Phosphorus removal mechanisms from domestic wastewater by membrane capacitive deionization and system optimization for enhanced phosphate removal

Process Safety and Environmental Protection

Jiaxi Jiang^{a,1}, David Inhyuk Kim^{a,b,1}, Pema Dorji^{a}, Sherub Phuntsho^{a}, Seungkwan Hong^{b}, Ho Kyong Shon^{a,*}

a Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), NSW 2007, Australia

b School of Civil, Environmental & Architectural Engineering, Korea University, Seongbuk-gu, Seoul 02841, Republic of Korea

[1] These authors contributed equally to this work.

*Corresponding author.

E-mail address: Hokyong.Shon-1@uts.edu.au (H.K. Shon).

Postal address: University of Technology Sydney, Faculty of Engineering & Information
Technology, School of Civil and Environmental Engineering, City Campus, PO Box 123
Broadway, NSW 2007 Australia

Abstract

Membrane capacitive deionization (MCDI) is an emerging technology for effective removal of charged pollutants from the water sources including domestic wastewater. In this work, a lab-scale MCDI system was employed to investigate its feasibility for effective phosphorus removal from domestic wastewater. The effect of phosphate equilibrium reactions on the ion sorption behaviour was studied in sodium phosphate buffer solution at typical pH range maintained in a real domestic raw wastewater effluent (between 6.5 and 8.5). The results demonstrated that phosphate equilibrium system has positive impact on the degree of inorganic phosphorus (P) adsorption capacity in aqueous solution. In addition, the ion selectivity of P over other co-existing anions (Cl^-,SO_4^{2-}) were experimentally studied using a synthetic wastewater solution. And it was found that the preferential electrosorption sequence of the competitive anions is: $\mathrm{Cl}^- > \mathrm{SO}_4^{2-} >$ P, while the initial ion concentration order in the synthetic feed solution is: Cl^- (1.90 mM) $>$ P (0.40 mM) $>$ SO_4^{2-} (0.32 mM). The experiments with diverse operating conditions revealed that the optimal adsorption of inorganic phosphorus over chloride and sulphate can be achieved in some extent with slower flow rates and higher applied potentials (less than 1.23 V).

Keywords: Membrane capacitive deionization; Phosphate removal; Phosphate equilibrium system; Electrosorption; Selectivity.

1. Introduction

Phosphorus (P) is an essential nutrient for the growth of plants and animals (Filippelli, 2002). Under natural conditions, P is the limiting nutrient in surface water because it prevent the growth of algae and aquatic plants in water bodies. The natural background level of total phosphorus (TP) and phosphate are typically less than 0.03 mg/L and range between 0.005 and 0.05mg/L, respectively (Kotoski, 1997). However, many open water sources such as lakes, streams, oceans and reservoirs, are currently experiencing excess of phosphorus from human activities, which can speed up eutrophication in aquatic system and cause water quality impairment, aquatic species biodiversity decrease, adverse human health impacts, and increase the cost of water treatment, etc. (Chislock et al., 2013; Wilkinson, 2017).

To mitigate or prevent the risk of eutrophication, the environmental authorities regulate the TP concentration in the wastewater effluent from the wastewater treatment plants (WWTPs) globally. Current WWTPs treatment methods used for P removal include physical, chemical and biological processes (Mohammed and Shanshool, 2009; Strom, August 2006). In contrast, the above nutrient removal methods, to some extent, have drawbacks in terms of life-cycle costs, operation complexity, safety, portability, and further maintenance requirements.

Capacitive deionization (CDI), on the other hand, is a promising technology that uses electrophoretic driving forces to remove charged ions from an aqueous solution (Pekala et al., 1998). It was shown to have great application potential for seawater and brackish water desalinations (Biesheuvel et al., 2017; Dorji et al., 2018), water softening (Tuan et al., 2015), selective removal of specific ions (Choi et al., 2016), resources removal and recovery (Huang et al., 2017; Kim et al., 2018), and water reclamation (Anderson et al., 2010). CDI operates at a low voltage, generally less than 1.23 V, to avoid faradaic reactions that can result in water electrolysis (Liang et al., 2017; Shanbhag et al., 2017; Zhang et al., 2018). Unlike other wastewater treatment measures, CDI process functions as an electrosorbent without requiring any additional chemical. Benefits of applying CDI technology include higher water recovery, lower operation cost, lower energy requirements, higher removal efficiency of charged ions, high portability, and no water softening requirement prior to purification. (Anderson et al., 2010; Porada et al., 2013; Zarzo and Prats, 2018).

CDI technology has been receiving increased attention for P removal and recovery. Huang (2014) was the first to evaluate the feasibility of applying a commercial CDI unit to treat phosphate-containing wastewater using single salt feed solution. Huang (2017) subsequently studied the pH-dependent phosphate electrosorption capacity in MCDI under both constant voltage (CV) and constant current (CC) mode of operations. However, the earlier works on CDI for P removal which fundamentally investigated the P removal has failed to reflect the very nature of phosphate ions in wastewater. So far, very few studies have focused on understanding the effect of phosphate equilibrium reactions particularly at pH between 6.5 and 8.5, which is the typical pH range maintained for the residential raw wastewater. The inorganic phosphate within this pH range mostly exists in the form of dihydrogen phosphate ion ($\mathrm{H_2PO_4^-}$) and hydrogen phosphate ion ($\mathrm{HPO_4^{2-}}$) (Mogens Henze, 2008), which is predominantly in a weakly acidic and weakly basic conditions, respectively. The proportion of these phosphate species in this pH range (6.5-8.5) is shown in Fig. S1 and Table S1 of the supporting information, in compliance with following reversible reaction:

$$\mathrm{H_2PO_4^-} \leftrightarrows \mathrm{H^+} + \mathrm{HPO_4^{2-}} \qquad (1)$$

the corresponding acid dissociation constant $\mathrm{K_{a2}}$ (mol/L) at 25 °C is:

$$K_{a2} = \frac{[\mathrm{H^+}][\mathrm{HPO_4^{2-}}]}{[\mathrm{H_2PO_4^-}]} \cong 6.2 \times 10^{-8} \qquad (\mathrm{P}K_{a2} \approx 7.21) \qquad (2)$$

Generally, the ion selectivity and degree of ion electrosorption capacity mainly depend on the hydrated size, ionic charge, ion concentration, and degree of ion complexation

(Hou and Huang, 2013). Fan, Liou & Hou (2017) investigated preferential adsorption sequence of co-existing ions in single-pass-mode (SP-mode) CDI. And they observed that the co-existence of other ions can significantly affect the phosphate removal from the wastewater. However, these reported works did not closely reflect the real ionic composition present in domestic wasteater considering the complexity of the co-existence of other ions. They conducted their studies in a mixed environment covering different ionic charge and non-equal ion concentration (Fan et al., 2017). In another work, Huang (2017) analysed pH-dependent ion selectivity between P and Cl^- in SP-mode membrane CDI (MCDI) with equivalent ionic strength. However, more in-depth research is required to fully understand the phosphate electrosorption capacity and competitive ion selectivity in more complex and realistic electrolytes with ionic contents.

