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Electro-assisted removal and selective recovery of Cu(II) from aqueous solution with a chitosan-containing composite electrode application in capacitive deionization

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ABSTRACT

This study presents a simple and effective method of enhanced removal and selective recovery of Cu(II) from aqueous solution using a chitosan composite electrode in a capacitive deionization system. The electrode was composed of chitosan, polyvinyl alcohol (PVA), and activated carbon powder. Its physico chemical and electrochemical characteristics were investigated by SEM, BET, FT-IR analyses and by cyclic voltammetry, respectively. The electrical potential for the electrosorptive removal of Cu(II) and the regeneration of the electrode were determined, and its Cu(II) selectivity was examined. It was shown that the Cu(II) removal capacity and kinetics were dependent on the applied potentials and reached a maximum capacity at 0.6 V with a composition of chitosan:PVA:ACP of 1:1:3. This result explains the significant influence of the electrical potential by the formation of an electrical double layer on the surface of the chitosan electrode, accelerating the removal of Cu(II). The electrode was successfully regenerated under a reverse electrical potential above 2.5 V with flowing deionized water without the use of chemicals. Moreover, the particular selectivity of Cu(II) from various cation mixture solutions using this system was confirmed. This finding implies that the suggested chitosan composite electrode system may be suitable for industrial utilization for the removal and therefore concentration of Cu(II) from wastewater.

Keywords: Cu(II) adsorption; Chitosan composite electrode; Electrical double layer; Cu(II) selectivity

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1. Introduction

Cu(II) is present in wastewater effluents from industries because it is used in coatings, wire, electronic parts and as a catalyst [1–2]. Cu(II) is known to be toxic to the environment and humans due to its non-degradable property, and thus the removal of Cu(II) from wastewater and industrial effluents is necessary [3–6]. The most commonly studied methods for the removal of Cu(II) from wastewater include precipitation, membrane separation, and adsorption [7]. Among them, adsorption using chitosan is expected to be promising in actual industrial applications due to its abundance in nature, bio-degradability, and adsorptive removal performance [8].

Chitosan has been widely studied as a biopolymer for the adsorption of heavy metal cations such as mercury, lead, zinc, cadmium, chromium, and Cu(II) due to the inherent $–NH_2$ and –OH groups in its matrix [9]. These functional groups can provide selective removal of Cu(II) in wastewater due to ion affinity [10–15]. However, chitosan possesses a few unfavorable aspects when present as flakes or powder. Its hydrophilic nature enables chitosan to dissolve in solution

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and makes it difficult to recover after use. Extensive studies have focused on enhancing its chemical and mechanical stability by modifying chitosan with chemical reagents such as glutaraldehyde [16], epichlorohydrin [17], and genipin [18] via cross linking. Granulation and coating of substrates are also commonly used techniques for the actual application of chitosan. However, such modification can cause a decrease in ion removal (adsorption) capacities and kinetic rates by limiting mass transfer; and therefore, there are difficulties in application at low-level ion concentrations [19].

To overcome this obstacle, electrosorptive removal methods can be considered [20]. The working principle is similar to an electrical double layer capacitor (EDLC). By applying an electrical potential, charged ions move toward a reversely charged electrode and are adsorbed in the electrical double layer. After that, the charged ions are removed by a short-circuit process. During the process, neither reduction nor oxidation occurs. Based on this principle, several studies are reported to remove Cu(II) from aqueous solution using electrosorptive techniques. Ordered meso porous carbon [21], activated carbon [22], and MnO_2/carbon fiber [23] were used as electrode materials, and its adsorption performance was tested with Cu(II) concentrations of under 200 ppm. Both adsorption capacities and rates are significantly affected by the applied electrical potential. It was revealed that 0.4 V was the optimal applied potential at which copper deposition did not occur, and the electro sorption constant rate increased from 0.018 min^{-1} (without electrical potential) to 0.038 min^{-1} at 0.4 V [22].

In this study, we report the electrosorptive removal of Cu(II) from aqueous solution using a chitosan composite electrode. The electrode was composed of chitosan, polyvinyl alcohol, and activated carbon powder. The effect of applied potentials, initial Cu(II) concentration, pH, and the composition of materials in the electrode on the electrosorptive removal of Cu(II) were investigated. Interestingly, aside from the conventional electrosorptive removal system using EDLC theory, the adsorbed Cu(II) cannot be easily removed via simple short-circuiting due to the interaction between chitosan and Cu(II). Electro sorbed ions on the chitosan composite electrode except for Cu(II) are removed from the electrode via short-circuiting process. This result indicates that Cu(II) can be concentrated during desorption (regeneration of electrode). Moreover, from an economic standpoint, it is important to selectively recover Cu(II) from solution. Thus, regeneration of electrodes, cyclic performance, and selectivity studies with the multi-cation component system were also performed.

2. Experimental

2.1. Preparation of chitosan composite electrodes

The chitosan solution was prepared by dissolving 2 wt% of chitosan flakes (medium molecular weight, 75–85% deacetylated, Sigma-Aldrich) in acetic acid (99%, Samchun); 15 wt% of PVA (average molecular weight 31,000–50,000, 98–99 hydrolyzed, Sigma-Aldrich) dissolved in deionized water was also prepared. The chitosan and PVA solutions and ACP (specific surface area > 1,300 m^2/g, Daedong AC Crop) were mixed with a mechanical stirrer for 2 h. The mixture was cast onto conductive graphite sheets (Dongbang Carbon Co., Korea) with a thickness of 450 μm using a doctor blade. The coated electrode was dried at 373 K in an oven for 30 min and immersed in 1 M NaOH solution for 1 h. It was rinsed with deionized water several times to reach a neutral pH and was cut into 10 × 10 cm^2 pieces and kept in deionized water before use. The net dry weight of chitosan composite on the graphite sheet was 0.2–0.3 g. The prepared samples were denoted as C113, C212, C311, and C014, respectively, in accordance with the dry weight contents of chitosan:PVA:ACP. For comparison, PVA electrode was also prepared using glutaraldehyde [24] as a cross linking agent and denoted as C010.

