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Capacitive deionization (CDI) for removal of phosphate from aqueous solution

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ABSTRACT

In this investigation, a commercial capacitive deionization (CDI) unit is utilized to treat phosphate wastewater. CDI deionization studies were performed to evaluate the effects of various experimental parameters, including initial pH, flow rate, and initial concentration on the removal of phosphate. The optimal pH value was around 5–6. The CDI removal efficiencies obviously decreased as the flow rate (1.6–8.0 L/min) or the initial phosphate concentration (50–300 mg P/L) increased. The highest removal of phosphate and reduction in conductivity were 86.5 and 81.5% obtained at a flow rate of 4.8 L/min, and an initial phosphate concentration of 50 mg P/L, and the lowest were approximately 77.4 and 73.1% obtained at an initial phosphate concentration of 300 mg P/L. A three-stage treatment yielded a reduction in conductivity and a removal of phosphate up to 98 and 93%, obtained at a phosphate concentration of 300 mg P/L. A pseudo-first-order rate model was adopted to describe the kinetics of electrosorption, and the k value was found to be about 0.88 min^{-1} at an initial phosphate concentration of 300 mg P/L. The energy consumption clearly increased with an increase in the initial phosphate concentration and decreased with an increasing in the flow rate. The optimal operating condition was a flow rate of 4.8 L/min for per unit of phosphorus removed, and the energy consumption for the treatment of wastewater was 7.01 kWh/kg P (removed) (or 1.65 kWh/m^3). The advantages of the CDI process are low cost and the lack of need for any chemical to be used. CDI is a suitable technology for removing phosphate from wastewater.

Keywords: Capacitive deionization (CDI); Electrosorption; Phosphate; Desalination

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1. Introduction

Phosphorus (P) is commonly present in low concentrations in wastewater. It is present almost solely as phosphates, including organic phosphate, inorganic phosphate (orthophosphate), and polyphosphate (particulate P). Its release to surface water is an environmental concern, because it is a critical and often limiting nutrient for the growth of organisms in most ecosystems, and so it is a major cause of eutrophication [1]. Discharges of wastewater from industry and agriculture as well as domestic sewage are major sources of phosphate pollution, so phosphate wastewater management is an important environmental issue [2]. The photoelectronic industry, specifically for the manufacturer of TFT-LCD, produces large amounts of wastewater with high concentrations of phosphate. Many phosphate removal methods, including chemical coagulation, biological treatment, crystallization, advanced chemical precipitation, ion exchange, magnetic, and adsorption, have been widely examined [2–7].

Capacitive deionization (CDI), which is regarded as one of the most efficient and economic technologies for desalination, is an electrochemically controlled method for removing salt from aqueous solutions. Desalination occurs, when a saline solution flows through an unrestricted capacitor type module that comprises numerous pairs of high surface area electrodes, such as carbon aerogel electrodes [8–10], nanoporous activated carbon cloth [11], carbon nanotube electrodes [12], and reduced graphene oxide and activated carbon composite electrodes [13]. The charged ions are attracted within the electrical double layer formed between the solution and the electrode interface, when the electrode is electrically charged by an external power supply. The CDI deionization system was developed as a potential technology for removing inorganic ions from aqueous solutions to treat water/wastewater [9,14–18]. Although CDI systems are commercially available, and various demonstration desalination projects are ongoing, the phosphate removal capabilities of CDI are not currently being extensively studied and emphasized.

In this investigation, electrosorption experiments were carried out using a CDI unit to study the efficiency treatment of phosphate-containing wastewater and to evaluate the effect of operational conditions on treatment efficiency and energy consumption.

2. Experimental methods and materials

2.1. Materials and analytical method

Synthetic solutions were prepared from deionized water made by CDI (tap water inlet) that was spiked with KH_2PO_4 to a phosphate concentration of approximately 300 mg P/L, which is the concentration in a wastewater stream from a certain TFT-LCD factory in Taiwan. The total hardness and conductivity for tap water and deionized water are 108.7, 3.2 mg/L as $CaCO_3$ and 254, 8.3 μS/cm. The pH adjustment used NaOH in this study. Phosphate concentration was measured by ion chromatography (IC, 732 IC Detector, A Supp 1 column, Metrohm). A portable WTW Cond 330i meter was used to determine the conductivity of the feed and the purified water. The electrical energy consumption of the CDI unit was measured using a power meter (SONDAR, SPG-26MS).

