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Alfredy, Tusekile

Hindawi

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Research Article

Capacitive Deionization for the Removal of Paraquat Herbicide from Aqueous Solution

Tusekile Alfredy ^{1,2}, Joyce Elisadiki ³, and Yusufu Abeid Chande Jande ^{1,2}

¹Department of Materials and Energy Sciences and Engineering, The Nelson Mandela African Institution of Science and Technology, P.O. Box 447 Arusha, Tanzania

²Water Infrastructure and Sustainable Energy Futures (WISE-Futures) Centre, The Nelson Mandela African Institution of Science and Technology, Nelson Mandela Road, Tengeru, P.O. Box 9124, Arusha, Tanzania

³Department of Physics, College of Natural and Mathematical Sciences, University of Dodoma, P.O. Box 338 Dodoma, Tanzania

Correspondence should be addressed to Yusufu Abeid Chande Jande; yusufu.jande@nm-aist.ac.tz

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In comparison to other conventional methods like adsorption and reverse osmosis (RO), capacitive deionization (CDI) has only been investigated extensively for the removal of inorganic pollutants from water, demonstrating limited practicality. Herein, the study investigated the use of CDI for the removal of paraquat (PQ) herbicide from water by using commercial activated carbon (AC) electrodes. The CDI performance was examined as a function of the initial PQ concentration, applied voltage, flowrate, treatment time, and cycle stability testing in the batch mode approach. The applied voltage had a beneficial effect on the removal efficiency, whereas the removal efficiency of PQ declined as the initial PQ concentration increased. However, the electrosorption capacity gradually increased with the increase of initial feed solutions' concentration. The maximum removal efficiency and electrosorption capacity achieved at 5 mg/L and 20 mg/L PQ initial concentrations, an applied voltage of 1.2 V, and 5 mL/min flowrate were 100% and 0.33 mg/g and 52.5% and 0.7 mg/g, respectively. Washing the electrodes with distilled water achieved sequential desorption of PQ, and the process produces a waste stream that can be disposed of or treated further. Therefore, the CDI method is considered a promising and efficient method for removing organic pollutants from water including pesticides.

1. Introduction

The demand for safe and clean water has been rising as the earth's population keeps increasing. Activities that are associated with population growth have a great impact on environmental pollution as different compounds are released into the environment as a result of human and industrial activities [1]. Pesticides, hormones, food additives, laundry detergents, plasticizers, surfactants, wood preservatives, disinfectants, and flame retardants are examples of these contaminants discharged to the environment [2]. In recent decades, pesticides in agricultural activities are increasing to meet the food demand for population growth. The usage of various kinds of pesticides has contaminated all of life's necessities: food, water, and air [3]. Agricultural wastewater issues have gained much attention and become a burning issue because their

management is still challenging. The release of agricultural wastewater into the environment without proper regulation poses a major hazard to human health and the environment in general [4]. According to Dulio and Slobodnik [5] around two (2) million tons of effluent is being discharged into freshwater, polluting water sources.

Paraquat (PQ) (1,1'-dimethyl-4,4'-dipyridinium chloride) or methyl viologen, by brand name known as gramoxone, is amongst the commonly and widely used herbicide compounds in agriculture worldwide [6], and over 100 countries had been applying it since 1962 [7]. Paraquat is a broad-spectrum, nonselective contact herbicide used to suppress narrow leaf and broadleaf weeds in both nonagricultural and agricultural settings. It is applied in the cultivation of tobacco, rice, coffee, grapes, beans, apples, soybeans, sugarcane, and other crops [8, 9].