The main goal of this work is to explore the suitability of MCDI for effective P removal from domestic wastewater. To do so, the effects of the equilibrium reactions on P adsorption capacity when feed solution contains only $\mathrm{H_2PO_4^-}$ and $\mathrm{HPO_4^{2-}}$ were firstly investigated. In addition, the phosphate sorption capacity and ion selectivity in the presence of Cl^- and $\mathrm{SO_4^{2-}}$ as co-ions were experimentally studied by mimicking the real ionic composition of a domestic wastewater. An overall evaluation of individual operating parameters (different flow rate, pH, voltage, and sorption time) and their corresponding P removal performance then covered to study the potential of applying MCDI - as one of the alternative WWTPs treatment option - for effective P removal from domestic wastewater.

2. Materials and methods

2.1. Lab-scale MCDI unit setup

The lab-scale symmetric two-electrode MCDI unit was used for the study purposes. It consists of a pair of commercial composite activated carbon electrodes coated by anionic and cationic exchange solutions which are manufactured by Siontech Co., Republic of Korea. Each single composite carbon electrode has a mass of 0.8 g with a dimension of 100 mm x 100 mm. A same-sized non-electrically conductive nylon spacer was placed between them to prevent the occurrence of short circuit.

The feed solution was pumped into the cell by a peristaltic pump which is made by Cole-Parmer Co., Ltd. The constant electrical voltage was appplied by a potentiostat WPG-100 (Wonatech Co., Republic of Korea). The physical adsorption equilibrium state prior to the electrosorption stage was attained by flushing out the entire MCDI unit with feed solution under single-pass, at zero volts, until the reading of effluent conductivity and pH were to be the same to that of in influent. All experiments were performed in triplicate to provide a relatively sound basis for statistical analysis. Fig. 1 shows a schematic diagram of the proposed single-pass mode (SP-mode) lab-scale MCDI unit set up.

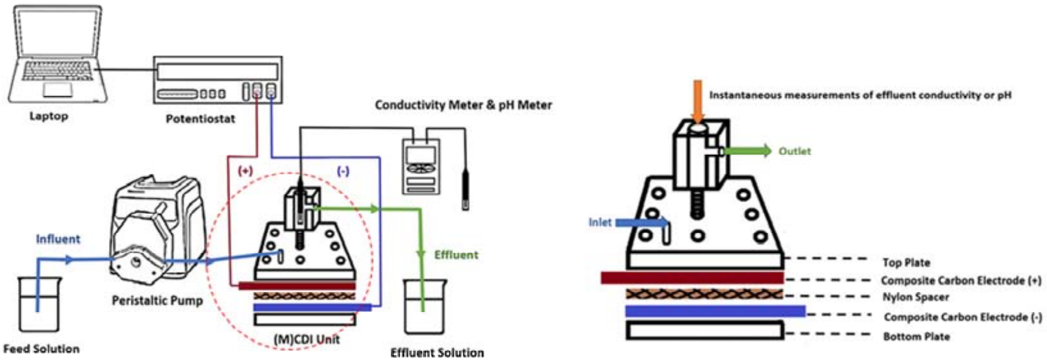

Figure 1. Schematic diagram of the proposed single-pass lab-scale MCDI unit setup

1.5-column fitting image

2.2. Feed solution preparation

Sodium phosphate buffer solution were used in preparing a synthetic solution for the investigation of the impact of phosphate equilibrium system on P removal. As it can maintain the feed solution at a relatively constant pH without additional acid/base needed, which can cause the increase of feed total dissolved solid (TDS). $NaHPO_4$ and Na_2HPO_4 were used in making buffer solution because they are commonly available and affordable. The desired pH value was achieved by adjusting the ratio between these two chemicals. The proportions of $H_2PO_4^-$ on HPO_4^{2-} at pH equals to 6.6, 6.9, 7.2, 7.5 and 7.8 are 4:1, 2:1, 1:1, 1:2 and 1:4, respectively (Table S1).

Synthetic wastewater solution were used in experiments to examine the ion selectivity of P over co-existing ions and optimizing operating conditions for enhanced phosphate removal. As it simulates the major chemical compositions and their mass concentrations, solution pH, and conductivity in typical raw domestic wastewater; but is free of organic pollutants, solid particles, and the like. Toifl (2014) discussed that the characteristics of the desirable composition for synthetic wastewater should be commonly available, affordable, non-volatile and non-biological. Table 1 presents the formulation for synthetic wastewater used in this study. Few drops of HCl was added to adjust synthetic wastewater solution pH between 7 and 8, without significantly increasing the TDS in the feed solution.

Table 1. Composition of synthetic wastewater used in the study

Constituents		Molar Weight (g/mole)	Concentration (mM)
Sodium citrate	$Na_3C_6H_5O_7$	258.06	1.16
Ammonium chloride	NH_4Cl	53.49	0.90
Sodium phosphate dibasic	Na_2HPO_4	141.96	0.40
Calcium chloride dihydrate	$CaCl_2 \bullet 2H_2O$	147.01	0.50
Potassium bicarbonate	$KHCO_3$	100.12	0.50
Magnesium sulphate heptahydrate	$MgSO_4 \bullet 7H_2O$	246.47	0.32

* *HCl was added to adjust pH between 7 and 8*

2.3. Experimental operating conditions

The SP-mode lab-scale MCDI system, which is more relevant to actual wastewater treatment measures, was used in this study in order to obtain reliable experimental results. The details of proposed experimental conditions and control parameters are described in Table 2. Experiment 1, corresponding to section 3.1 in this paper, studied the effects of phosphate equilibrium reactions on P adsorption capacity when feed solution contains only $\mathrm{H_2PO_4^-}$ and $\mathrm{HPO_4^{2-}}$. Experiment 2, corresponding to section 3.2 in this paper, investigated the P electrosorption capacity and ion selectivity in the presence of $\mathrm{Cl^-}$ and $\mathrm{SO_4^{2-}}$. Moreover, an overall evaluation of individual operating parameters and their corresponding P removal performance were covered in Experiment 3, corresponding to section 3.3 in this paper.