2.2. CDI pilot

The CDI pilot plant utilized in this research was developed by AQUA EWP. Fig. 1 schematically depicts the CDI unit that was used. The influent water is pumped from a storage tank through a 10-μm filter for pretreatment and through a flow meter to measure the influent flow. It then flows into two carbon electrode cells that are connected in parallel. Electrodes used are made from activated carbon, and the surface area is 100 cm^2 (with dimensions of 10×10 cm) with 200 sheets of pairs. The working size of the tested unit is around 2,880 cm^3. The control panel circuits are all 240 VAC with a mean current of 5 A and a single-phase electrical supply.

The power is delivered in parallel to two cells with a voltage of 7.5–8.0 VDC. The voltage is further divided by a series connection to the cell terminals at about DC 1.5 V, such that no electrolysis reactions occurred. The operational cycle of CDI takes 2.5 min and comprises two main steps, which are the regeneration step (Regen-step1, Regen-step2, and Prepurify step) and the purification step (Purify step).

The regeneration step lasts for 30 s (Regen-step1), while the power supply is turned off and continues for another 30 s, while the power with the opposite polarity is turned on during the first 20 s (Regen-step 2) of the second 30 s. The regeneration step is complete after 60 s. The purification step follows the Prepurify step with 10 s and lasts for 90 s to purify the feed solution. In this period, the valve to the purified water tank is opened; the valve to the wastewater tank is closed and the power is turned on. Table 1 presents the operating sequence of the commercial CDI unit.

2.3. Experimental method

A series of laboratory experiments was conducted to investigate the effect of operational conditions (phosphate concentration, flow rate, and pH level) on the CDI desalting efficiency and energy consumption.

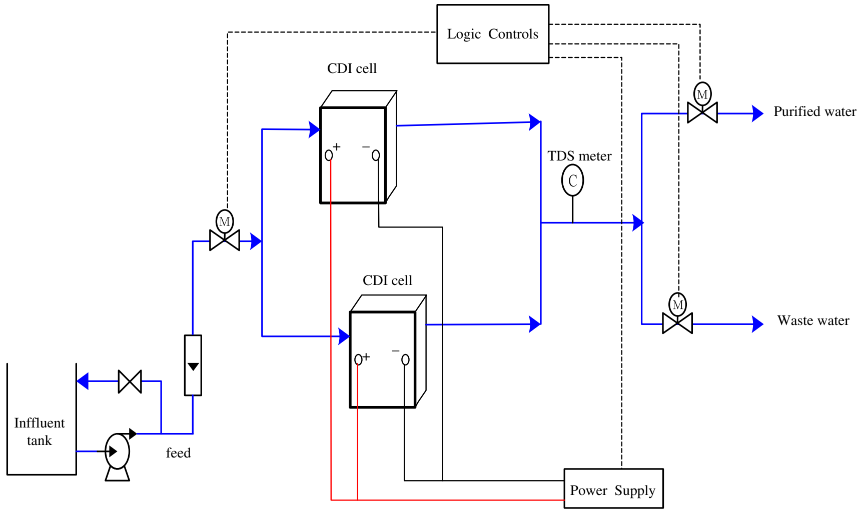

Fig. 1. The CDI schematic diagram.

Table 1
The sequence of operation for the commercial CDI unit

Process	Time (s)	Feed pump	Valve to purify tank	Valve to waste tank	Power supply voltage* (V)
Regen-step1	30	OFF	OFF	OFF	0
Regen-step2	20	ON	OFF	ON	8
Prepurify step	10	ON	OFF	ON	0
Purify step	90	ON	ON	OFF	8

*The power is delivered in series to four cells with a voltage of 7.5–8.0 VDC.