Exposure to PQ can be extremely harmful to the body organs, including the lung, brain, muscles, liver, adrenal glands, and kidney, either accidentally or deliberately and even results in death [10, 11]. Various studies reported on the linkage between Parkinson's disease and paraquat usage [12, 13]. Paraquat can enter into the water supplies and is considered a threat to human health even at a low level. Because of the cationic charge present on the molecule, paraquat's (PQ) high solubility in water (620 g/L) increased the contamination risk of PQ to water sources [14]. The maximum allowable PQ level in drinking water has set to be 0.01 mg/L [11, 15]. Thus, removing PQ from water and decreasing PQ poisoning is of great significance when it comes to water pollution. Therefore, the development of low-cost, high-efficiency technology for removing PQ from water is vital.

Pesticides and different organic matters have been removed from water using a variety of techniques including adsorption [16, 17], membrane separation processes [18, 19], photodegradation [20], and advanced oxidation processes [21, 22]. Because of its high removal efficiency, ease of design, and cheap operational cost, adsorption has been extensively explored among the methods listed above [4, 23–25]. Despite its interesting attributes, the adsorption process faces numerous challenges including a short lifespan due to low regeneration capacity [26] and usage of acid or alkali during the regeneration process which results in secondary water pollution [27]. Organic pollutants are removed effectively using membrane separation technology. On the other hand, membrane processes face challenges such as membrane fouling or deterioration, making them impractical and costly in terms of energy consumption, installation, and maintenance [28–30]. The photodegradation approach can degrade organic pollutants under ambient conditions by using visible light from the sun as energy and O₂ in the air as an oxidant, as well as oxidation of organic compounds even at low concentrations [31–33]. However, the major disadvantage of this process is the insufficient sunlight utilization and ambiguous reaction mechanism [20]. Additionally, advanced oxidation processes (AOPs) have been successfully used to decompose many hazardous chemical compounds to acceptable levels at or near ambient temperature and pressure and produce no further hazardous by-product or sludge that requires additional handling, but the techniques are capital demanding (costly) and require complicated chemistry to be tailored to specific applications, and in some applications, quenching of excess peroxide is required [34, 35]. Therefore, technologies that will overcome the challenges of regeneration of adsorbents, fouling, and energy consumption in the water treatment arena are highly needed.

Capacitive deionization (CDI) is an emerging desalination method that is being investigated as an alternative to the above-mentioned technologies. In CDI, ions from an electrolyte are adsorbed on electrodes under the influence of both an applied electric field and inherent chemical surface charges [36]. When the electric field is removed, the ions held in the electric double layers (EDLs) at the electrode surface are released back into the bulk solution. Therefore, short-circuiting the electrode or applying a reverse or zero voltage during the discharge process makes it simple to

regenerate the adsorbent with CDI [27]. Also, CDI's energy expenditure during its operation is low [37], but also, it has high water recoveries, low fouling, and secondary pollution prevention [38, 39].

Various materials including intercalation electrode materials such as MXenes [40], manganese oxides [41], Prussian blue (PB) and its equivalents [42], and carbon-based materials like graphene [43], carbon nanofibers [44], activated carbon (AC) [45], and carbon nanotubes (CNTs) [46] have been investigated as CDI electrode materials. However, carbon-based materials are the most commonly utilized materials for removing various contaminants from water (both inorganic and organic pollutants) because of their environmental friendless and cost-effective materials [47, 48] together with the high surface area [49, 50]. In the removal of organic contaminants from water, CDI with AC electrodes has shown promising performance. Senoussi and Bouhidel [51], for example, used granular activated carbon as a CDI electrode to remove textile cationic dyes from industrial wastewater in their investigation. The maximum removal efficiency and electrosorption capacity achieved was 98% and 1.75 mg/g at 2 V and 10 mL/min flowrate. Lester Yaal et al. [52] looked into using activated carbon as an electrode material in a CDI to remove salt and trace organic contaminants (bisphenol A, estrone, carbamazepine, and pentoxifylline) from water. The removal efficiency of the trace organic contaminants follows the order of bisphenol A > estrone > carbamazepine > pentoxifylline. The removal efficiency of bisphenol A was reported to be over 90% by the authors. Based on that, we anticipate that CDI with AC electrodes can also be used to remove PQ herbicide from water since it is cationic in nature.