2.2 Preparation of counter electrode

The ACP electrode was prepared as a counter electrode as follows. A well-blended mixture of ACP and poly (vinylidenefluoride) (PVDF, average molecular weight 530,000, Sigma-Aldrich) was dissolved in di-methylacetamide (99.5%, Daejung, Korea) with a total binder content of 15 wt%. After drying, it was cast onto graphite sheets using a doctor blade. The coated electrode was dried in a vacuum oven at 323 K. The dried electrode was heated at 363 K and was then uniformly pressed using a roll press. The resulting electrode was further immersed in deionized water to remove residual DMAc. After that, it was cut into size of 10 × 10 cm^2, and kept in deionized water before use.

2.3. Characterization

The surface morphologies of the prepared chitosan composite electrodes were observed using scanning electron microscopy (SEM, S-4800, HITACHI). The specific surface area (S_{BET}) of the electrode samples were measured by the Brunauer-Emmet-Teller (BET) equation. The total micropore volume (V_{micro}) and the total mesopore volume (V_{meso}) of the electrode samples were determined using the MP method [25] and BJH method [26], respectively, from the liquid nitrogen adsorption at 77 K on Micromeritics ASAP-2400 system after degassing at 100°C for 3 h. The surface functional groups on the chitosan composite electrodes were identified using an FT-IR spectrometer with attenuated total reflectance (FT-IR/ATR, VERTEX 80/80v, Bruker). The electrochemical characteristics were determined using cyclic voltammetry with a potentiostat (WMPG-1000, WonATech).

2.4. Electrosorptive removal properties

All electro sorption tests were conducted in a batch-mode experiment with a continuous flowing Cu(II) solution using chloride salts at a flow rate of 2 ml/min using a peristaltic pump. Fig. 1 shows schematic diagrams of the test cell and experimental device. Between the chitosan and ACP electrodes, porous polyurethane foam was positioned to maintain the gap distance (200 μm) and the function of the flow path for Cu(II) solution. The Cu(II) adsorption capacity was calculated with following equations.

$$q_e = \left(C_0 - C_e\right)\left(\frac{V}{m}\right) \tag{1}$$

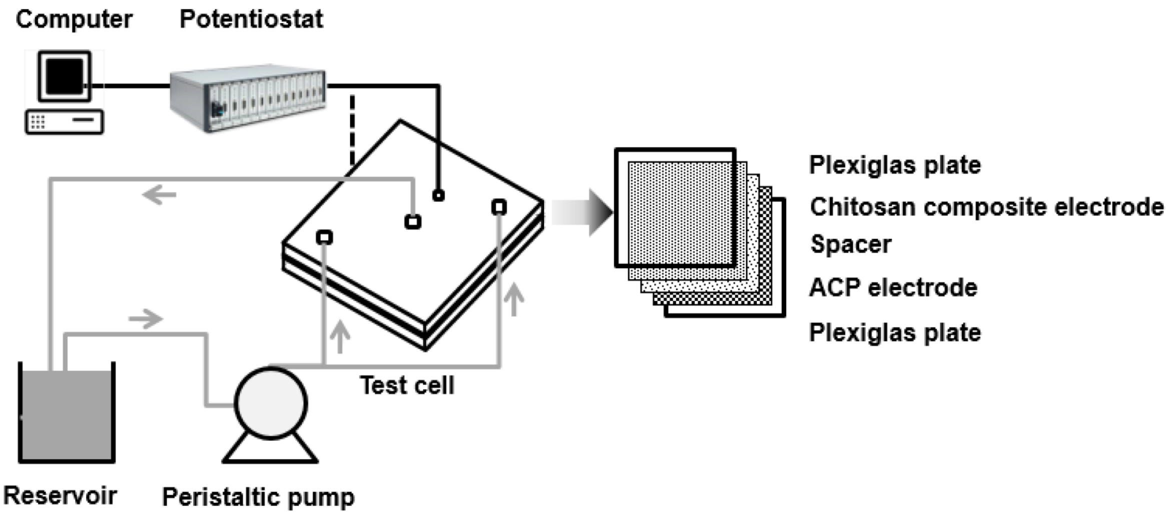

Fig. 1. Schematic overview of experimental setup for Cu(II) recovery system.

where q_e is the adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg/l) of the cations, V is the volume of the solution (L), and m is the CPA composite dry weight (g). The concentration of cations in the effluent solutions were analyzed using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Optima 7300D, PerkinElmer).

2.5. pH of solution

The adsorption properties are strongly dependent on the initial pH of the solution. The amine groups in the chitosan molecules can be protonated at pH 2–4, which causes the electrostatic repulsion of Cu(II) due to the formation of $–NH_3^+$ sites [27,28]. Precipitation of Cu(II) to $Cu(OH)_2$ can occur at high pH, and thus it is important to maintain an initial pH of less than 6. In all experiment, the pH was adjusted to approximately 6 by adding HCl and $Cu(OH)_2$ to the stock solution.

2.6. Regeneration of electrode after electro sorption

Before the regeneration of electrode, deionized water was fed into the cell to remove the remaining ions from the electrode interface at open circuit. Reverse electrical potentials with a potential range from 0 to 3.5 V between two electrodes system were applied by feeding deionized water and HCl solution for 900 min at a flow rate of 2 mL/min using a peristaltic pump.

2.7. Selectivity

To investigate Cu(II) selectivity from divalent cations, a stock solution containing Cu(II), Cd(II), Ni(II), Co(II), and Mg(II) was prepared using chloride salts of each reagent (purity 98–99.5%). The Cu(II) selectivity in the effluent solution during electrodesorption was determined using the selectivity factor for Cu(II) with respect to other metal cations and was calculated using the following equation:

$$\mathrm{S} = \frac{C_{d,Cu}}{C_{d,M}} \tag{2}$$

where S is the selectivity factor and $C_{d,Cu}$ and $C_{d,M}$ (mg/l) are the concentration of desorbed cations. Here, M represents cations such as Cd(II), Ni(II), and Co(II). The desorbed metal ion amounts of the samples obtained in the desorption process was calculated as follows:

$$\mathrm{C}_{d,M} = \frac{C_d V}{m} \tag{3}$$

where C_d is desorbed metal ion concentration in the solution, V is the collected solution volume (L), and m is the mass of chitosan in adsorbent layer. Moreover, the system was tested in synthetic LCD wastewater [29] to demonstrate the effectiveness of this system in actual application for the selective recovery of Cu(II).