These experiments were performed as follows. First, the pH level of the feed flow was gradually increased from 3 to 10 at a flow rate of 4.8 L/min and a phosphate concentration of 300 mg P/L. Second, the phosphate concentration of the feed solution was gradually increased from 50 to 300 mg P/L; the flow rate was kept at 4.8 L/min and the operating pH was around 4.7. Finally, the flow rate was slowly increased from 1.6 to 8.0 L/min at a phosphate concentration of 300 mg P/L and a pH of 6.0. The results obtained concerning the purified water in each cycle indicated the performance of cumulative electrosorption throughout the experimental period, rather than instantaneous adsorption. Three times repetitions were done for each experiment.

In this study, the electrosorption removal efficiency Eq. (1) was calculated as follows.

$$\text{Electrosorption removal efficiency } (\%) = \frac{C - C_0}{C_0} (\%) \tag{1}$$

where C_0 and C (mg P/L) represent the phosphate concentrations in the influent and treated streams, respectively.

3. Results and discussion

3.1. CDI removal efficiencies for various feed pH values

Fig. 2 plots the removal efficiencies of CDI in the removal of phosphate from synthetic phosphate aqueous solution, and the consequent reduction in conductivity for various feed pH values. The results demonstrate that the pH was a significant parameter in controlling the process of electrosorption.

As the pH of the aqueous solution is changed, different phosphate species dominate the solution. The following three equilibrium reactions describe the speciation of orthophosphate [19].

$$\begin{aligned} H_3PO_4 &= H^+ + H_2PO_4^- \quad && pKa_1 = 2.1 \\ H_2PO_4^- &= H^+ + HPO_4^{2-} \quad && pKa_2 = 7.2 \\ HPO_4^{2-} &= H^+ + PO_4^{3-} \quad && pKa_3 = 12.3 \end{aligned}$$

The $H_2PO_4^-$ and HPO_4^{2-} species are present in the pH region between 5 and 10. The concentration of $H_2PO_4^-$ species is higher at pH values below around 7 than at those above 7 and is highest at a pH around 5, whereas the HPO_4^{2-} species dominate for pH values of between 7 and 10 [20]. As the pH falls below 5, the

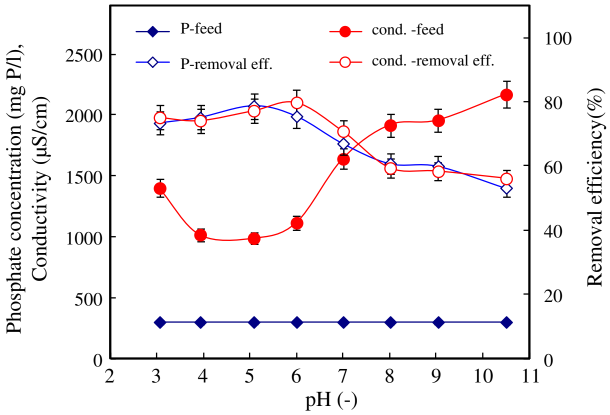

Fig. 2. Effect of pH on phosphorus and conductivity removal efficiency (at phosphate concentration 300 mg P/L, flow rate 4.8 L/min).

concentration of $H_2PO_4^-$ decreases and that of the non-charged H_3PO_4 species gradually increases.

In this study, phosphate and conductivity uptake clearly decreased as pH increased. This decreasing tendency can be attributed to the competition between phosphate ions and hydroxyl ions. The concentration of hydroxyl ions increases with increasing pH, and thus, the competition between phosphate ions and hydroxyl ions to the adsorption sites of electrodes is enhanced [21]. A higher concentration of hydroxyl ions promoted the opposite reactions to those described above, so phosphate adsorption was lower in solution with a higher pH. Therefore, the adsorption reaction was much more favorable at a lower pH. The removal of phosphate and consequent reduction in conductivity were around 80% at pH values of 5–6. Hence, CDI is effective in treating phosphate solution in an acidic environment.