To the authors' knowledge, no study investigated the application of AC as CDI electrode materials for removing PQ contaminants from water. Therefore, this study investigated the suitability of commercial AC as CDI electrode materials for the removal of PQ from an aqueous solution for the first time. The influence of various CDI operational factors, such as initial concentration of PQ, applied voltage, flowrate of the solution, treatment/charging time, and cycle stability of AC for PQ removal, was examined in batch mode experiments.

2. Materials and Methods

Finar Chemicals India provided the commercial AC used in this study. Before the experiments, AC was rinsed multiple times with distilled water until the effluent's pH was neutral, then filtered using the filter unit, and dried at 90°C for 3 hours. The AC used in this study was previously characterized by the literature [53]. It had 1295 m²/g BET surface area, type IV isotherms, and many microspores, and the FTIR data revealed the presence of the following bonds: C-O, O-H, C-H, and O-H. Sigma-Aldrich provided paraquat (1,1'-dimethyl-(4,4'-bipyridilium dichloride, 99.3%), carbon black (conductive material), and polytetrafluoroethylene (PTFE, 60 wt % dispersion in H₂O) as a binder, while Chem-Lab NV in Belgium provided ethanol (100%). All of

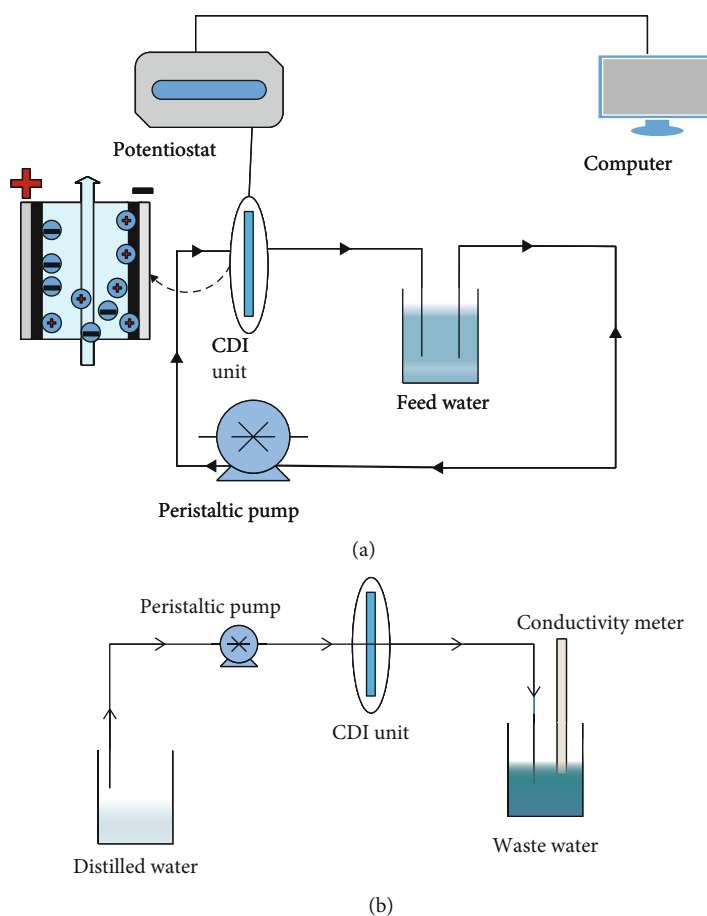


FIGURE 1: Schematic diagram of the CDI experiment setup: (a) purification; (b) regeneration.

the chemicals used were analytical grade and did not need to be purified further.