3. Results and discussion

3.1. Characteristics of chitosan composite electrodes

Physical properties such as porosity, specific surface area, pore size distribution, wettability, and mechanical properties are important characteristics for the electrode in electrosorptive ion adsorption from an aqueous solution [30–32]. The prepared electrodes were easily wet with an aqueous solution and maintained their shape under various experimental conditions, such as hydraulic pressure and applied potential. Figs. 2a–c show the surface and cross-sectional views of prepared chitosan electrodes. Smooth and flat surfaces can be seen for C410 (Fig. 2a), and rougher surfaces are found with increasing ACP content in composite electrodes. The cross-sectional images also confirmed more accessible Cu(II) inside the chitosan composite. Such morphologies are desirable for better access of Cu(II) to the functional group of chitosan while a potential is applied. Moreover, as shown in Table 1, the average pore

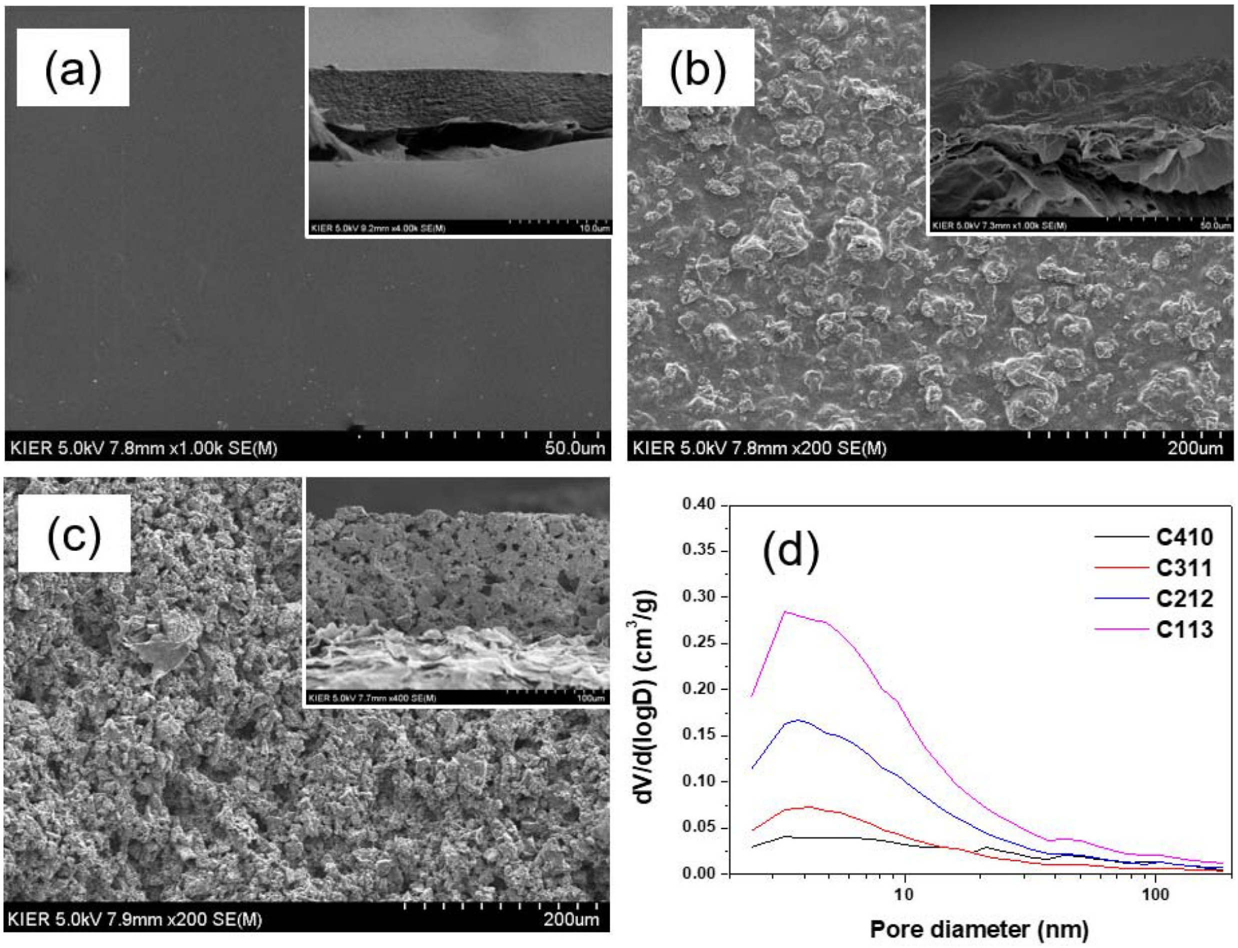

Fig. 2. SEM images and pore size distribution of prepared chitosan composite electrodes (a) C410, (b) C311, (c) C113. Insets are cross-sectional view of each electrode.

Table 1
Physical characteristics of chitosan-PVA-activated carbon composite electrodes

Sample	SBET (m^2/g)	Average pore diameter (nm)	V micro (cm^3/g)	V meso (cm^3/g)
C410	17.13	16.19	0.0077	0.0455
C311	23.93	9.87	0.0118	0.0517
C212	95.10	3.64	0.0164	0.0640
C113	184.93	2.78	0.0102	0.1024

diameter of Chitosan-PVA composite electrode determined by BET analysis was 16.19 nm and it was decreased to 2.78 nm by increasing ACP contents in electrode. The V_{meso} and S_{BET} surface areas increased from 0.0455 cm³/g, 17.13 m²/g to 0.1024 cm³/g, 184.93 m²/g and with increasing content of ACP in the electrode. Considering the effect of high specific surface area and mesopore volume on enhancing electrosorptive capacities [33,34], the C113 electrode might expect to have higher electro sorption capacities than other electrodes.