Table 2. Proposed experimental conditions and control parameters

Corresponding Section in This Paper	Study Objective	Feed Solution	Experiments Number	Operating Conditions						
				Initial ionic strength (mM)			Initial influent pH	Flow rate (mL/min)	Voltage (V)	Adsorption duration (min)
				$[\mathrm{P}]$(	$[\mathrm{Cl^-}]$	$[\mathrm{SO_4^{2-}}$				
3.1.	Equilibrium reaction study	Sodium phosphate buffer solution	1.1	4			6.6,6.9,7.2,7.5,7.8	8	1.2	10
			1.2	0.4			6.6, 7.2, 7.8			
			1.3	0.4	3.6		6.6, 7.2, 7.8			
3.2	Electrosorption capacity and ion selectivity study	Synthetic waste water solution	2	0.4	1.9	0.32	7.2	8	1.2	10
3.3	Optimization of operating parameters	Synthetic waste water solution	3.1 (Reference Experiment)	0.4	1.9	0.32	7.2	8	1.2	10
			3.2					8	1.2	8
			3.3					8	0.6	10
			3.4					24	1.2	10

2.4. Sample analysis

The validity of experimental results was guaranteed by performing triplicate experiments and carefully collecting samples in every 30 seconds. All the samples that had been digested by phosphorus test kit (Phosphate Test (o-phosphate) 114842) were measured by Merck Millipore UV/VIS Spectrophotometer (Spectroquant^{R} NOVA 60, USA) for effluent P concentration.

The salt adsorption capacity (SAC) (mg/g) in SP-mode was calculated using equation (3):

$$\text{SAC (mg/g)} = \frac{\text{Q}\times\int_0^t \Delta\text{C}\, dt \times\text{M}}{m} \tag{3}$$

where Q is the volumetric flow rate (mL/min); ΔC is the concentration difference(mM) at time t; M is the molar mass of the salt (mg/mmol); and m represents the total electrode mass (g).

The average salt adsorption rate (ASAR) (mg/g-min) in SP-mode was determined according to equation (4):

$$\text{ASAR (mg/g-min)} = \frac{\text{SAC}}{\Delta\text{t}} \tag{4}$$

where Δt is the time difference from start to any time t.

The average ion removal efficiency (E) (%) in SP-mode was determined as follows:

$$\text{E (\%)} = \frac{\int_0^t \Delta\text{C}\, dt}{\text{C}_0 \times \text{t}} \times 100\% \tag{5}$$

where C_0 is the influent concentration.

The relative ion removal ratio (RE) in SP-mode was expressed by equation (6):

$$\text{RE } = \frac{E(A)}{E(B)} \tag{6}$$

where RE represents the selectivity of salt A compared to salt B. RE value greater than 1 means salt A has higher selectivity than salt B, which means salt A will be more preferentially removed from aqueous solution over salt B.

3. Results and discussions

3.1. Phosphate equilibrium system study

As indicated previously, the major composition of influent total phosphorus in domestic wastewater is inorganic phosphorous, often in the form of orthophosphate. Henze et al. (2008) reported it constitutes around 75% of total phosphorus concentration with concentration ranging from 5 to 15mg/L.

To probe the effects of equilibrium system on degree of P adsorption capacity, highly concentrated sodium phosphate buffer solution ($[\mathrm{P}]_0$ = 4 mM) was fed through the MCDI system. The experimental results, as shown in Fig. 2, suggested that the P was most quickly removed under about neutral pH from the synthetic water in the early stage of adsorption (0 – 2 min). For instance, at end of 90s, the instantaneous effluent P concentration in neutral solution (pH 7.2) dropped from 4.0 to 2.2 ± 0.06 mM, while the P concentrations with the initial solution pH at 6.6, 6.9, 7.5, and 7.8 is declined to slightly higher levels at 2.5 ± 0.1, 2.8 ± 0.07, 3.0 ± 0.07 and 2.6 ± 0.15 mM, respectively. It implies that such system, constituted by equal amount of monovalent and divalent phosphate ions, is likely to quickly respond to reversible reactions at equilibrium. At the beginning of adsorption stage, phosphate equilibrium reactions continuously provides system sufficient amount of HPO_4^{2-} to screen carbon electrode surface charge. Meanwhile, such equilibrium reaction provides adequate amount of $\mathrm{H_2PO}_4^-$ to be adsorbed inside the carbon electrode pores.

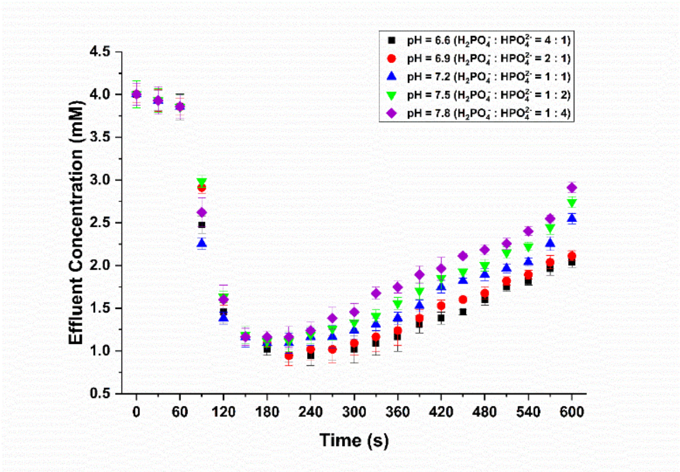

Figure 2. Effects of equilibrium system on variation of the effluent P concentration for highly concentrated feed streams when feed solution containing phosphate salt only. Electrosorption process operated at 1.2 V. (Experimental conditions: $[P]_0$ = 4 mM, Flow rate = 8 mL/min.)

Single column fitting image

Interestingly, however, after first two minutes of adsorption, the effluent P concentration of both neutral and weakly basic conditions are higher than that of weakly acidic condition. This shows the overall P removal capacity is more efficient in the lower range of initial pH than that is in higher initial pH, due to the fact that the adsorption capacity also depends on the initial concentration and hydrated radii of ions. Since $H_2PO_4^-$ which is predominate in weakly acidic solution has smaller hydrated radius (0.302 nm) compared to HPO_4^{2-} (0.327 nm), it take less space within and near the carbon electrode pores and has faster diffusion rate to rapidly remove from aqueous solution into the micropores (Hassanvand et al., 2017; Huang et al., 2017). Besides, larger number of phosphate ions are needed for charge neutralization near the carbon electrode surface when the monovalent $H_2PO_4^-$ outnumbers the divalent HPO_4^{2-} - only one electron is consumed for each $H_2PO_4^-$. This also increases the overall P adsorption capacity.

