was retained by utilizing a peristaltic pump. Experiments were conducted as per the protocols. The residual chloride levels were monitored closely as per the method specified in IS 3025 Part 32 (Diaz *et al.* 2014).

2.3 Kinetic Studies

Kinetic study was conducted to identify the rate-limiting phase in the electrosorption of chloride onto graphene. Both reaction-based and diffusion-based kinetic models were assessed. The experimental data were analyzed in reaction-based kinetics using the pseudo-first-order rate proposed by Lagergren, the pseudo-second-order model proposed by Ho, and the Elovich model. In addition, Weber-Morris quadratic diffusion model and the pore diffusion model were also studied.

2.4. Energy Requirement

Power required to remove one gram of chloride in one hour was calculated as follows,

$$P = \frac{EIt}{(C_{in} - C_{out})V} \quad \dots (1)$$

where, P is power required to reduce chloride concentration in kWh/m³, t is duration of CDI electrosorption, V is volume of water treated. Energy requirement analysis was carried out using varying operational parameters like electrolytic concentration, duration of CDI process, voltage, pH, spacing between electrodes, and flow rate.

3. RESULTS AND DISCUSSION

3.1 Effect of Operational Parameters

Five operational parameters, each with five levels were selected for investigation. A total of 5⁵ investigations were required to be conducted. The Taguchi approach was implemented to decrease the number of experimental trials as shown in Table 3.

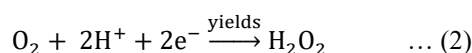
Table 3. Taguchi orthogonal array of an experimental run

S. No.	Potential in V	Flow rate in ml/min	Electrolytic concentration in mg/L	pH	Spacing b/w electrodes in cm
1	0.5	2	250	3	0.5
2	0.5	4	500	5	1
3	0.5	6	750	7	1.5
4	0.5	8	1000	9	2
5	0.5	10	1250	11	2.5
6	1	2	500	7	2
7	1	4	750	9	2.5
8	1	6	1000	11	0.5
9	1	8	1250	3	1
10	1	10	250	5	1.5
11	1.5	2	750	11	1
12	1.5	4	1000	3	1.5
13	1.5	6	1250	5	2
14	1.5	8	250	7	2.5
15	1.5	10	500	9	0.5
16	2	2	1000	5	2.5
17	2	4	1250	7	0.5
18	2	6	250	9	1
19	2	8	500	11	1.5
20	2	10	750	3	2
21	2.5	2	1250	9	1.5
22	2.5	4	250	11	2
23	2.5	6	500	3	2.5
24	2.5	8	750	5	0.5
25	2.5	10	1000	7	1

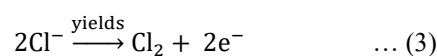
Fig. 3(a) shows percentage of chloride removal when 0.5 V voltage is increased to 2.5 V. An increase in voltage ionizes the electrolytic solution and thickens the electric double layer (EDL). Further, an increase in EDL thickness increases the electrostatic force of attraction that causes removal of more chloride (Qi *et al.* 2022). Redox reactions in the electrolytic solution reduce EDL ion concentration and thickness when voltage surpasses 2 V. As EDL thickness lowers, the electrostatic attraction reduces and thus limits the removal efficiency.

Fig. 3(b) shows the effect of pH variation on chloride removal efficiency. As pH increases over 3, chloride concentration decreases. The maximum chloride drop was 46.5% at pH 7. With a pH increase above 7, chloride

concentration decreases till it reaches pH 11. When the pH of the electrolytic solution is acidic, the cathode reaction is as follows (eq 2):

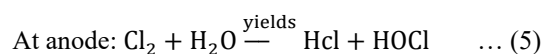
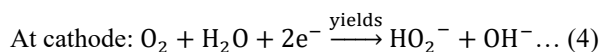


Conversely, chloride ions undergo oxidation, as shown in equation (3)



The redox process depletes chloride ions, resulting in lower chloride ion concentrations in electrolytic solutions and thin EDLs. Decreased EDL

thickness reduces chloride ion removal. When pH exceeds 7, the following redox reaction happens.



Electrons produced in the alkaline range prefer redox processes to the ionization of chloride at electrolytic concentrations. Compared to the acidic range, the chloride removal efficiency decreases as the concentration of chloride ions available for electrosorption is reduced in the electrolytic solution (Alkhadra *et al.* 2022).