3.2. Cyclic voltammetry test

CV measurements were performed to confirm the potential window for electrosorptive removal of Cu(II) in this system. Fig. 3a presents cyclic voltammograms for the C113 and ACP electrode system in 20 mg/L of Cu(II) solution at various potentials with a scan rate of 10 mV/s. One current peak observed at around 0.75 V in the potential widow of –1.0 V to 1.0 V. It indicates that reduction of Cu(II) to Cu metal occurred on the surface of the electrode [22]. In the potential range from –0.6 to 0.6 V, typical capacitive behavior was observed without evident oxidation/reduction suggested that electrodes can form an electrical double layer under charging potential [35]. On the other hands, current peaks corresponding to the complex formation between Cu(II) and a mine group in chitosan were not observed in the experimental condition. The environmental conditions are known to be important parameters in the formation of Cu(II) and a mine complexes. Thus, another CV measurement was carried out in 200 mg of Cu(II) solution with various scan rates. As shown in Fig. 3b, a small current peak corresponding to the Cu(II) complex [36] is observed at 0.35 V with a scan rate of 2 mV/s and it shifted to higher voltage

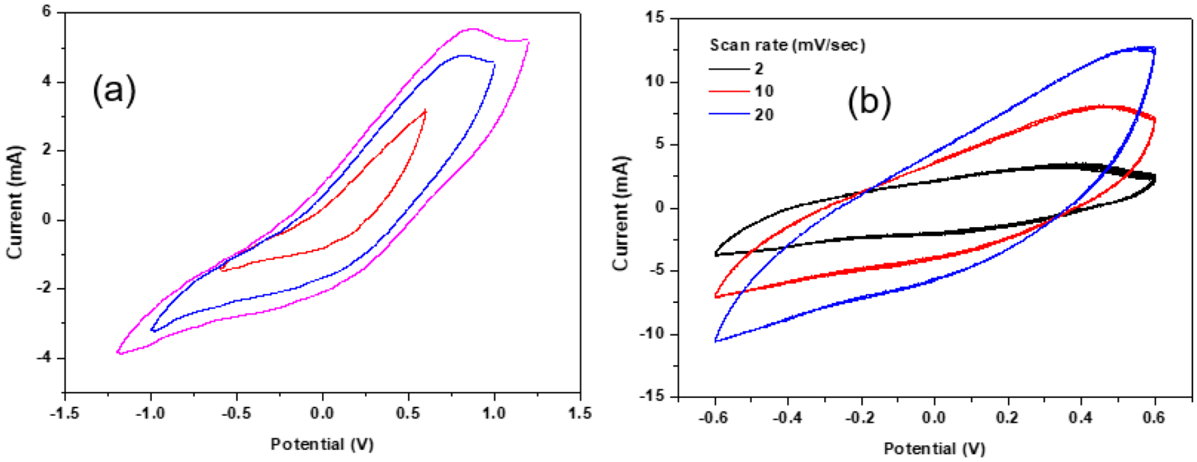

Fig. 3. Cyclic voltammograms obtained using a two-electrode configuration (C113 vs. ACP electrodes) of (a) various potential windows in a 20 ppm $CuCl_2$ solution with a scan rate of 10 mV/s, and (b) various scan rates in a 200 ppm $CuCl_2$ solution.

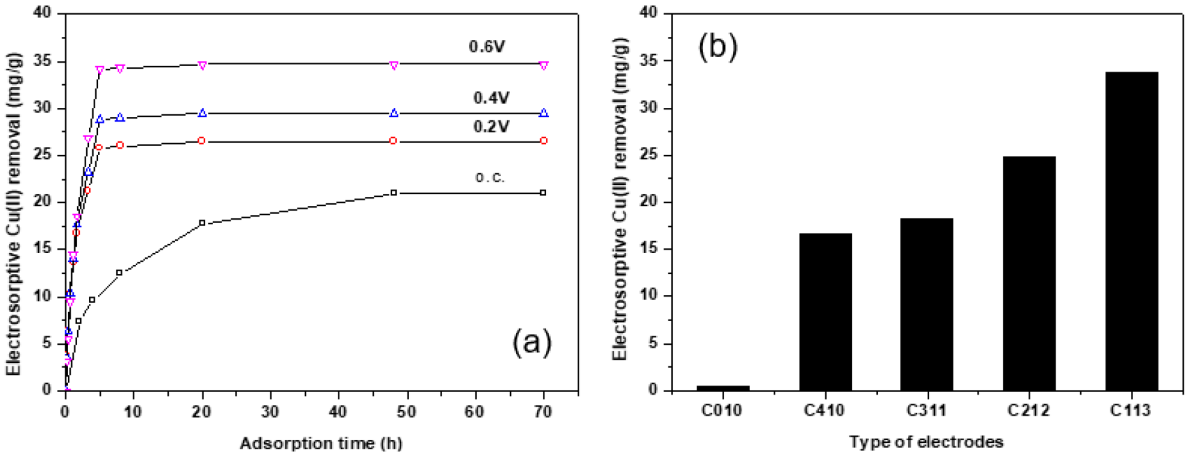

Fig. 4. Effect of (a) electrical potential and (b) ACP content on electrosorptive Cu(II) removal (C_o = 40 ppm, V = 200 ml, feed rate = 2 ml/min).

by increasing the scan rate. Based on these results, the following electro sorption tests were performed under the potential limit to 0.6 V to prevent deposition of Cu during electro sorption.

3.3. Electrosorptive removal performance

The electrosorptive Cu(II) removal performances were investigated using the C113/ACP electrode system at various applied potentials. A test of physisorption without electrical potential (open circuit, o.c.) was also conducted to confirm the effect of electrical potential on electro sorption. As shown in Fig. 4a, adsorption equilibrium was reached after 48 h for 18 mg/L of Cu(II) for the o.c. condition. The maximum capacities increased up to 35.5 mg/L at 0.6 V, and adsorption equilibrium was reached faster in 4 h under electrical potential. These results indicate that electrochemical polarization showed significant enhancement of Cu(II) transfer from bulk solution onto the electrode [22]. Moreover, a higher electrical potential (0.6 V) was preferable to improve the capacitance of the chitosan/ACP electrode system for Cu(II) adsorption.

Fig. 4b shows the effect of mixture composition on electrosorptive Cu(II) removal capacities. No significant Cu(II) adsorption was detected when C010 (PVA-GA cross linked film electrode) was used. This means that the hydroxyl group on the PVA matrix and the chitosan matrix do not effectively influence electrosorptive and adsorptive Cu(II) removal. By increasing the amounts of chitosan and ACP in the composite electrodes, the maximum capacities increased from 16.7 mg/L for C410 to 35.5 mg/L for CPA113. This indicates that the amounts of ACP affect electrosorptive Cu(II) removal performance compared to chitosan. Thus, the optimized proportion obtained from the experiment for chitosan/PVA/ACP was selected as 1:1:3 (C113).