The above experimental results are consistent with findings from previous study by Huang et al. (2017) in which they concluded that, for solution containing only $H_2PO_4^-$ and HPO_4^{2-}, the optimal P removal performance is observed under acidic solution (initial pH valued at 5 and 6) where dihydrogen phosphate ion ($H_2PO_4^-$) is predominant. Figure 3 presents the schematic diagram of P adsorption mechanism on composite carbon electrode when feed solution containing phosphate salt only. At the beginning of adsorption stage, phosphate equilibrium system has a great influence on P removal. The quick swift between the divalent and monovalent ions in order to maintain the system at equilibrium state provides sufficient amount of divalent HPO_4^{2-} to screen the surface charge at the electrode. Meanwhile, it provides adequate amount of $H_2PO_4^-$ to be adsorbed inside the carbon electrode pore. Therefore, the phosphate equilibrium system leads to a rapid removal of the P in first two minutes. However, the overall P adsorption capacity was greatly varied with solution pH, as it directly determines the types and proportions of various P species in system. The optimal P adsorption capacity occurred at the lower range of initial pH

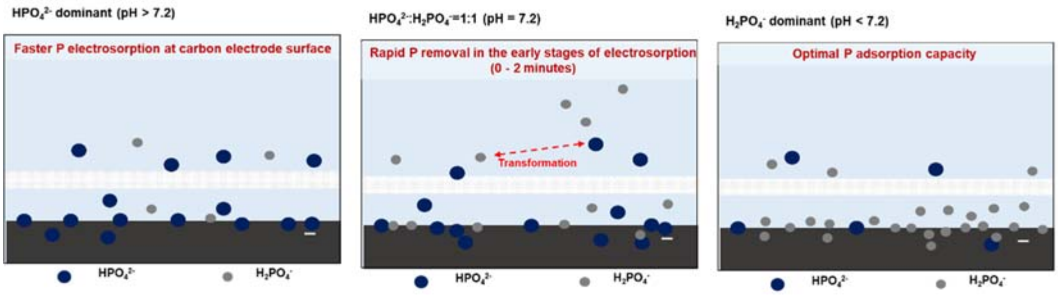

Figure 3. Schematic diagram of P adsorption mechanism on composite carbon electrode when feed solution containing phosphate salt only. Electrosorption process operated at 1.2 V. (Experimental conditions: $[P]_0$ = 4 mM, Flow rate = 8 mL/min.)

1.5-column fitting image

Nevertheless, further CDI tests with an initial P concentration of 0.4 mM was carried out to more closely simulate the P concentration present in a typical domestic wastewater

(Metcalf et al. 2003). The experimental results in Fig. 4(a) show that at a low phosphate concentration of 0.4 mM, the equilibrium reactions during adsorption stage and types of P species is unlikely to affect the P removal performance. Another set of experiments were run in which 0.4 mM P was present together with the 3.6 mM NaCl solution to reflect the background TDS of a real wastewater. It is noticeable from Fig 4(b) that the trends in the P removal in the presence of background TDS were consistent as observed in Fig. 2 earlier. In other words, effluent P concentration curves in both highly concentrated feed streams (Fig. 2) and high TDS feed solutions (Fig. 4(b)) reflected an identical trend.

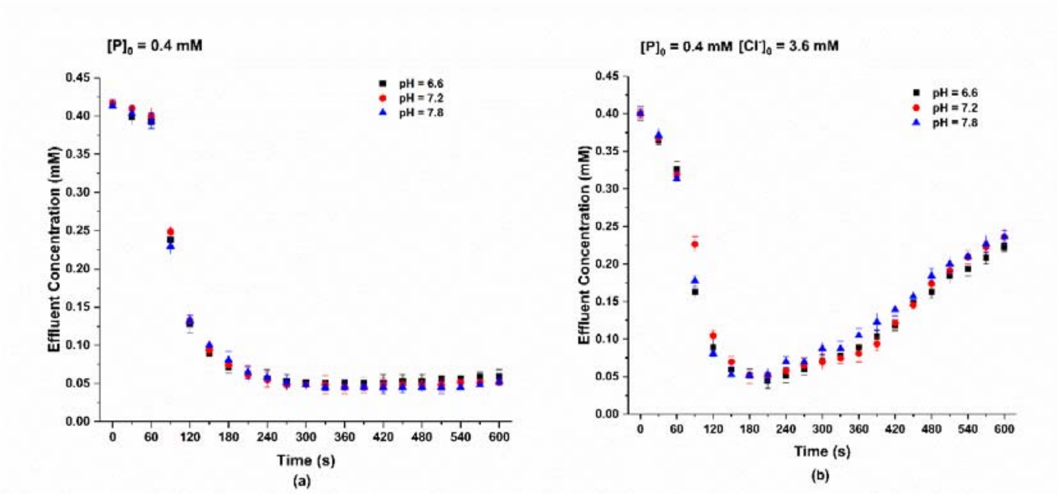

Figure 4. Effects of equilibrium system on variation of the effluent P concentration for feed simulating inorganic phosphorus concentration in real domestic wastewater at (a) low concentration of TDS, $[P]_0$ = 0.4 mM (b) high concentration of TDS, $[P]_0$ = 0.4 mM, $[Cl^-]_0$ = 3.6 mM. (Experimental conditions: Flow rate = 8 mL/min; Voltage = 1.2 V)

1.5-column fitting image

Fig. 5 shows that, the SAC of P using 4 mM phosphate as feed solutions ranged from 5.9 ± 0.05 to 7.1 ± 0.05 mg/g, which are around 6.5 to 7.5 times higher than that when 0.4 mM phosphate solutions (0.93 – 0.95 mg/g) was used as feed solution under the three different pH conditions. In contrast, the SAC of P in high TDS mixed solution (0.4 mM phosphate plus 3.6 mM NaCl) is less than that of a low TDS phosphate feed solution (0.4 mM phosphate) among all pH values, ranged from 0.76 to 0.79 mg/g. These results demonstrates that, a higher initial P concentration makes more P preferentially removed from the aqueous solution by MCDI process. The co-existence of Cl^- in the phosphate containing feed solution reduces the P removal performance by MCDI process due to effect of competing co-ions. Therefore, in-depth studies were conducted to understand the P electrosorption capacity and the preferential adsorption sequence of co-existing ions in more complex electrolyte according to the typical ionic contents in domestic wastewater.

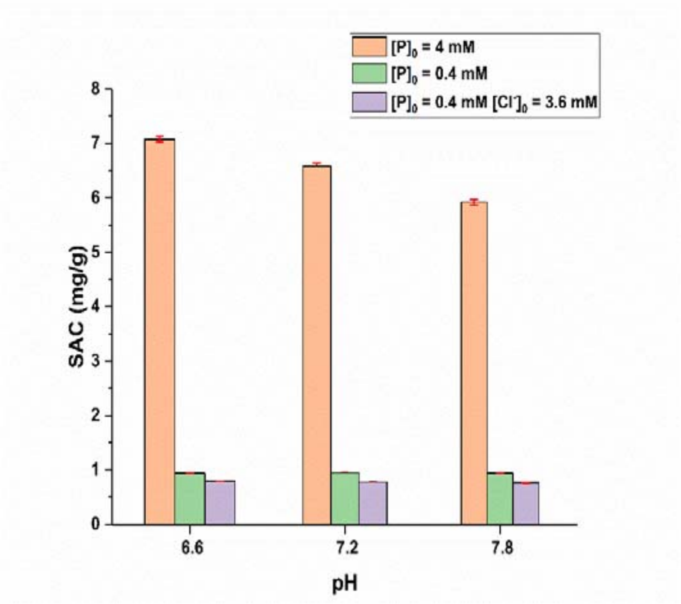

Figure 5. Experimental salt adsorption capacity for both concentrated feed streams ($[P]_0$ = 4 mM), low TDS feed streams ($[P]_0$ = 0.4 mM), and high TDS feed streams ($[P]_0$ = 0.4 mM, $[Cl^-]_0$ = 3.6 mM). (Experimental conditions: Flow rate = 8 mL/min; Voltage = 1.2 V)