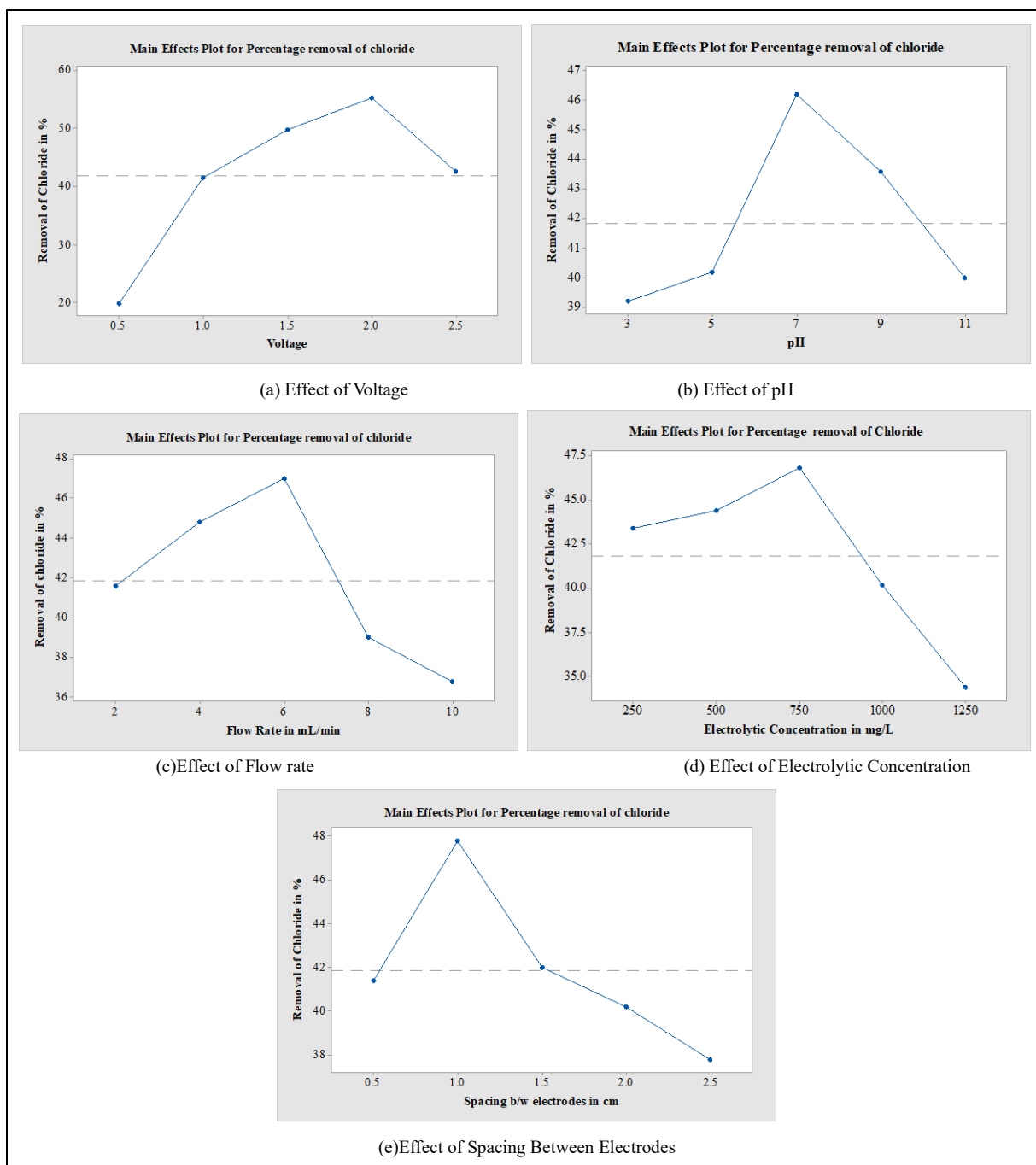


Fig. 3: Removal of chloride with operational parameters of CDI process

Fig. 3(c) shows the chloride removal efficiency when the flow rate was varied from 2 to 10 mL/min at a constant interval of 2 mL/min. Increasing the flow rate reduces chloride reduction. Increasing the flow rate by up

to 6 mL/min reduces ion retention in the CDI electrolyte and lowers electrolytic solution resistance. The electrosorptive capacitance of graphene increases as resistivity decreases, thus, increasing current density.