2.1. Fabrication of AC Electrodes for CDI Cell. In this study, an AC electrode was prepared by mixing 80 wt % of AC as an active material, 10 wt % of conductive carbon black, and 10 wt % of PTFE binder. The mixture was then added with 20 to 30 mL of ethanol and agitated to achieve homogeneity until a dough-like paste formed. The paste was pressed to the required thickness, cut into 3.5 cm by 3.5 cm pieces, and dried in a vacuum oven at 50°C overnight before being tested for leftover solvents. Finally, the electrodes were assembled into a CDI cell to test its electrosorption capacity and removal efficiency. Both AC electrodes used in the CDI tests have a combined mass of about 0.6 g.

2.2. Capacitive Deionization Experimental Setup and Procedure. The electrosorption experiments were carried out in a batch mode in a laboratory-scale CDI reactor (Figure 1(a)) to evaluate the effectiveness of commercial AC in removing PQ. A solution tank, a peristaltic pump, a pair of electrodes, an electrochemical workstation potentiostat (equipped with IviumSoft electrochemistry software), a digital conductivity meter, and a digital pH meter were all part of the CDI system.

To ensure electrolyte flow and prevent short circuit, a pair of AC electrodes were put on stainless steel sheet current collectors, separated by a plastic mesh placed between the carbon electrodes. To seal the cell, rubber gaskets were added, and all of the components will be covered with plexiglass and tightened with screws. A 20 mg/L aqueous paraquat (PQ) solution was prepared by dissolving 20 mg of paraquat dichloride in deionized water to fill a round bottom flask with 1000 mL of the solution. The above-prepared solution was kept in the refrigerator at 4 to 5°C and was utilized for about a month without showing any signs of PQ degradation. Using the series dilution approach, a PQ solution with concentrations of 5, 10, and 15 mg/L was prepared by diluting the stock solution (20 mg/L) in a 100 mL volumetric flask.

During CDI operation, 40 mL of PQ solution with varying concentrations (5 to 20 mg/L) was supplied to the CDI cell using a peristaltic pump (MasterflexLive™, L/S® series), and the circulated feed solution was returned to the feed tank with a flowrate of 5 and 10 mL/min. To evaluate PQ herbicide electrosorption, electric potentials of 0.8, 1.0, and 1.2 V were provided to the CDI cell at electrode terminals via a potentiostat/galvanostat (Vertex.1A.EIS 1A/10 V/1 MHz EIS, Ivium Technologies, the Netherlands), as well as a control experiment (with no voltage applied) for comparison. After 1 hour, the solution in the feed tank

was taken, and the concentration of PQ in the solution was analysed using a UV-VIS spectrophotometer. In addition, to determine the change in PQ concentration over time, 2 mL of PQ solution was drawn after every 10 min interval, and the change in PQ concentration was determined using a UV-Vis spectrophotometer. Desorption of PQ pollutants was done by recirculating distilled water through the CDI system for approximately 30 min (Figure 1(b)). The removal efficiency RE (%) and electrosorption capacity r (mg/g) were calculated using Equations (1) and (2), respectively. Distilled water was used as a blank in this study (containing no paraquat).

$$RE = \frac{C_o - C_f}{C_o} \times 100\%, \quad (1)$$

$$\Gamma = \frac{(C_o - C_f)}{m} \times V, \quad (2)$$

where C_o and C_f represent the initial and equilibrium PQ concentrations (mg/L), respectively; V is the total volume of the solution (mL); and m is the mass of active material in both electrodes in grams [54].

3. Result and Discussion

3.1. The Measurement of the Absorption Spectrum of PQ. A UV-Vis spectrophotometer (UVmini-1240, Serial No. 10934402550, Shimadzu Corp.) equipped with a quartz cuvette with 10 mm of the optical path was used to measure the PQ absorption spectrum corresponding to PQ concentrations of 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 mg/L. The used UV-Vis emits electromagnetic light with wavelengths ranging from 190 to 1100 nm. The UV-Vis spectrophotometer method was used to determine the concentration of the solution, with the absorption of light by the solution being a function of concentration. The standard paraquat calibration curve depicts the linear relationship between concentration and absorbance (Figure 2).