3.2. Effect of feed solution phosphate on electrosorption efficiency

Fig. 3 plots the dependence of desalting efficiency on the initial feed phosphate concentration (50,100, 150, 200, 250, 300 mg P/L) at a constant flow rate of 4.8 L/min with a pH of around 4.7 (except the test run of 50 mg/L at pH 5.7). The phosphate concentration and conductivity removal efficiencies clearly decreased as the initial feed phosphate concentration increased. The removal of phosphate and the reduction in conductivity were highest, 86.5 and 81.5%, respectively, at a low phosphate concentration (50 mg/L) and lowest, 77.4 and 73.1%, respectively, at a high phosphate concentration of 300 mg/L.

3.3. Effect of flow rate on electrosorption efficiency

Fig. 4 plots the variation of phosphate removal and conductivity reduction with flow rate. The flow rate range is from 1.6 to 8.0 L/min with the retention time around 30 to 60 s. For a complex water sample from the Purify step (0–90 s) in the CDI unit, the phosphate removal efficiency decreased from 77.3 to 48.3%, as the flow rate increased from 1.6 to 8.0 L/min at an initial phosphate concentration of 300 mg P/L and an operating pH of 6.0. When the sample was taken 30–90 s into the CDI purify step (excluding the purified water that flowed in the initial 30 s) at lower flow rates (1.6–3.2 L/min), the reduction in conductivity clearly increased from 74.2 to 85.7% and from 76.7 to 80.8% at flow rates of 1.6 and 3.2 L/min, respectively. These results reveal that a flow rate of over 4.8 L/min should be used in this CDI unit to prevent an insufficiency of water for cleaning residual waste in the prepurify step.

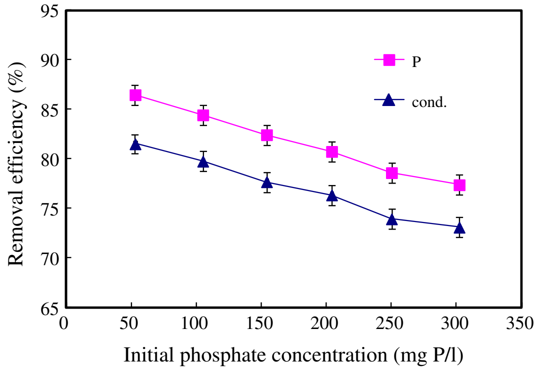

Fig. 3. Effect of initial feed phosphate concentration on phosphorus and conductivity removal efficiency (at pH = 4.7 (except the 50 mg/L test run at pH 5.7), flow rate 4.8 L/min).

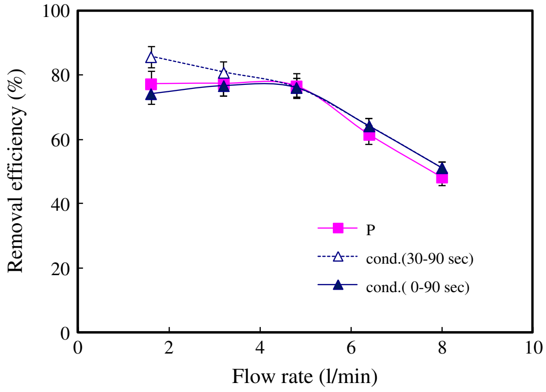

Fig. 4. Effect of flow rate on phosphorus and conductivity removal efficiency (at phosphate concentration 300 mg P/L, pH = 6.0).

3.4. Electrosorption rate constants

Adsorption kinetics is an important characteristic of an adsorbent. To investigate the kinetics of electrosorption of phosphate, the electrosorption rate constant was determined by fitting pseudo-first-order adsorption kinetics, defined as follows [22].

$$C = C_0 e^{-kt} \tag{2}$$

where k is the adsorption rate constant (min^{-1}), and C and C_0 (mg P/L) denote the purified solution concentration at time (t) and the feed concentration, respectively.