Chloride removal reduces as the flow rate exceeds 6 mL/min, possibly due to a further decrease in the residence period of chloride ions. Chloride retention

duration is less than the period needed for efficient sorption onto graphene, thus, reducing contact time.

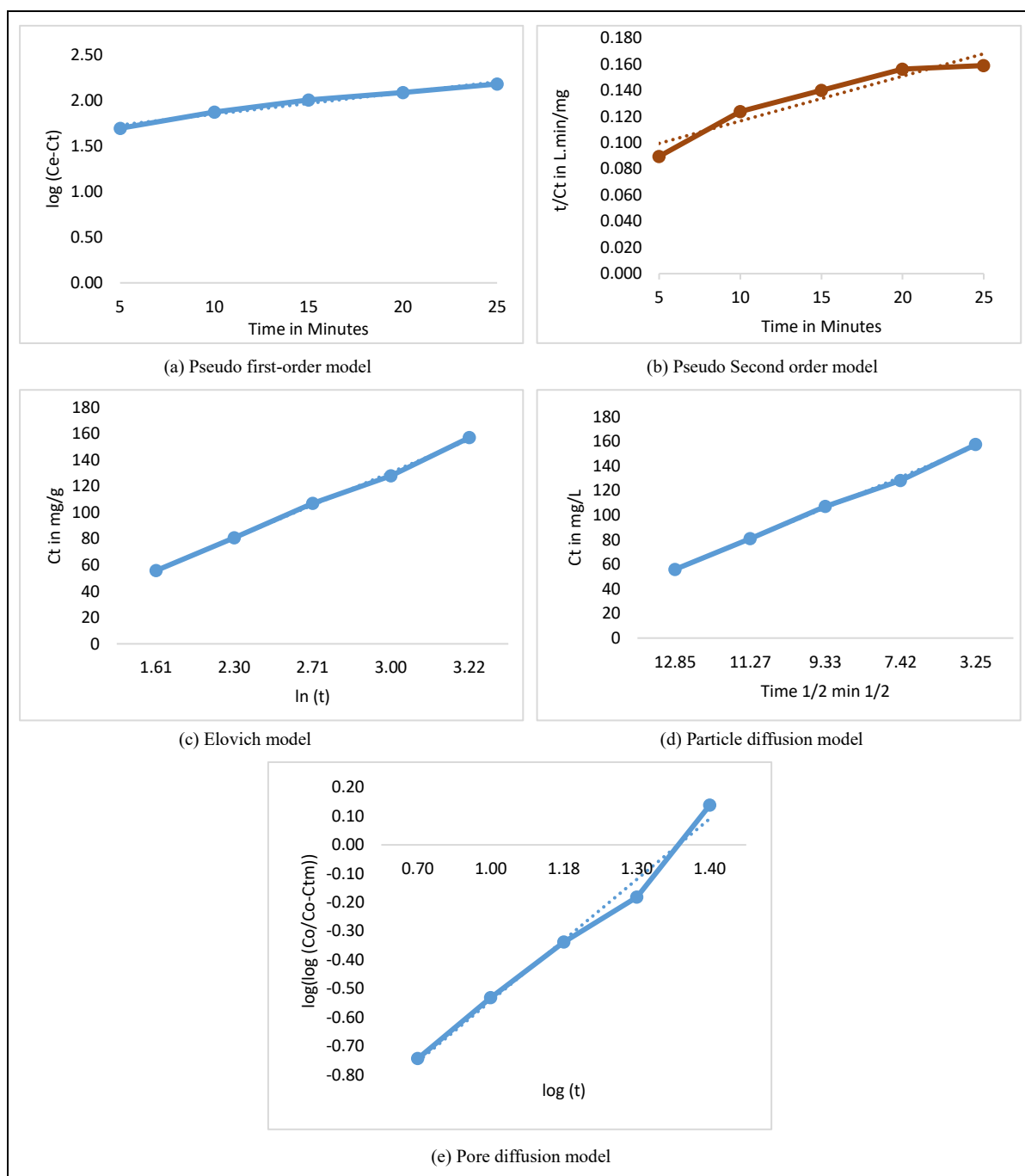


Fig.4: Kinetic model of chloride removal

Fig. 3(d) shows chloride removal % vs concentration. Electrosorption is affected by electrolytic concentration. Graphene removal efficiency increases with electrolytic concentration. Chloride removal efficiency of graphene increases until the electrolyte concentration reaches 750 mg/L. As feed concentration drops, resistance reduces, lowering ionic concentration

and increasing ion flow to the electrode. As EDL thickness increases, pseudocapacitance increases, causing chloride electrosorption onto graphene (Angizi *et al.* 2023). When chloride concentration in feed water increases beyond the optimum value, the resistance increases, resulting in reduced EDL thickness and capacitance. The decreased static force of attraction

creates a concentration gradient between the electrode and electrolyte. The concentration gradient drives the desorption of chloride ions from the electrode surface to the electrolytic solution. Thus, graphene chloride removal efficiency decreases with an increase in chloride concentration.