After CDI experiments, the equilibrium concentration of paraquat herbicide was measured using the calibration curve of paraquat standard for paraquat concentrations ranging from 2 to 20 mg/L, as shown in Figure 2. In determining the paraquat solution's absorption spectrum pattern between 190 and 640 nm, the solution's maximum wavelength data was 257.5 nm. The maximum wavelength determined was used for later PQ absorption spectrum solution measurements.

3.2. CDI Performance. Electrosorption tests were carried out to study the CDI performance on the PQ removal from water using commercial AC electrodes. The variable CDI operational parameters investigated were concentration (5, 10, 15, and 20 mg/L), applied voltage (0.8, 1.0, and 1.2 V), flowrate of 5 and 10 mL/min, treatment/charging time (10, 20, 30, 40, 50, and 60 min), and cycle stability of AC electrode for PQ removal for comparison.

3.2.1. Effect of Voltage on the PQ Removal. At a flowrate of 5 mL/min, Figure 3 depicts the changes in concentration

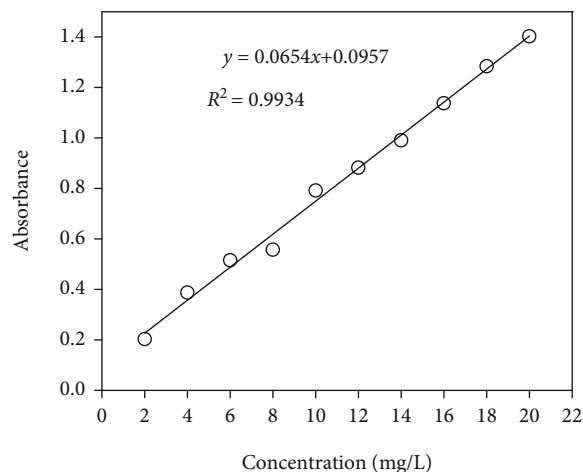


FIGURE 2: Calibration curve of PQ standard.

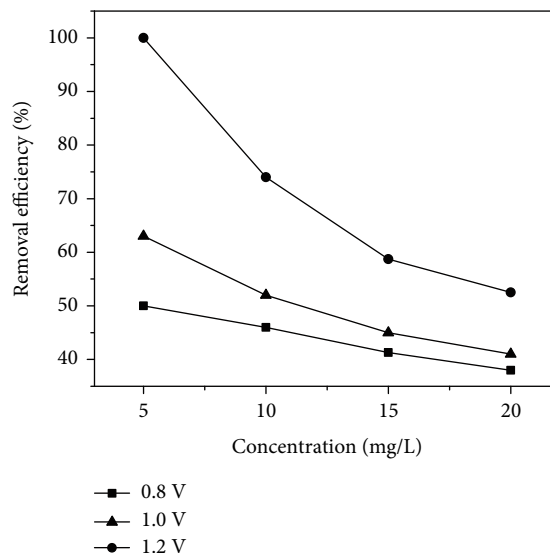


FIGURE 3: Removal efficiency of PQ at different applied voltages at a flowrate of 5 mL/min.

and removal efficiency as a function of applied voltage. The voltages above 1.2 V were not investigated to prevent water electrolysis and undesired faradaic reactions on the electrode [55], thus controlling the applied voltage became an important factor [56]. Because of the larger electrostatic forces caused by the increased potential, the removal efficiency rose as the applied voltage was increased from 0.8 to 1.2 V [57]. Herein, higher PQ removal was achieved at 1.2 V with the initial concentration of 5 mg/L, as presented in Figure 3.