3.4. Electro sorption kinetics of Cu(II)

To understand the adsorption/electro sorption kinetic of Cu(II) on the chitosan composite electrode, two classical pseudo-first-order and pseudo-second-order models were employed [37–39]. The linearized forms of both kinetic models are as follows:

$$C_{d,M} = \frac{C_d V}{m} \tag{3}$$

$$-k_1 t = ln\left[\frac{(q_e - q_t)}{q_e}\right] \tag{4}$$

where q_e (mg/g) is the amount of adsorbed Cu(II) at equilibrium, q_t (mg/g) is the quantity of Cu(II) adsorbed in the chitosan composite electrode at time t, and k_1 (min^{-1}) and k_2 (g/(mg min)) are the pseudo-first-order and pseudo-second-order reaction rate constants, respectively.

The linearized plot fitting of the kinetic models to experimental data is shown in Fig. 5, and its kinetic parameters are listed in Table 2. Both kinetic models fitted well with the experimental data, but the regression coefficient (R^2) for the pseudo-second-order models were relatively higher than for pseudo-first-order. This can be explained by considering that the pseudo-second-order mechanism includes the majority of metal adsorption kinetics for the adsorption of divalent metals on heterogeneous sorbent [40]. Complexation could occur by sharing electrons between the a mine in chitosan and Cu(II), with or without applied electrical potential. This is the probable explanation for the Cu(II) adsorption mechanism on the surface of the chitosan electrode.

3.5. FT-IR

FT-IR spectra were used to observe the Cu(II) adsorption behavior during electro sorption. Three C113 electrodes, before adsorption (as-prepared), after physisorption, and after electro sorption, were collected. To prepare the Cu(II) physisorbed electrode, the C113 was immersed in 200 mL of a 100 ppm Cu(II) solution for 48 h with shaking and washed with deionized water several times. To prepare the Cu(II) electro sorbed electrode, 200 mL of a 100 ppm Cu(II) solution was fed into the electrochemical cell at 2 mL/min with a cell potential of 0.6 V for 300 min. As shown in Fig. 6, the FT-IR spectra and transmittance were significantly altered after adsorption of Cu(II). This reveals that the same Cu(II) adsorptive interactions accrued between the chitosan matrix and Cu(II) during physisorption and electro sorption. More specifically, the transmittance changes in the frequency range of 3100–3500 cm^{-1} were observed, char-

Table 2
Parameters of kinetic models studied for Cu(II) electrosorption

Cell potential (V)	Pseudo first order			Pseudo second order		
	q_e (mg/g)	$k_1 \times 10^3$ (min^{-1})	R^2	q_e (mg/g)	$k_2 \times 10^3$ (g/mg min^{-1})	R^2
o.c.	18.48	1.130	0.916	19.85	0.405	0.990
0.2	23.60	7.720	0.980	24.89	0.370	0.989
0.4	26.25	8.150	0.972	27.72	0.253	0.985
0.6	34.15	9.300	0.951	33.08	0.110	0.983

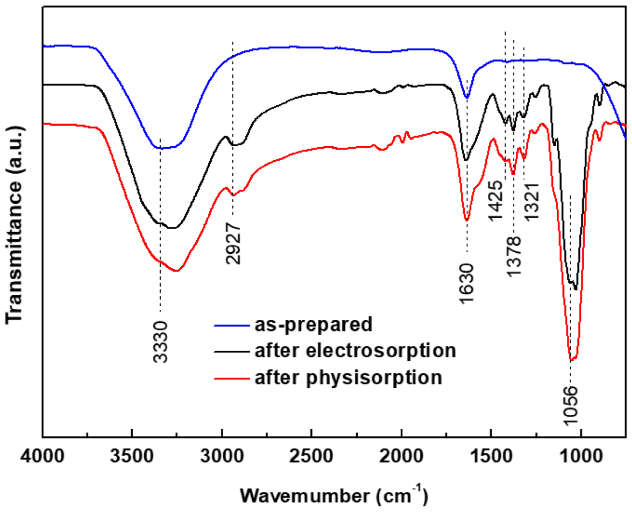

Fig. 6. FT-IR spectra of C113 electrodes before (as-prepared) adsorption, after physisorption, and after electro sorption of Cu(II).

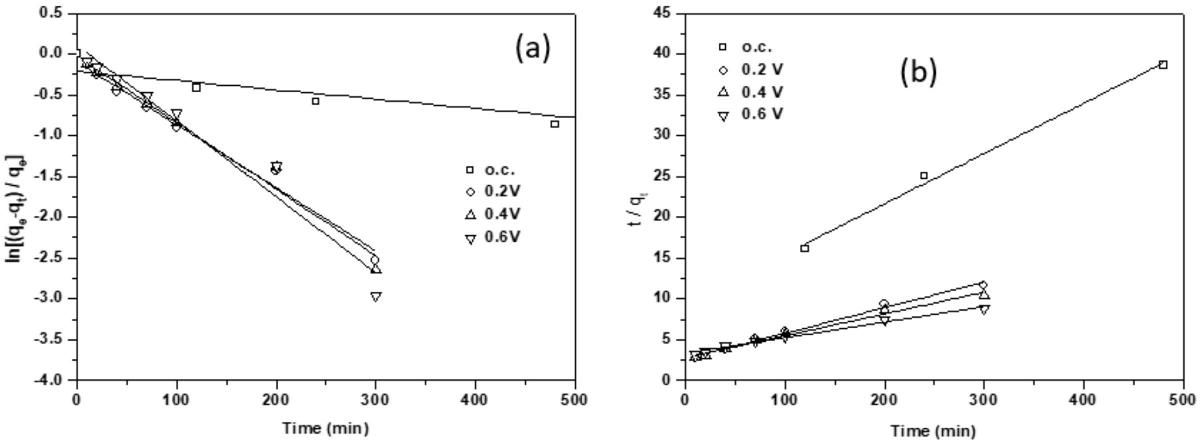

Fig. 5. Linearized plots of pseudo-first- (a) and pseudo-second- (b) order kinetic models at various electrical potentials (C_o = 40 mg/l, V = 200 ml, feed rate = 2 ml/min).

acterized as N-H amino groups. This led to the consideration that N-H amino groups are involved in the formation of chelated chitosan compounds with Cu(II) [41] in good agreement with the kinetic analysis. Other changes in transmittance were also observed at 1638 cm^{-1} for N-H bending and 1050 cm^{-1} for C-N stretching. Many peaks related to OH and CH groups in the frequency ranges of 1250 to 1500 cm^{-1} and 2700 to 3400 cm^{-1} were also observed [5] and its transmittance was decreased similarly after Cu(II) adsorption. This appears to be due to the contribution of the OH group to the chelation of chitosan with Cu(II).