Table 3 shows electrode spacing variation, while Fig. 2 shows chloride removal. Another significant

factor in chloride electrosorption on graphene is electrode distance. Graphene chloride removal effectiveness increases with electrode spacing, regardless of electrolytic concentration. Chloride ions travel less with reduced spacing, allowing for a thick EDL. A dense EDL eliminates chloride ions, producing excellent removal efficiency at 1.0 cm.

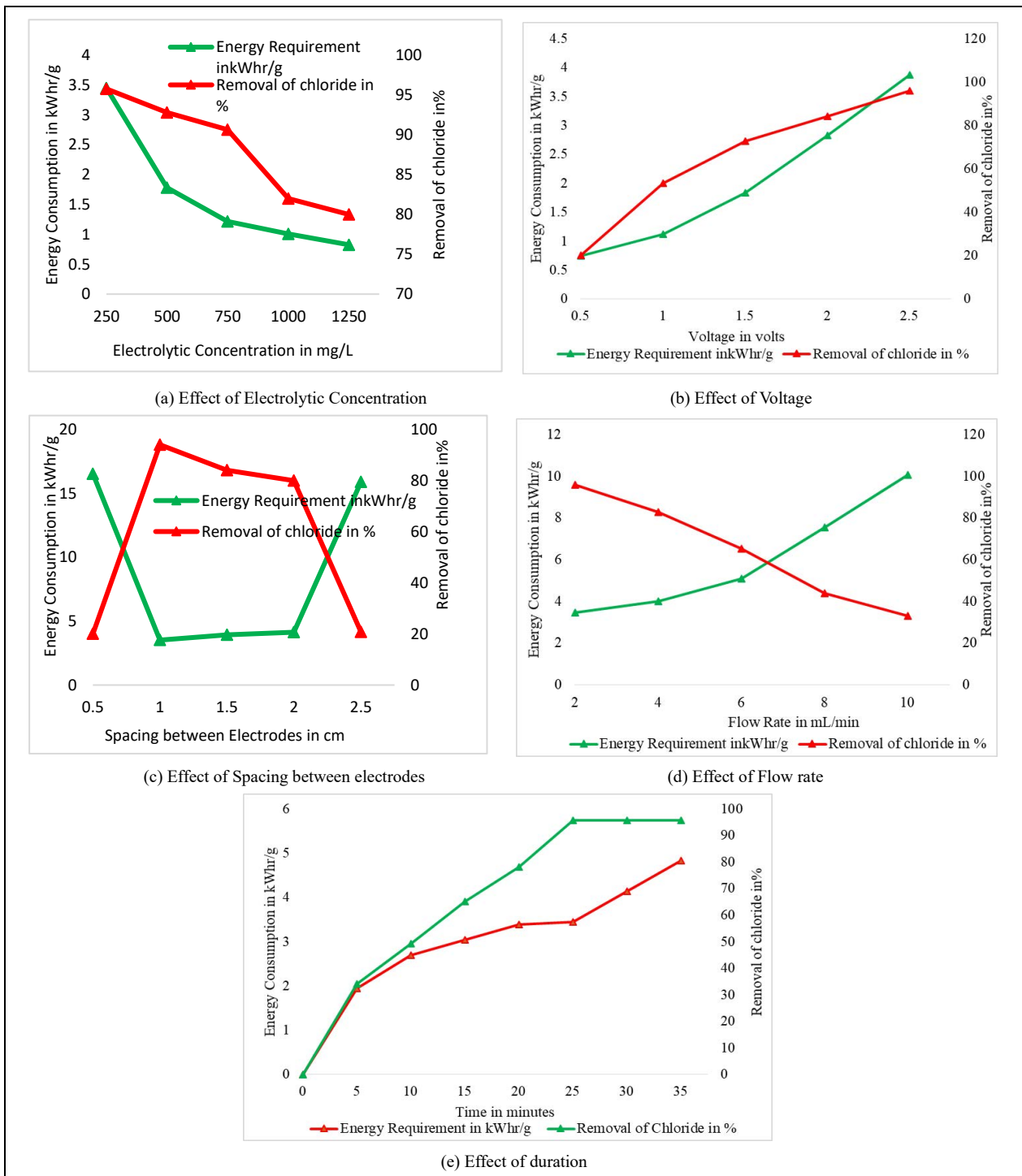


Fig. 5: Energy consumption

Conversely, decreasing graphene electrode spacing decreases removal efficiency. Although reducing graphene electrode spacing increases removal efficiency in theory, it causes electric field overlap. The abrupt voltage surge and DC supply excess indicate short-circuiting due to overlapping. When separation exceeds 1.0 cm, chloride ions must travel farther. The electrostatic force of attraction decreases when graphene electrodes are farther apart, reducing chloride ion elimination.

3.2 Kinetics

A peristaltic pump was used to pump an electrolytic concentration of 250 mg/L chloride at a 6 mL/min flow rate. The spacing between the electrodes was kept at 0.8 cm, as determined from the optimization studies. The chloride concentration of the output at 5-minute intervals was analyzed until the electrosorption process reached equilibrium. Equilibrium concentration was used to analyze the kinetics of chloride transport towards graphene (Fig. 4 and Table 4).

Table 4. Kinetic Parameters

Model	Kinetic Parameter	R ² Value
First Order	0.27 min ⁻¹	0.9738
Second Order	0.004 g/mg.min	0.9072
Elovich Kinetics	0.04 mg/g.min	0.9982
Particle Diffusion	25.056 mg/gmin ^{0.5}	0.9982
Pore Diffusion model	0.2112	0.9861

The electrosorption of chloride on graphene follows Elovich kinetics and intra-particle diffusion model based on R². When intra-particle diffusion is linear with intercept, then the diffusion is not alone as a rate-limiting step. On the other hand, it involves some boundary layer concepts simultaneously (Vareda, 2023). Elovich model is suitable for sorption involving chemisorption without desorption. Hence, from this study, it may be concluded that the intra-particle diffusion and chemisorption process governs chloride removal by electrosorption on graphene.

3.3 Energy Analysis

The energy requirement was analyzed by varying operational parameters such as electrolytic concentration, duration of CDI process, voltage, pH, spacing between electrodes, and flow rate (Fig. 5).