3.2.2. Effect of PQ Initial Concentration on the Removal Efficiency. One of the most critical parameters affecting the operation of the CDI system is the initial concentration of the feed solution, as it might affect the effluent concentration of the outlet stream [58]. Herein, the CDI tests were carried out to investigate the influence of the initial concentration of PQ herbicide by varying the PQ concentration from 5 to

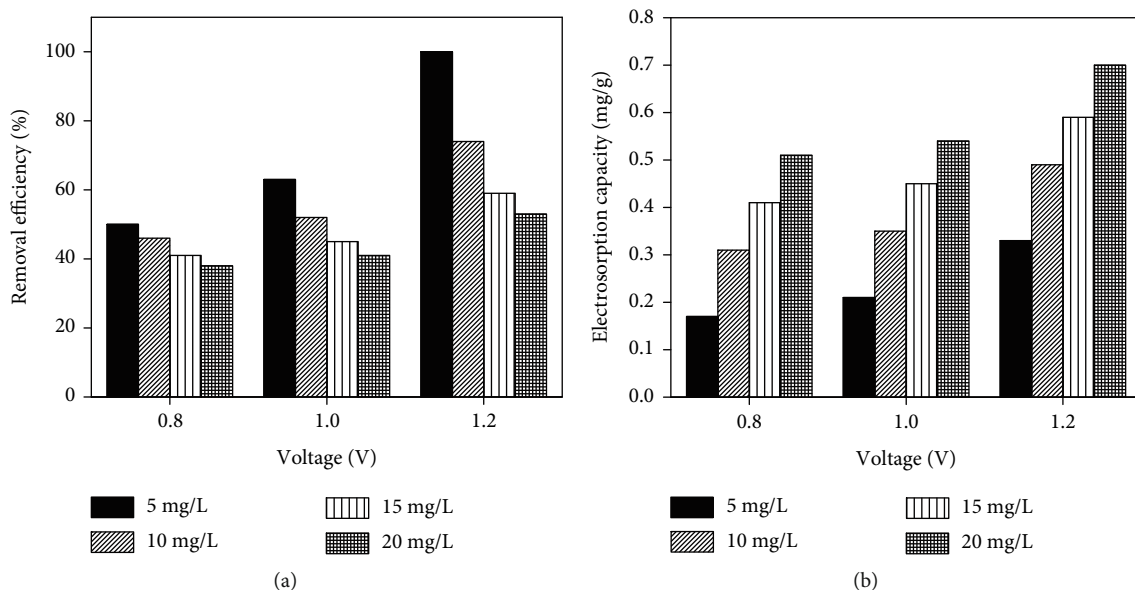


FIGURE 4: The removal efficiency and the electrosorption capacity of AC electrodes at various initial concentrations of PQ at different cell voltages and flowrate of 5 mL/min.