Single column fitting image

3.2 The influence of co-existing anions in domestic wastewater on P removal

By using the synthetic wastewater as feed solution, it has been observed that the presence of co-existing anions can have a significantly negative impact on the degree of P adsorption capacity in a mixed electrolyte solution due to their competitive adsorption onto the carbon electrode. Fig. 6 illustrates that, for a feed solution containing mixed of different ionic species, the overall P SAC was 0.53 ± 0.06 mg/g, which is lower than the value 0.95 mg/g observed in Fig 5 using similar P concentration of 0.4 mM but only phosphate as feed solution. The overall salt adsorption capacity of $\mathrm{Cl^-}$ and $\mathrm{SO_4^{2-}}$ observed were 1.6 ± 0.06 and 1.45 ± 0.12 mg/g, respectively. Above observations imply that a preferential electrosorption sequence of the competitive anions was: $\mathrm{Cl^-} > \mathrm{SO_4^{2-}} >$ P, while their initial ion concentration in the synthetic feed solution were $\mathrm{Cl^-}\ (1.90\ \mathrm{mM}) > \mathrm{P}\ (0.40\ \mathrm{mM}) > \mathrm{SO_4^{2-}}\ (0.32\ \mathrm{mM})$. The fastest $\mathrm{Cl^-}$ removal among all the co-existing anions at stage of adsorption is mainly because it has the highest initial concentration amongst all the anions present in the synthetic wastewater (Fan et al., 2017). Similar to the results shown in Fig. 5, ions with higher concentration gradient is likely to have a stronger diffusive force to overcome solution resistance, leads to faster ion transportation across the electrode pores (Fan et al., 2017; Hassanvand et al., 2018). A preferential electrosorption of $\mathrm{SO_4^{2-}}$ over that of P was observed at the similar initial concentration. This preferential adsorption of $\mathrm{SO_4^{2-}}$ is likely due to the larger charge effect of divalent ions (Tang et al., 2017). Specifically, due to the tendency to achieve electroneutrality at the charged electrode surface, divalent sulphate ions are selectively removed to screen the electrode surface charge than P. The removal of phosphate underperformed than that of $\mathrm{SO_4^{2-}}$. These results show that the co-existence of other anions in the wastewater solution can be a significant challenge for effective removal of P by the MCDI process, and hence the MCDI process has to be systematically optimized by increasing the pH or adjusting operating conditions to achieve highly efficient P removal.

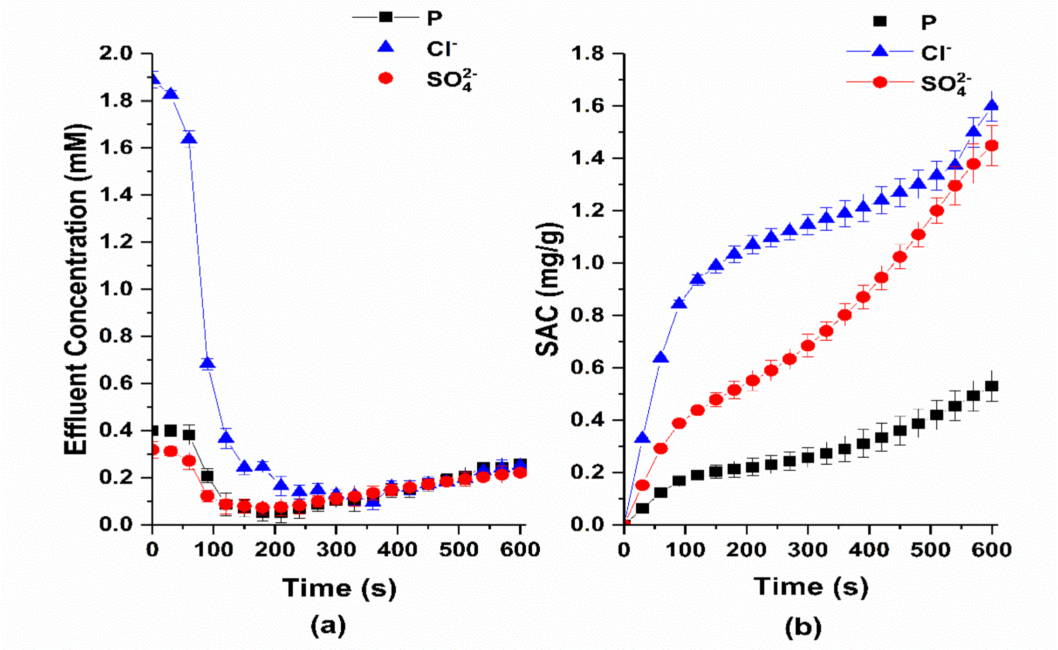

Figure 6. The electrosorption competition of Cl^-, SO_4^{2-} and P based on (a) ion analysis of the effluent stream, and (b) salt adsorption capacity in MCDI in a mixed electrolyte at 1.2 V. (Experimental conditions: Flow rate = 8 mL/min, Feed solution pH = 7.2)

1.5-column fitting image

3.3 Optimization of MCDI system for highly efficient P removal

A controlled experimental operating conditions such as adsorption time, applied potential, and flow rates were studied using a lab-scale SP mode MCDI unit as shown in Table 2. The reference experiment was conducted under the following operating conditions: synthetic wastewater feed solution at pH 7.2, applied constant voltage at 1.2 V, pumped flow rate at 8 ml/min, and 10 min adsorption duration. The desalination performance of controlled experiments was evaluated in accordance with its average salt adsorption capacity (ASAC), overall ion removal efficiency (E), and relative ion removal ratio (RE).