The adsorption kinetics at various phosphate feed concentrations are fitted with pseudo-first-order adsorption kinetics by using a regression analysis based on the method of least squares (Fig. 5). The results demonstrate that pseudo-first-order kinetics fit the experimental data. Furthermore, the concentration of the solution affects the rate of electrosorption. Table 2 displays the fitting parameters, including the electrosorption rate k and the regression coefficient R^2. The rate constant was 0.87–0.88 min^{-1} for a solution concentration of 100–300 mg P/L, falling to 0.72 min^{-1} as the solution concentration was increased to 600 mg P/L. The electrosorption rate at 600 mg/L was 20.8% lower than that at 100 mg/L.

Table 2
The electrosorption parameters of the pseudo-first-order kinetics at various solution concentrations (at 25℃, flow rate = 4.8 L/min)

P (mg/L)	100	200	300	600
k (min^{-1})	0.87	0.88	0.88	0.72
R^2	0.997	0.995	0.995	0.996

3.5. Effect of multi-stage treatment

When stronger treatment is required, the CDI units can be connected to three stages in series. In this study, tanks are utilized and the water is treated three times through a single unit instead of through three CDI units in series. Purified volume to wastewater volume ratio is 3:1. Fig. 6 presents the experimental result. The figure reveals that initial phosphate concentration and conductivity were 300 mg P/L and 1,187 μS/cm, respectively. The phosphate removal efficiency reached 93% for the 300 mg P/L stream, when the three-stage treatment process was used. The three-stage removal of phosphate salt by CDI treatment reduced the conductivity of the water to 20.9 μS/cm.

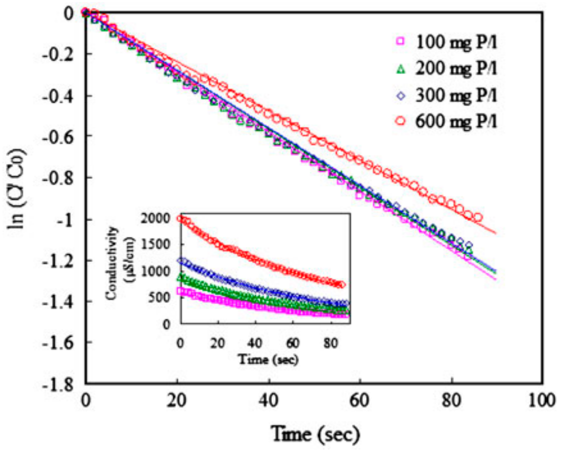

Fig. 5. The electrosorption kinetics of CDI at various solution concentrations (at 25℃, flow rate = 4.8 L/min) (the inset illustrates the effect of conductivity on purify time at various phosphate concentrations).

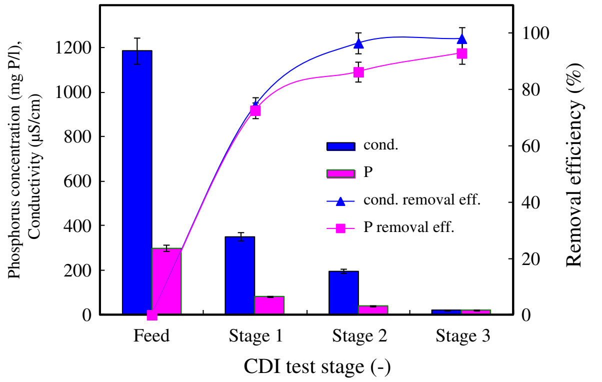

Fig. 6. Effect of treating stage in series on phosphorus, conductivity removal efficiency (at phosphate concentration 300 mg P/L, pH = 6.0, flow rate 4.8 L/min).

3.6. Energy consumption of CDI

Fig. 7 plots the effects of operating flow rate and initial phosphate concentration on the electrical energy consumption in terms of kWh/m^3 of phosphate removed. The energy consumption falls as the flow rate increases, but it increases as the initial phosphate concentration increases. Notably, the energy consumption in terms of kWh/m^3 of purified water was reduced from 2.41 to 1.19 kWh/m^3 of purified water by increasing the flow rate from 1.6 to 8.0 L/min, based on a phosphate concentration of 300 mg P/L. The energy consumption of the unit increased gradually from 0.97 to 1.65 kWh/m^3 of purified water as the initial feed concentration was increased from 50 to 300 mg P/L at a flow rate of 4.8 L/min.