Since chloride removal efficiency is maximum when the initial concentration is 250 mg/L, the energy requirement is also high at 3.45 kWh/g. The least energy of 0.826 kWh/g is required when the initial concentration of feed water is 1250 mg/L (Fig. 5a). The energy requirement is 0.741 kWh/g when the applied potential is 0.5V and 1.12 at 1.0 V. The energy requirement increases as voltage increases, reaching a maximum of 3.96 kWh/g

at the applied potential of 2.5V (Fig. 5b). When the spacing was increased to 1.0 cm, the energy requirement of the system decreased to 3.52 kWh/g with 94% chloride removal. After that, as the distance between the electrodes increases, the energy requirement of the system increases and reaches a maximum of 15.89 kWh/g (Fig. 5c). The energy requirement increases with a higher flow rate and decreases with a decrease in flow rate up to 2 mL/min. The maximum energy of 10.48 kWh/g is required when the flow rate is 10 mL/min, whereas a minimum energy of 3.45 kWh/g is required when the flow rate is 2 mL/min (Fig. 5d). The maximum energy required to remove chloride is 4.833 kWh/g (Fig. 5e).

4. CONCLUSION

Graphene was employed as the active electrode material in fabricating a CDI cell. The electrode was fabricated by applying a coating of graphene, PVdF, and DMA as a binder and solvent onto a copper plate. Based on the R² value and kinetic experiments, chloride electrosorption on graphene follows Elovich kinetics and the intraparticle diffusion model. Furthermore, it can be deduced that the elimination of chloride through electrosorption on graphene is regulated by intraparticle diffusion and chemisorption processes. Graphene exhibits energy requirements of a maximum of 4.833 kWh/g and a minimum of 1.945 kWh/g. The efficiency of the CDI process is contingent upon the transportation of ions from an aqueous solution through the pores of the electrode material, in addition to the specific surface area, specific capacitance, and formation of an electric double layer (Rafael *et al.* 2016). The thickness of electrode is the governing parameter for ion transport. Therefore, prioritizing the thickness of the coated electrode material will be essential in the near future.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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