In order to find the optimal applied potential for the maximum removal performance and relative high ion removal ratio of P over chloride and sulphate, a series of CV controlled experiments were performed. Compared to the results in Experiments 3.1 and 3.2, electrode saturation time has slight positive effect on the overall P removal performance (Fig. 7(a)). The relative ion removal ratio of P over $\mathrm{Cl^-}$ is 0.80 ± 0.06 for $\mathrm{RE}(\frac{\mathrm{P}}{\mathrm{Cl^-}})$ at 8 min versus 0.73 ± 0.05 at 10 min. This observation shows an increased P over $\mathrm{Cl^-}$ selectivity at a shorter adsorption period. The relative ion removal ratio of P over $\mathrm{SO_4^{2-}}$ in both cases were same, all reaching 1.11. By contrast, comparing results Experiments 3.1 and 3.3, Fig. 8 illustrates that the overall removal efficiency of P increased from 37 ± 4.50 to 57 ± 4.90%, when the applied potential was raised from 0.6 to 1.2 V. This indicates that, approximately 25% more P has been selectively removed per minute at 1.2 V (0.07 mg/g-min) compared to 0.6 V (0.05 mg/g-min). As can be inferred from Fig. 7 (b), relative ion removal ratio of P over $\mathrm{Cl^-}$ increased with increase in adsorption voltage - 0.55 ± 0.04 for $\mathrm{RE}(\frac{\mathrm{P}}{\mathrm{Cl^-}})$ at 0.6 V versus 0.73 ± 0.05 for that at 1.2. While, the relative ion removal ratio of P over $\mathrm{SO_4^{2-}}$ dropped from 1.6 ± 0.13 at 0.6 V to 1.11 ± 0.07 at 1.2V applied voltage. Comparing results of Experiments 3.1 and 3.4 the relative ion removal ratio of P over $\mathrm{SO_4^{2-}}$ and $\mathrm{Cl^-}$ at 8 mL/min flow rate were 1.11 ± 0.07 and 0.73 ± 0.05, respectively. While the relative ion removal ratio of P over $\mathrm{SO_4^{2-}}$ (0.96 ± 0.07) and $\mathrm{Cl^-}$ (0.96 ± 0.13) at flow rate of 24 mL/min share the same proportion. It suggests that the co-existing ions in this case have similar selective removal capacity. It is also worth mentioning that the effluent concentration of all studied ions under the flow rate of 24 mL/min were higher than that operated under a flow rate of 8 mL/min during adsorption process. Similarly, the removal efficiency of all ions at 8 mL/min is two times higher than that of 24 mL/min (Fig. 9). This shows that the overall removal efficiency of P, $\mathrm{Cl^-}$ and $\mathrm{SO_4^{2-}}$ was hampered by the increased feed solution flow rates, which reduces the residence time for ion adsorption. The fact that relatively small amount of ions would be potentially transported into activate carbon electrodes at higher flow rates, leads to the observation of more concentrated effluent streams (Biesheuvel and Van der Wal, 2010; Dorji et al., 2018; Kim et al., 2015; Zhao et al., 2013).

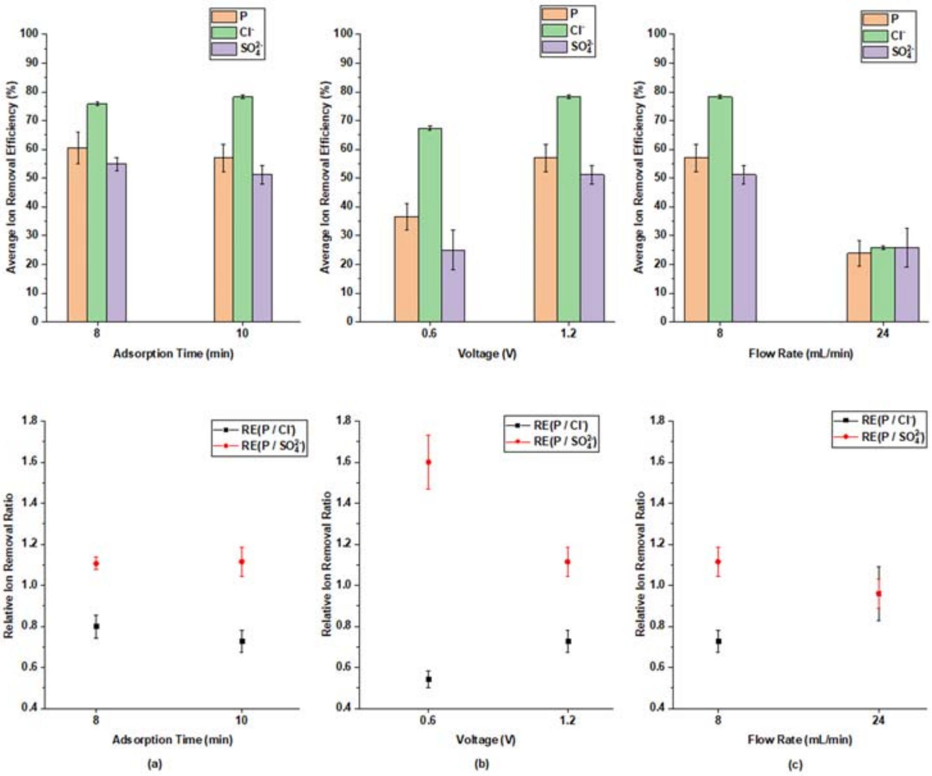

Figure 7. Experimental average ion removal efficiency (E) and relative ion removal ratio (RE) results for SP mode MCDI operated at various (a) adsorption time, (b) voltage, (c) flow rate. The details of individual control parameters are described in Table 2.