3.6. Recovery of Cu(II)

Recovery of electrode, in other words removal of adsorbed Cu(II) from chitosan electrode, was examined using two parameters: pH and reverse electrical potentials. Before the desorption test, the simple charged Cu(II) ions in EDL without bonding between Cu(II) and the functional group of chitosan were removed by flowing deionized water for 75 min. Approximately 3 mg of Cu(II) were rinsed for the C113 electrode. Fig. 7a shows pH-dependent Cu(II) desorption characteristics from the chitosan electrode. In all, 32 mg of Cu(II) was removed at pH 3.0 (32 mg) from the chitosan composite electrode. By considering the washed amounts of Cu(II), almost all of the remaining Cu(II) was successfully removed in acidic condition, but only small amounts of Cu(II) were removed at pH values greater than 4. This means that Cu(II) can be more effectively desorbed from chitosan electrode in acidic conditions [42,43].

Electrodesorption was achieved by applying reverse electrical potential ranging from 0 (o.c.) to 3.5 V under flowing deionized water and an acidic solution (pH 3). In addition, to avoid deposition of desorbed Cu(II) on the opposite electrode, a cation exchange membrane was installed in front of the ACP electrode before electrodesorption [44]. Fig. 7b shows the electrodesorption of Cu(II) from the chitosan electrode. Significant amounts of Cu(II) were successfully removed by increasing electrical potentials but no further increase was observed in the acidic condition. Thus, the desorption efficiency appears to be solely dependent on the applied electrical potential.

3.7. Selectivity and regeneration properties

The selectivity for Cu(II) from a divalent cation mixture solution of $CuCl_2$, $NiCl_2$, $CdCl_2$ and $CoCl_2$ was investigated. Electro sorption, washing, and electrodesorption processes were conducted. The initial concentration of each cation in the solution was 100 ppm. Table 3 shows the concentration of cations after each step. The observed trend for the selectivity factor of metal-ion electro sorption followed the order Cu(II) >> Cd(II), Ni(II) > Co(II), and this result was similar to previous studies using chitosan-based composite materials [12–15]. Moreover, the regeneration of the Cu(II) and its selectivity performance were also important in this process. The electro sorption, washing, and electrodesorption cycles were repeated five times. As shown in Fig. 8, almost similar amounts (28 ~ 29 mg/g) of Cu(II) were observed in electrodesorption process. This result shows that the reusability and stability of the chitosan composite electrode is suitable for use in a continuous Cu(II) recovery process under experimental conditions.

Additional experiments were performed to evaluate the actual application for the selective recovery of Cu(II) in more complex cationic mixtures of synthetic LCD wastewater. Its initial concentration of cations and metal ion recovered amounts are shown in Table 4. As expected, higher selectivity factors for divalent cations ($C_{d,Cu}/C_{d,Mg}$ = 68.00) were observed. Moreover, selectivity factors of 67.95 and 34.00 for B(III) and K(I) were also found. These results showed

Table 3
Selectivity of Cu(II) on chitosan composite electrodes

Metal ions	C_o (ppm)	$C_{d,M}$ (ppm)	S
Cu(II)	96.04	28.31	1
Cd(II)	97.91	4.12	6.87
Ni(II)	103.56	1.92	14.74
Co(II)	102.67	1.36	20.82

Experimental conditions: T = 303 K, V = 200 mL, flow rate = 2 ml/min, electro sorption at –0.6 V for 300 min, washing of 75 min with deionized water, electrodesorption at 2.5 V for 12 h with deionized water.

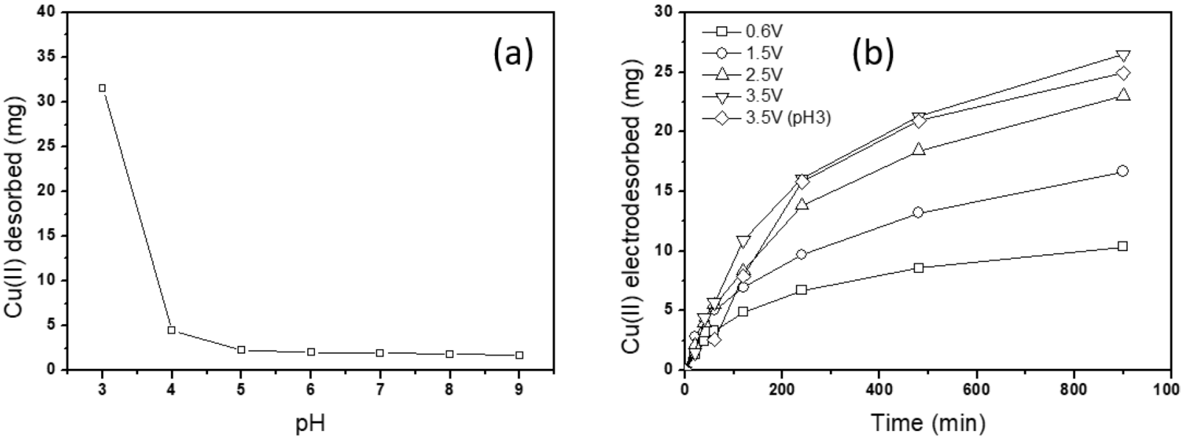

Fig. 7. Removal and recovery of Cu(II) from chitosan electrode (C113) with effect of (a) pH and (b) reverse electrical potentials.