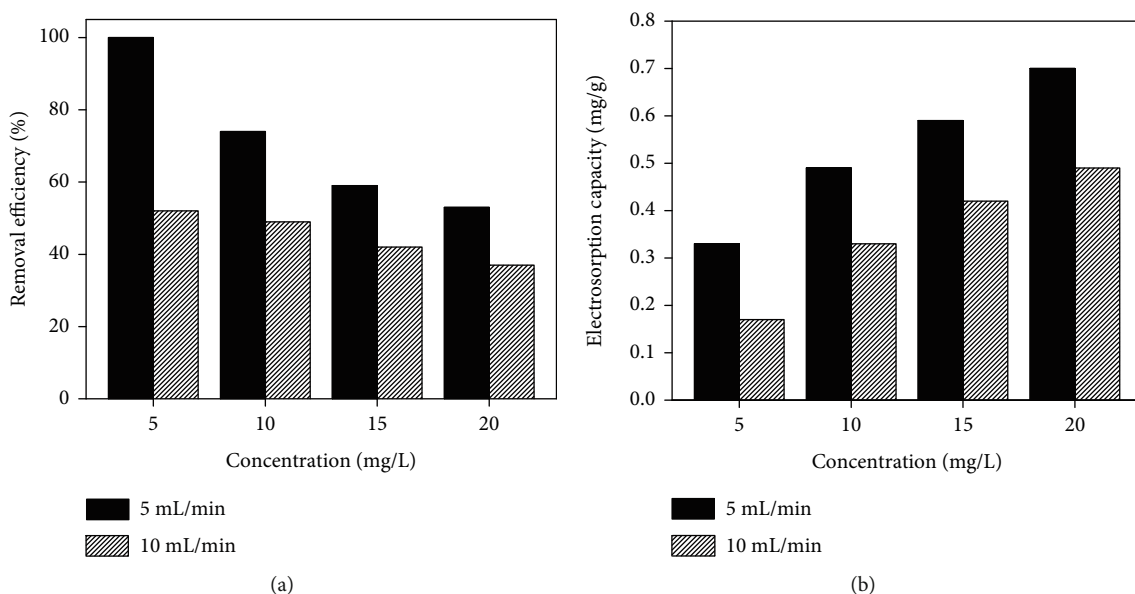


FIGURE 5: Effect of flowrate on the (a) removal efficiency and (b) electrosorption capacity of PQ onto AC electrodes at various initial feed concentrations.

20 mg/L at a constant flowrate of 5 mL/min and a voltage of 1.2 V. Figure 4(a) shows that removal efficiencies declined as PQ initial concentration increased, a tendency that has been observed in several relevant studies [57]. The PQ removal efficiency of 100%, 74%, 58.7%, and 52.5% was attained when using the PQ initial concentrations of 5, 10, 15, and 20 mg/L, respectively. The decline of removal efficiency as the initial feed concentration increases could be attributed to the quicker saturation of electric double layers (EDLs) at a higher inlet concentration [58, 59]. Figure 4(b) demonstrates that the electrosorption capacity is dependent on the initial concentration

of the solution; electrosorption capacity increases as the concentration of the solution increases. The electrosorption capacity of the AC electrode rose by 4.1 times as the PQ concentration increases from 5 to 20 mg/L. The expansion of diffuse double-layer capacity, which is mostly dependent on the electrolyte solution concentration, could explain the favourable effect of the initial concentration on the AC electrodes' electrosorption capacity [57].

3.2.3. *Effects of Flowrate on PQ Removal.* Flowrate is also among the important parameters to consider in CDI

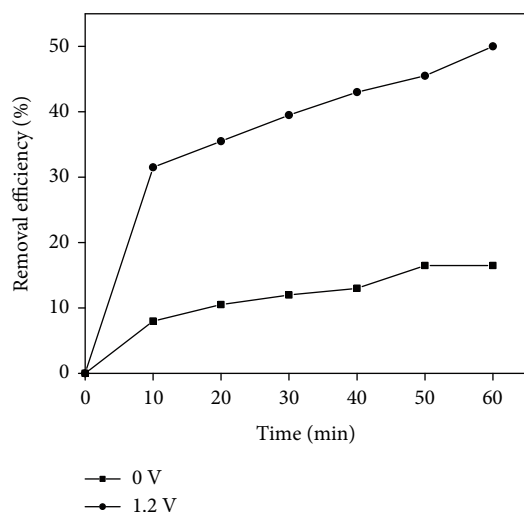


FIGURE 6: PQ removal versus time.

performance [60]. In the present study, the influence of two different flowrates on the CDI operation for removing PQ by keeping the applied voltage of 1.2 V was investigated. Figure 5 depicts the removal efficiency and electrosorption capacity improvement at a flowrate of 5 mL/min. Increasing the flowrate was found to decrease CDI performance because the contaminated water is not given enough time to interact with the electrode surface resulting in reduced performance as also observed by the literature [61]. Less residence time gives the ions a short time to migrate towards the electrodes for electrosorption, resulting in reduced desalination performance [60, 62]. In this study, the flowrate of 5 mL/min for the AC electrode is recommended as the optimum condition for the removal of PQ from water as it shows good performance in all concentrations under study.