1.5-column fitting image

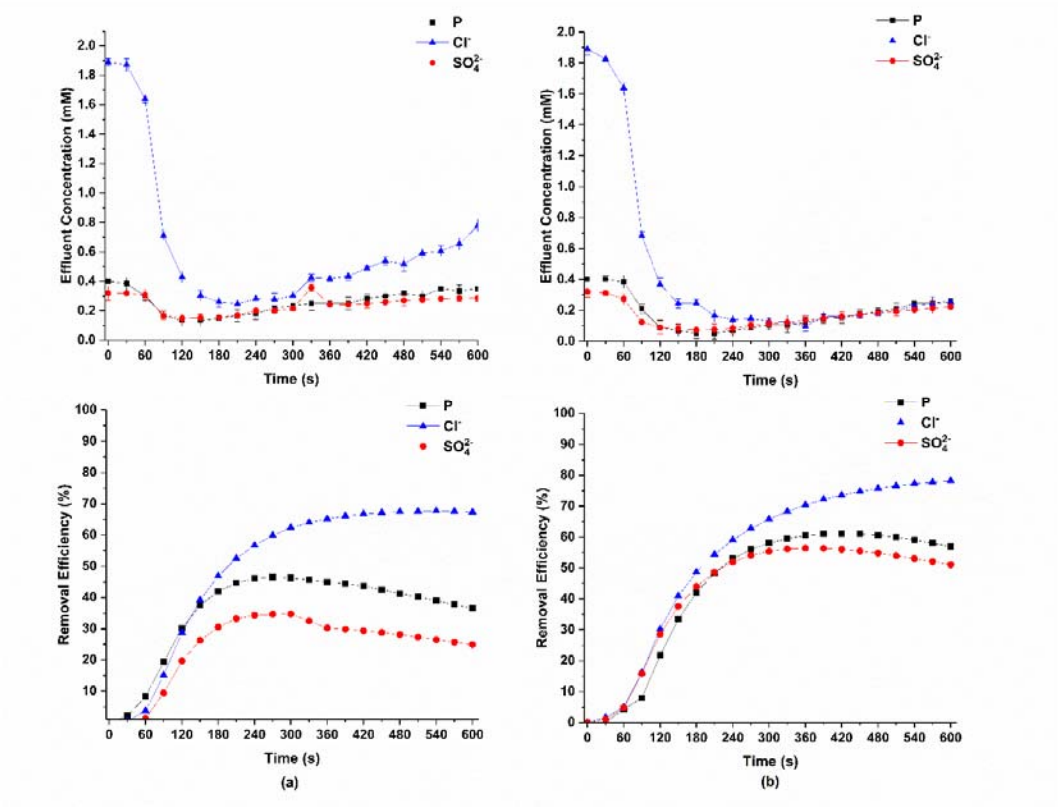

Figure 8. The effect of applied voltage on the variation of removal efficiency of phosphorus and other anions for MCDI electrosorption process operated at (a) 0.6 V, and (b) 1.2 V. (Experimental conditions: Flow rate = 8 mL/min, Feed solution pH = 7.2)

1.5-column fitting image

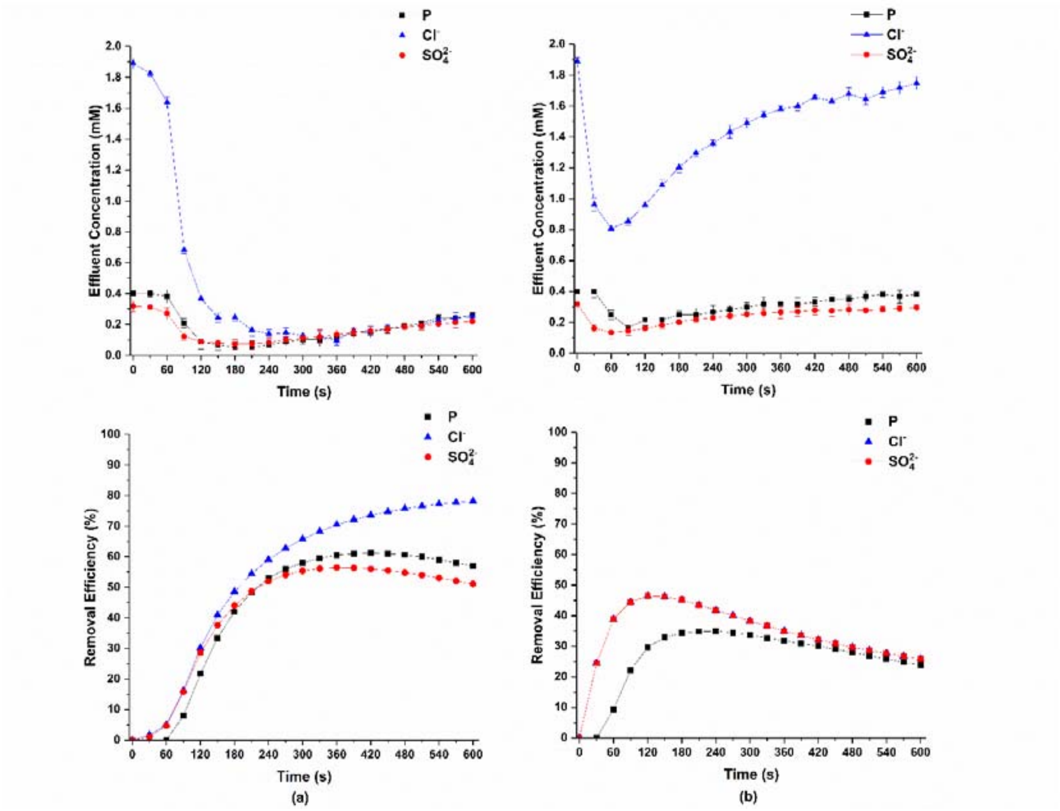

Figure 9. The effect of applied flow rate on the variation of removal efficiency of phosphorus and other anions for adopted flow rate at (a) 8mL/min, and (b) 24mL/min. (Experimental conditions: Voltage = 1.2 V, Feed solution pH = 7.2)

1.5-column fitting image

Table 3 demonstrates the *p*-values of three different operating parameters - adsorption time, applied potential, and flow rate - in the statistical model. The *p*-factors in statistical analyses of voltage and flow rate were all less than 0.05, indicating significant selectivity of P over other competitive anions. In contrast, the *p*-values of adsorption time in both P over Cl^{-} and P over SO_4^{2-} were greater than alpha value 0.05, showing that this factor was insignificant. In summary, the above experimental statistical analyses demonstrate that the optimal adsorption of inorganic phosphorus over chloride and sulphate can be achieved to some extent by conducting adsorption process with lower feed flow rates and higher applied potentials (less than 1.2 V). The 2-minute adsorption time difference does not correlate with higher selectivity of P removal in this study.

Table 3. *p*-values of the operating parameters in the statistical analyses

Parameter		$RE(\frac{P}{Cl^-})$			$RE(\frac{P}{SO_4^{2-}})$		
		Value	Standard error	p-Value	Value	Standard error	p-Value
Adsorption time (min)	8	0.8	0.06	0.26 9	1.11	0.03	0.135
	10	0.73	0.05		1.11	0.07	
Voltage (V)	0.6	0.55	0.04	0.023	1.6	0.13	0.007
	1.2	0.73	0.05		1.11	0.07	
Flow rate (mL/min)	8	0.73	0.05	0.028	1.11	0.07	0.037
	24	0.96	0.13		0.96	0.07	

4. Conclusions

The removal of inorganic phosphorus from the domestic wastewater using MCDI and its system optimization for enhanced phosphate removal has been explored by closely investigating the key mechanisms such as phosphate equilibrium and competitive sorption, and adjusting operating conditions and solution compositions. This study shown that the single-pass mode MCDI process has a great potential for effective P removal from the municipal wastewater. The following are the key findings of the study:

1) In the early stage of adsorption, phosphate equilibrium system has a significant impact on the degree of inorganic phosphorus (P) adsorption capacity and hence its removal. Because the phosphate equilibrium reactions continuously provide system sufficient amount of HPO_4^{2-}which quickly be adsorbed onto the electrode surface to achieve charge neutrality. However, the overall P removal is more efficient in the lower range of the initial solution pH as the $H_2PO_4^-$ (0.302 nm) with smaller hydrated radius takes less space within and near the carbon electrode pores and preferentially

removed from aqueous solution.