A higher flow rate results in low-energy consumption in kWh/m^3. Additionally, the energy consumption

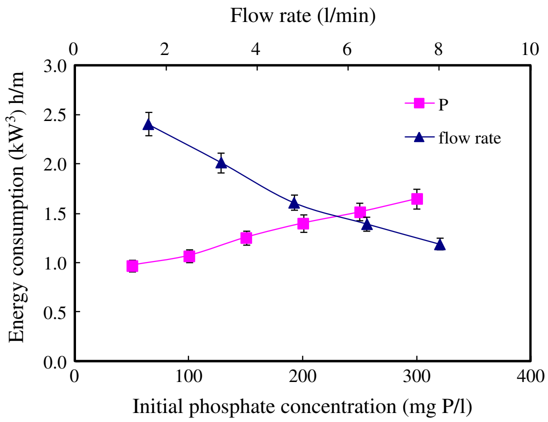

Fig. 7. Effect of initial feed phosphate concentration and flow rate on energy consumption (based on treating per cubic meter of wastewater).

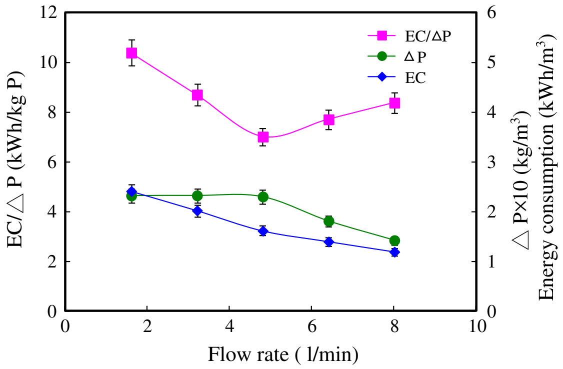

Fig. 8. Effect of flow rate on specific energy consumption (based on the removed amount in phosphorus) (EC: energy consumption per cubic meter (kWh/m^3), ΔP: phosphate removal amount per cubic meter (kg P/m^3), EC/ΔP: specific energy consumption (kWh/kg P)).

in kWh/kg P(removed) declined from 10.38 to 7.01 as the flow rate increased from 1.6 to 4.8 L/min, but it increased from 7.01 to 8.37 kWh/kg P (removed) as the flow rate was increased from 4.8 to 8.0 L/min (Fig. 8). These results suggest that CDI is a more economic approach for removing phosphate than other treatment methods, such as crystallization (3.9 €/kg P (removed)) [23]. Consequently, both the electrosorption removal efficiency and the energy consumption must be considered in determining the optimal operational flow rate. In this investigation, for treating 300 mg P/L phosphate solution, the optimal flow rate was 4.8 L/min as this rate minimized the energy consumption. In selecting the treatment capacity of a CDI unit, both the flow rate, and the power consumption must be taken into account, as the unit will only be cost-effective when the flow rate, and power consumption are within the optimal range.

4. Conclusion

A commercial CDI unit was used to study its desalting performance, and energy consumption for various values of its operational parameters. CDI was found to be an effective process for removing phosphate from water streams, offering such advantages as low-energy consumption and the lack of need for any chemicals. The results herein indicate that phosphate removal efficiency is inversely related to solution pH, initial phosphate concentration, and the applied flow rate, while CDI energy consumption is directly related to the phosphate concentration and inversely related to the flow rate.

CDI is found to be a promising alternative to conventional methods of removing phosphate from wastewater with a high concentration of phosphate (such as 300 mg P/L). Moreover, the CDI system can be combined with other methods, such as Fluidized-Bed Crystallization, to form an integrated process for treating wastewater with an excessive phosphate concentration of over 300 mg P/L, like that produced by TFT-LCD factories. We believe that CDI can play a role in treating phosphate-containing wastewater suitably and cost-effective.

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