3.2.4. Variation of PQ Concentration with Time. With treatment/charging time, the ionic concentration in the solution decreases as part of the ion adsorb on the electrodes [63]. For a 5 mL/min flowrate and an initial PQ concentration of 20 mg/L, the change in PQ concentration with time at 0 and 1.2 V was examined (Figure 6). When a potential of 1.2 V was applied, the concentration dropped significantly in the first 10 minutes, indicating that PQ was rapidly electrosorbed onto the electrode surface. This could be owing to a large number of active sites on electrode surfaces that are available for electrosorption. As time increases the active sites and PQ concentration is decreased, electrosorption decreased until an electrosorption equilibrium concentration was reached. The PQ removal efficiency was up to 16.5% at 0 V; however, when voltage of 1.2 V was supplied, the removal efficiency improved to 50%.

3.2.5. Regeneration of Spent AC Electrodes. The electrode materials' recyclability and stability are important factors in determining the commercial success of the developed materials for industrial CDI applications. The results of recyclability testing of AC CDI electrodes using 20 mg/L of PQ feed solution are shown in Figure 7. The recyclability

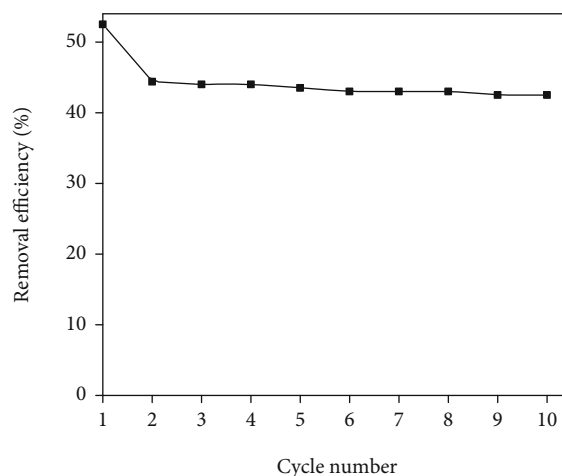


FIGURE 7: Reusability studies of AC electrodes at 1.2 V using a feed solution of 20 mg/L at 5 mL/min.

tests were carried out for ten (10) cycles, with the removal efficiency of the electrode materials being examined for each cycle. The CDI cycles were performed at 1.2 V and 5 mL/min flowrate for 1 h. The saturated AC electrode was regenerated by washing the AC electrode with distilled water for approximately 30 min until the conductivity of the concentrate approaches the distilled water's conductivity. As demonstrated in Figure 7, the PQ removal efficiency reduces from 52.5% to 44.4% after the first cycle of reuse and then to 42.5% after 10 cycles of reuse. The removal efficiency dropped by 19% after the electrodes have been washed and reused for 10 cycles.

4. Conclusion

The suitability of commercial AC as CDI electrode materials for the removal of PQ pollutants from water was studied in the current study. The effect of different experimental factors, including initial solution concentration, cell voltage, flowrate, treatment time, and cycle stability on PQ removal during the CDI operation process was studied. The result showed that CDI can be thought as an alternative for the removal of PQ from wastewater. Increasing the applied voltage (ranging from 0.8 to 1.2 V) led to improved PQ removal in the feed solution while the increase in flowrate decreases the CDI performance. Furthermore, because of the limited electrosorption sites on the AC surface, an increase in PQ concentration had a detrimental impact on the removal efficiency of AC electrodes. Furthermore, the study demonstrates that the spent AC can be regenerated by washing it with water, which is environmentally friendly and reused for some time without a significant loss of its electrosorption capacity. Therefore, with consideration of CDI operating parameters, CDI is regarded as an alternative method for removing different organic pollutants from water, including PQ herbicide.

Data Availability

All data generated or analyzed during this study are included in this manuscript.

Conflicts of Interest

There are no conflicts of interest declared by the authors.

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