2) From the co-existing anions selectivity study, it can be concluded that in the presence of higher $\mathrm{Cl^-}$ ion concentrations, it is more favorably removed compared to P from the mixed electrolyte due to its stronger diffusion force; divalent ion such as sulphate showed higher electrosorption capacity among similar concentrated monovalent ion P due to valence. The preferential electrosorption sequence of the competitive anions present in the wasetwater was: $\mathrm{Cl^-} > \mathrm{SO_4^{2-}} >$ P, while the initial ion concentration in the feed water was with the order: $\mathrm{Cl^-} > \mathrm{P} > \mathrm{SO_4^{2-}}$.
3) The optimal adsorption of P over chloride and sulphate can be achieved with lower feed flow rates and higher applied potentials (less than 1.2 V).

The above findings summarized in this study may contribute to the enhanced understanding of the application of MCDI as an alternative treatment measure for the effective phosphorus removal from the wastewater effluent.

Acknowledgements

This work is supported by the Korea Agency for Infrastructure Technology Advancement (KAIA) grant funded by the Ministry of Land, Infrastructure and Transport (Grant 6IFIP-B116953). This work was also partly supported by the Bhutan Trust Fund for Environmental Conservation or BTF-EC (MB0167Y16). The support was also provided to HKS by the Australian Research Council (ARC) through Future Fellowship (FT140101208).

References

Anderson, M.A., Cudero, A.L., Palma, J., 2010. Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete? Electrochimica Acta 55, 3845-3856.

Biesheuvel, P., Bazant, M., Cusick, R., Hatton, T., Hatzell, K., Hatzell, M., Liang, P., Lin, S., Porada, S., Santiago, J., 2017. Capacitive Deionization--defining a class of desalination technologies. arXiv preprint arXiv:1709.05925.

Biesheuvel, P., Van der Wal, A., 2010. Membrane capacitive deionization. Journal of Membrane Science 346, 256-262.

Chislock, M.F., Doster, E., Zitomer, R.A., Wilson, A., 2013. Eutrophication: causes, consequences, and controls in aquatic ecosystems. Nature Education Knowledge 4, 10.

Choi, J., Lee, H., Hong, S., 2016. Capacitive deionization (CDI) integrated with monovalent cation selective membrane for producing divalent cation-rich solution. Desalination 400, 38-46.

Dorji, P., Choi, J., Kim, D.I., Phuntsho, S., Hong, S., Shon, H.K., 2018. Membrane capacitive deionisation as an alternative to the 2nd pass for seawater reverse osmosis desalination plant for bromide removal. Desalination 433, 113-119.

Fan, C.-S., Liou, S.Y.H., Hou, C.-H., 2017. Capacitive deionization of arsenic-contaminated groundwater in a single-pass mode. Chemosphere 184, 924-931.

Filippelli, G.M., 2002. The Global Phosphorus Cycle. Reviews in Mineralogy and Geochemistry 48, 391-425.

Hassanvand, A., Chen, G.Q., Webley, P.A., Kentish, S.E., 2017. A comparison of multicomponent electrosorption in capacitive deionization and membrane capacitive deionization. Water Res 131, 100-109.

Hassanvand, A., Chen, G.Q., Webley, P.A., Kentish, S.E., 2018. A comparison of multicomponent electrosorption in capacitive deionization and membrane capacitive deionization. Water Research 131, 100-109.

Hou, C.-H., Huang, C.-Y., 2013. A comparative study of electrosorption selectivity of ions by activated carbon electrodes in capacitive deionization. Desalination 314, 124-129.

Huang, X., He, D., Tang, W., Kovalsky, P., Waite, T.D., 2017. Investigation of pH-dependent phosphate removal from wastewaters by membrane capacitive deionization (MCDI). Environmental Science: Water Research & Technology 3, 875-882.

Kim, D.I., Gwak, G., Dorji, P., He, D., Phuntsho, S., Hong, S., Shon, H., 2018. Palladium Recovery through Membrane Capacitive Deionization from Metal Plating Wastewater. ACS Sustainable Chemistry & Engineering 6, 1692-1701.

Kim, J.S., Kim, C.S., Shin, H.S., Rhim, J.W., 2015. Application of synthesized anion and cation exchange polymers to membrane capacitive deionization (MCDI). Macromol. Res 23, 360-366.

Kotoski, J.E., 1997. Information on Phosphorus Amounts & Water Quality.

Liang, P., Sun, X., Bian, Y., Zhang, H., Yang, X., Jiang, Y., Liu, P., Huang, X., 2017. Optimized desalination performance of high voltage flow-electrode capacitive deionization by adding carbon black in flow-electrode. Desalination 420, 63-69.

Mogens Henze, Y.C., 2008. 3-Wastewater Characterization Biological Wastewater Treatment: Principles, Modelling and Design IWA Publishing.

Mohammed, S.A., Shanshool, H.A., 2009. Phosphorus removal from water and waste water by chemical precipitation using alum and calcium chloride. Iraqi Journal of Chemical and Petroleum Engineering 10, 35-42.

Pekala, R., Farmer, J., Alviso, C., Tran, T., Mayer, S., Miller, J., Dunn, B., 1998. Carbon aerogels for electrochemical applications. Journal of non-crystalline solids 225, 74-80.

Porada, S., Zhao, R., van der Wal, A., Presser, V., Biesheuvel, P.M., 2013. Review on the science and technology of water desalination by capacitive deionization. Progress in Materials Science 58, 1388-1442.

Shanbhag, S., Bootwala, Y., Whitacre, J.F., Mauter, M.S., 2017. Ion Transport and Competition Effects on NaTi2(PO4)3 and Na4Mn9O18 Selective Insertion Electrode Performance. Langmuir 33, 12580-12591.

Strom, P.F., August 2006. Technologies to Remove Phosphorus from Wastewater

Tang, W., He, D., Zhang, C., Waite, T.D., 2017. Optimization of sulfate removal from brackish water by membrane capacitive deionization (MCDI). Water Research 121, 302-310.

Tuan, T.N., Chung, S., Lee, J.K., Lee, J., 2015. Improvement of water softening efficiency in capacitive deionization by ultra purification process of reduced graphene oxide. Current Applied Physics 15, 1397-1401.

Wilkinson, G.M., 2017. Eutrophication of Freshwater and Coastal Ecosystems Encyclopedia of Sustainable Technologies. Elsevier, Oxford, pp. 145-152.

Zarzo, D., Prats, D., 2018. Desalination and energy consumption. What can we expect in the near future? Desalination 427, 1-9.

Zhang, C., He, D., Ma, J., Tang, W., Waite, T.D., 2018. Faradaic reactions in capacitive deionization (CDI) - problems and possibilities: A review. Water Research 128, 314-330.

Zhao, R., Satpradit, O., Rijnaarts, H., Biesheuvel, P., Van der Wal, A., 2013. Optimization of salt adsorption rate in membrane capacitive deionization. Water research 47, 1941-1952.