Membrane Capacitive Deionization Using Ion-exchange Polymer Coated Electrodes for Resource Recovery from Wastewater

by David Kim

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under the supervision of Hokyong Shon

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Certificate of Original Authorship

Required wording for the certificate of original authorship

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, David Kim declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering/ Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Collaborative doctoral research degree statement

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree at any other academic institution except as fully acknowledged within the text. This thesis is the result of a Collaborative Doctoral Research Degree program with Korea University.

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Abstract

In the face of major global challenging issues of water scarcity, the water industry has been undergoing a paradigm shift. The limited availability of nutrients resources, such as nitrogen and phosphorus, and their oversupply as fertilizer are projected to risk the global demands for food production. Therefore, the global needs of renewable resources have driven the wastewater facilities to recycle nutrients. Wastewater has been considered an important source of recoverable nutrients and other valuable materials, and thus, resource recovery from wastewater has become attractive where technological innovation is being used to provide additional social, environmental, and economic benefits.

Membrane capacitive deionization (MCDI), driven by an electrochemical potential between two electrodes across ion-exchange membranes (IEMs), has been shown to be an effective system for recovering valuable nutritional resources dispersed in wastewater via the enrichment and selective collection of the ions present in small amounts in low salinity wastewater resources. In particular, the recovery of nitrogen and phosphorus from municipal wastewaters has been noted as one of the most feasible targets to prevent environmental issues, such as the eutrophication of water resources and procuring these biological nutrients essential for food production. However, the application potential of MCDI for the resource recovery has not been verified due to lack of its full investigation from practical perspectives.

In this study, the application potential of MCDI was explored to recover nutrient resources present in wastewater, especially converging the ion selectivity and performance efficiency during electrosorption and electrode regeneration. Carbon electrodes coated with a thin cation- or anion-exchange polymer layer which acted as an

IEM in the conventional MCDI have been mainly used as an advanced configuration for the electrosorptive process with both inducing lower membrane electrical resistance and inhibiting the electrosorption of the counter-ions during regeneration of electrodes.

The ion transport during resource recovery via MCDI, from feed water to a carbon electrode in electrosortpion and then from the carbon electrode into highly enriched brine solution in regeneration, was examined. The ion discharge was retarded by a reverse-ionic strength gradient induced by the enriched brine solution. The regeneration was further hindered when a dilute feed solution concentration was used (<10 mM), attributing to the enhanced resistance of the ion-exchange (IX) layer. Energy-efficient regeneration methods, such as short-circuiting, were constrained owing to lack of electrochemically repulsive force capable of overcoming the reverse gradient. The preferential desorption order under a mixture of cations was $K^+ > Na^+ > Mg^{2+}$, as mainly determined by their physiochemical properties, whereas the permselectivity through the cation-exchange membrane (CEM) was insignificant.

The application potential of MCDI using IX layer coated electrodes was systematically explored demonstrating its effective performance in resource recovery from wastewater, and the operating conditions were optimized considering the complex nature of the characteristics of real municipal wastewater. A higher salt adsorption capacity and charge efficiency could be attained owing to the lower resistance induced by the thinly coated layer facilitating faster ionic transport. The organic substances had an insignificant impact on the electrodes' performance in a longer operation, as the fairly adsorbed negatively charged organic compounds were well released in the consequent desorption stage. The fouling-free operation was attributed to the flat morphology of the coated IX layer surface with low roughness offering a smaller chance for the impurities to accumulate on the electrode surface.

The electrosorption selectivity followed the permselectivity through the IX layers, and was impacted by the change in their mobility under different applied potential. The selective electrosorption of NO_3^- can be enhanced by decreasing applied potential to increase relative ion mobility and by increasing water flow rate to reach faster electrode saturation. The recovery of phosphate has been examined considering the effect of phosphate speciation reactions at a typical pH range in wastewater (between 6.5 and 8.5). The overall P adsorption capacity was apparently higher in the lower pH, where $H_2PO_4^-$ dominantly presents in wastewater, owing to the smaller hydrated radii monovalent ions occupying less space within the electric double layer (EDL) for charge neutralization. However, the effect of phosphate speciation on selective phosphorus removal from wastewater was insignificant, as in reality it presents in a low amount compared to the other anions.

One of the major disadvantages of MCDI for resource recovery is the inability of electrodes to selectively remove target ions. Therefore, a nitrate selective composite electrode coated with an anion-exchange polymer with A520E resins was fabricated for enhanced recovery of nitrate. The low-contact resistance of the coated IX layer enhanced the electrosorption capacity, whereas the granular nitrate—selective resin incorporated in the IX layer rather increased the electrical resistivity. The adsorbed mole fraction of NO_3^- kept increased even after saturation, attributing to the ion exchange between Cl^- on the resin coating layer and NO_3^- contained in the bulk feed solution. However, its desorption efficiency for NO_3^- was lowered as the NO_3^- were temporarily intercepted by being exchanged with Cl^- ions in the resin at the IX layer during the ion migration towards the bulk brine solution.

The possible application of MCDI was further tested on the recovery of palladium from metal plating wastewater. The highly efficient adsorption of Pd from a single Pd solution, higher than 98.38% even at 0.3 V of low applied potential, was driven by both electrosorptive and physical adsorption. Its removal was remained to be high even under co-existence of different cations present in the metal plating wastewater, since the Pd species with high initial concentration and ionic charge valency competitively took place within the EDL. High concentration of Pd was obtained after five successive operation cycles (925.48 mg/L) from a 100 mg/L Pd catalyst solution. However, an apparent decrease in Pd removal and desorption in the successive cycles implied the deterioration of electrodes attributing to physisorption or complexation of Pd metal ions within the porous structure of electrode, resulting in reduced available surface of area of electrode for additional electrosorption.

This thesis finally concludes with recommendations to provide future insights into realizing the practical use of MCDI for the recovery of resources from wastewater. The operating conditions of MCDI are important in order to achieve selective and highly efficient resource recovery. Enriching the target resource above a desired amount could be limited due to the reverse-ionic strength gradient. Reversing polarity is expected work best for discharging ions into brine, but however, its optimized condition has to be determined carefully as its energy demand could compensate the feasibility of MCDI. Employing lower potential and higher flow rate for selective nitrate removal may rather result in poor total removal of ions in the wastewater, whereas selective collection of phosphate at the current technological level is likely to be challenging due to its low amount present in wastewater and low permselectivity through the IEM. The carbon electrodes can be customized for the enhanced extraction of target species by coating IX polymer solution. New coating techniques for a thinner selective layer incorporating micro-fine resins will further improve the charge efficiency and ion selectivity. The application of MCDI on recovery of precious metals requires preventive maintenance or cleaning strategies to inhibit the physisorption, complexation or crystal formation of the metallic species on the IX layer surface.

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