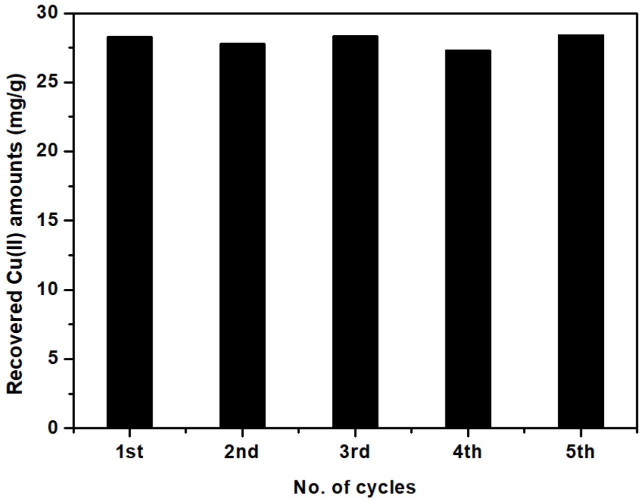

Fig. 8. Recovered Cu(II) amounts during electrodesorption process in 5 repeated electro sorption, washing, and electrodesorption process.

Table 4
Composition of wastewater and Cu(II) selectivity

Metal ions	C_o (ppm)	$C_{d,M}$ (ppm)	S
Cu(II)	59.90	9.52	–
Mg(II)	1.50	0.14	68.00
Fe(II)	0.10	N.D.[1]	–
Ni(II)	1.60	N.D.[1]	–
B(III)	12.11	0.14	67.95
K(I)	72.60	0.28	34.00

Experimental conditions: T = 303 K, V = 1000 ml, flow rate = 2 ml/min, electrosorption at -0.6 V for 300 min, washing of 75 min with deionized water, electrodesorption at 2.5 V for 12 h with deionized water.

1) Not detected.

that chitosan composite electrodes can preferentially adsorb Cu(II), indicating the selective adsorption effect of chitosan under electrical potential better than competitive cations with a different oxidation state. Thus, we conclude that the suggested chitosan composite electrode – ACP electrode system has a potential application for selective recovery of Cu(II) from a complex cationic mixture.

4. Conclusions

Chitosan composite electrodes composed of chitosan, PVA, and ACP were prepared and their electrosorptive Cu(II) removal capacities from aqueous solution and selectivity performance were determined. It was observed that the Cu(II) removal capacity and kinetics were dependent on the applied potentials, showing an optimum adsorption potential of 0.6 V with a chitosan:PVA:ACP composition of 1:1:3 (C113). Recovery of adsorbed Cu(II) from the chitosan electrode was investigated with varying pH and reverse electrical potential. The adsorbed Cu(II) was effectively removed from the chitosan electrode at pH 3.0 in an 1 M NaCl + HCl solution. Interestingly, it was also successfully removed under a reverse electrical potential of 2.5 V flowing deionized water without acidic or basic chemicals. This indicates that electrical potential can achieve but adsorption and desorption processes. Moreover, the chitosan composite electrode can preferentially adsorb Cu(II) from a multi-cation mixture, indicating a selective adsorption property. Hence, the chitosan composite electrode is expected to have great application in selective Cu(II) removal and recovery, due to its high adsorption performance, selectivity, and efficiency.

Acknowledgments

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References

[1] J. Yoo, T. Shim, J. Hur, J. Jung, Role of polarity fractions of effluent organic matter in binding and toxicity of silver and copper, J. Hazard. Mater., 317 (2016) 344–351.

[2] Y.S. Petrova, A.V., Pestov, M.K. Usoltseva, L.K. Neudachina, Selective adsorption of silver(I) ions over copper(II) ions on a sulfoethyl derivative of chitosan, J. Hazard. Mater., 299 (2015) 696–701.

[3] S.A. Al-Saydeh, M.H. El-Naas, S.J. Zaidi, Copper removal from industrial wastewater: A comprehensive review, J. Ind. Eng. Chem., 56 (2017) 35–44.

[4] U.C. Gupta, S.C. Gupta, Heavy metal toxicity in humans and its preventive and control measures, Curr. Nutr. Food Sci., 7 (2011) 221–231.

[5] N. Li, R. Bai, Copper adsorption on chitosan–cellulose hydrogel beads: behaviors and mechanisms, Sep. Purif. Technol., 42 (2005) 237–247.

[6] J. Ng, W. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interface Sci., 255 (2002) 64–74.

[7] S.T. Lee, F.L. Mi, Y.J. Shen, S.S. Shyu, Equilibrium and kinetic studies of copper(II) ion uptake by chitosan-tripolyphosphate chelating resin, Polymer., 42 (2001) 1879–1892.

[8] A. Altinisik, Y. Kadir, Chitosan/PVA coated magnetic nano particles for Cu(II) ions adsorption, Desal. Water Treat., 57 (2016) 18463–18474.

[9] N.A. Negm, R. El-Sheikh, A.F. El-Farargy, H.H. Hefni, M. Bekhit, Treatment of industrial wastewater containing copper and cobalt ions using modified chitosan, J. Ind. Eng. Chem., 21 (2015) 526–534.

[10] Y. Ren, M. Zhang, D. Zhao, Synthesis and properties of magnetic Cu(II) ion imprinted composite adsorbent for selective removal of copper, Desalination, 228 (2008) 135–149.

[11] B. Goze, O.A. Evirgen, Y.S. Acikel, Investigation of antagonistic and synergistic interactions on simultaneous adsorption of crystal violet and Cu(II) using chitin and chitosan, Desal. Water Treat., 57 (2016) 4059–4072.

[12] I.M. Vold, K.M. Vårum, E. Guibal, O. Smidsrød, Binding of ions to chitosan-selectivity studies, Carbohydr. Polym., 54 (2003) 471–477.

[13] J. Rangel-Mendez, R. Monroy-Zepeda, E. Leyva-Ramos, P. Diaz-Flores, K. Shirai, Chitosan selectivity for removing cadmium(II), copper(II), and lead(II) from aqueous phase: pH and organic matter effect, J. Hazard. Mater., 162 (2009) 503–511.

[14] M. Rhazi, J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, M. El Meray, Influence of the nature of the metal ions on the complexation with chitosan.: Application to the treatment of liquid waste, Eur. Polym. J., 38 (2002) 1523–1530.

[15] D. Liu, Z. Li, Y. Zhu, Z. Li, R. Kumar, Recycled chitosan nano fibril as an effective Cu(II), Pb(II) and Cd(II) ionic chelating agent: adsorption and desorption performance, Carbohydr. Polym., 111 (2014) 469–476.
[16] I. Sargin, A. Gulsin, Effect of glutaraldehyde cross-linking degree of chitosan/sporopollenin micro capsules on removal of copper(II) from aqueous solution, Desal. Water Treat., 57 (2016) 10664–0676.
[17] Y. Wei, S. Hudson, J. Mayer, D. Kaplan, The cross linking of chitosan fibers, J. Polym. Sci. A Polym. Chem., 30 (1992) 2187–2193.
[18] R.A. Muzzarelli, Genipin-cross linked chitosan hydrogels as biomedical and pharmaceutical aids, Carbohydr. Polym., 77 (2009) 1–9.
[19] S.R. Popuri, Y. Vijaya, V.M. Boddu, K. Abburi, Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads, Bioresour. Technol., 100 (2009) 194–199.
[20] J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala, J.F. Poco, Capacitive deionization of NaCl and $NaNO_3$ solutions with carbon aerogel electrodes, J. Electro chem. Soc., 143 (1996) 159–169.
[21] C.-C. Huang, J.-C. He, Electrosorptive removal of copper ions from wastewater by using ordered mesoporous carbon electrodes, Chem. Eng. J., 221 (2013) 469–475.
[22] S.-Y. Huang, C.-S. Fan, C.-H. Hou, Electro-enhanced removal of copper ions from aqueous solutions by capacitive deionization, J. Hazard. Mater., 278 (2014) 8–15.
[23] C. Hu, F. Liu, H. Lan, H. Liu, J. Qu, Preparation of a manganese dioxide/carbon fiber electrode for electrosorptive removal of copper ions from water, J. Colloid Interface Sci., 446 (2015) 359–365.
[24] C.-K. Yeom, K.-H. Lee, Pervaporation separation of water-acetic acid mixtures through poly (vinyl alcohol) membranes cross linked with glutaraldehyde, J. Memb. Sci., 109 (1996) 257–265.
[25] R.S. Mikhail, S. Brunauer, E.E. Bodor. Investigations of a complete pore structure analysis: I. Analysis of micropores, J. Colloid Interface Sci., 26 (1968) 45–53.
[26] E.P. Barrett, L.G. Joyner, P.P. Halenda. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, J. Am. Chem. Soc., 73 (1951) 373–380.
[27] F. Zhao, B. Yu, Z. Yue, T. Wang, X. Wen, Z. Liu, C. Zhao, Preparation of porous chitosan gel beads for copper(II) ion adsorption, J. Hazard. Mater., 147 (2007) 67–73.
[28] A. Heidari, H. Younesi, Z. Mehraban, H. Heikkinen, Selective adsorption of Pb(II), Cd(II), and Ni(II) ions from aqueous solution using chitosan–MAA nano particles, Int. J. Biol. Macromol., 61 (2013) 251–263.
[29] K.S. Jun, S.W. Kwon, B.H. Yang, Economic evaluation and environmental assessment on electrochemical copper recovery form IT wastewater, J. Korea Society of Waste Management, 30 (2013) 625–631.
[30] H. Li, L. Pan, T. Lu, Y. Zhan, C. Nie, Z. Sun, A comparative study on electrosorptive behavior of carbon nano tubes and graphene for capacitive deionization, J. Electroanal. Chem., 653 (2011) 40–44.
[31] K.-L. Yang, T.-Y. Ying, S. Yiacoumi, C. Tsouris, E.S. Vittoratos, Electro sorption of ions from aqueous solutions by carbon aerogel: an electrical double-layer model, Langmuir, 17 (2001) 1961–1969.
[32] H.J. Liu, J. Wang, C.X. Wang, Y.Y. Xia, Ordered hierarchical mesoporous/micro porous carbon derived from mesoporous titanium-carbide/carbon composites and its electrochemical performance in super capacitor, Adv. Energy Mater., 1 (2011) 1101–1108.
[33] D. Zhang, X. Wen, L. Shi, T. Yan, J. Zhang, Enhanced capacitive deionization of graphene/mesoporous carbon composites, Nano scale, 4 (2012) 5440–5446.
[34] K. Xia, Q. Gao, J. Jiang, J. Hu, Hierarchical porous carbons with controlled micro pores and meso pores for super capacitor electrode materials, Carbon, 46 (2008) 1718–1726.
[35] L. Zou, G. Morris, D. Qi, Using activated carbon electrode in electrosorptive deionisation of brackish water, Desalination, 225 (2008) 329–340.
[36] H. Çiftçi, U. Tamer, A.Ü. Metin, E. Alver, N. Kizir, Electrochemical copper(II) sensor based on chitosan covered gold nano particles. J. Appl. Electrochem., 44 (2014) 563–571.
[37] Y.-S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater., 136 (2006) 681–689.
[38] Y.-S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Process Saf. Environ. Prot., 76 (1998) 183–191.
[39] Y.-S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics, 59 (2004) 171–177.
[40] M.-W. Wan, C-C. Kan, B.D. Rogel, M.L.P. Dalida, Adsorption of copper(II) and lead(II) ions from aqueous solution on chitosan-coated sand, Carbohydr. Polym., 80 (2010) 891–899.
[41] Z. Modrzejewska, Sorption mechanism of copper in chitosan hydrogel, React. Funct. Polym., 73 (2013) 719–729.
[42] M.L.P. Dalida, A.F.V. Mariano, C.M. Futalan, C.-C. Kan, W.-C. Tsai, M.-W. Wan, Adsorptive removal of Cu(II) from aqueous solutions using non-cross linked and cross linked chitosan-coated bentonite beads, Desalination, 275 (2011) 154–159.
[43] S. Peng, H. Meng, Y. Ouyang, J. Chang, Nano porous magnetic cellulose–chitosan composite micro spheres: preparation, characterization, and application for Cu(II) adsorption, Ind. Eng. Chem. Res., 53 (2014) 2106–2113.
[44] J.-B. Lee, K.-K. Park, H.-M. Eum, C.-W. Lee, Desalination of a thermal power plant wastewater by membrane capacitive deionization, Desalination, 196 (2006) 125–134.