



Biomass based activated carbon electrodes for capacitive deionization in the context of nitrate and phosphate removal

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ABSTRACT

Capacitive deionization (CDI) technique is widely pursued for the removal and recovery of ionic contaminants from wastewater, as it does not leave secondary waste and can operate at low voltages < 1.2V vs. reversible hydrogen electrode (RHE) (Suss, 2015; Pastushok, 2019; Ge, 2018). Most studies in literature concentrate on desalination, however the removal of other ionic contaminants like nitrates, phosphates, sulphates, chlorides, and fluoride are also explored (Zhang, 2022; Zhang, 2023; Chen, 2022; Martinez-Vargas, 2022). In a previous work (Krishnamurthy, 2022), carbon-based electrodes were made from pine-based biomass and these electrodes were tested for their electrochemical properties, through a series of complementary experimental methods. The goal of the present work is to perform a techno-economic analysis (TEA) for the removal of ionic nitrate (NO_3^-) and phosphate (H_2PO_4^-) contaminants from wastewater using the electrochemical properties. The basis for the design was the removal of nitrates and phosphates from a wastewater stream available at a flowrate of 44l/s and an initial nitrate and phosphate concentration of 1 mM. The final concentration was fixed to be 0.1 mM after the removal of the ionic contaminants. The TEA was based on the information obtained from the characterization of the electrodes. The results showed that CDI process was economical for nitrate removal compared to that of the phosphate removal due to the higher capacitance value. Sensitivity analysis was further performed to evaluate the effect of the capacitance, the electrode replacement and the outlet concentration on the capital and the operating expenditure values.

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Abbreviations: CDI, Capacitive deionization; BET, Brunauer–Emmett–Teller; CAPEX, Capital expenditure; OPEX, Operating expenditure.

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Figures and tables

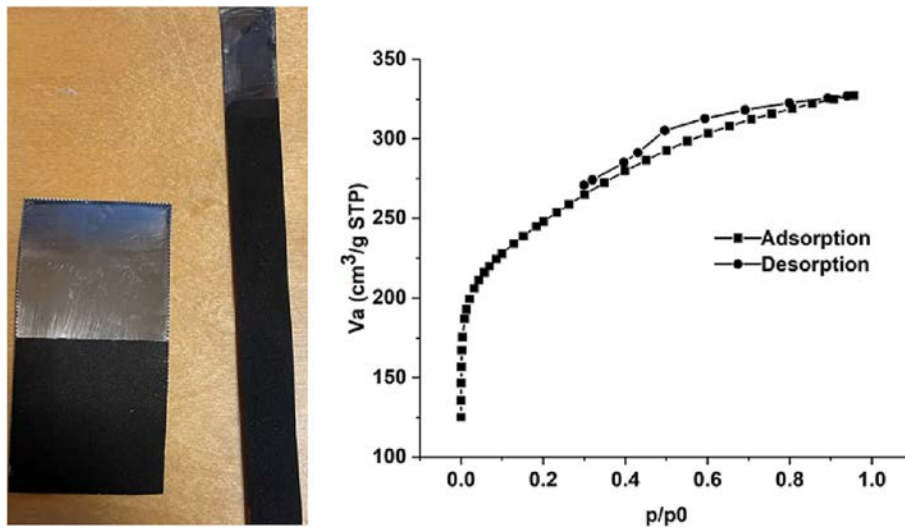


Fig. 1. On the left, are electrodes made for this work. These are done by spray coating carbon on to a stainless-steel substrate. About 2 mg of carbon was coated from every cm² of area. On the right, adsorption-desorption curves for N₂ adsorption at 77 K are shown. The carbon synthesized from the pyrolysis of pine wood has a BET surface area of 700–800 m²/g while a commercial activated carbon from MERCK has a BET surface area of 903 m²/g.

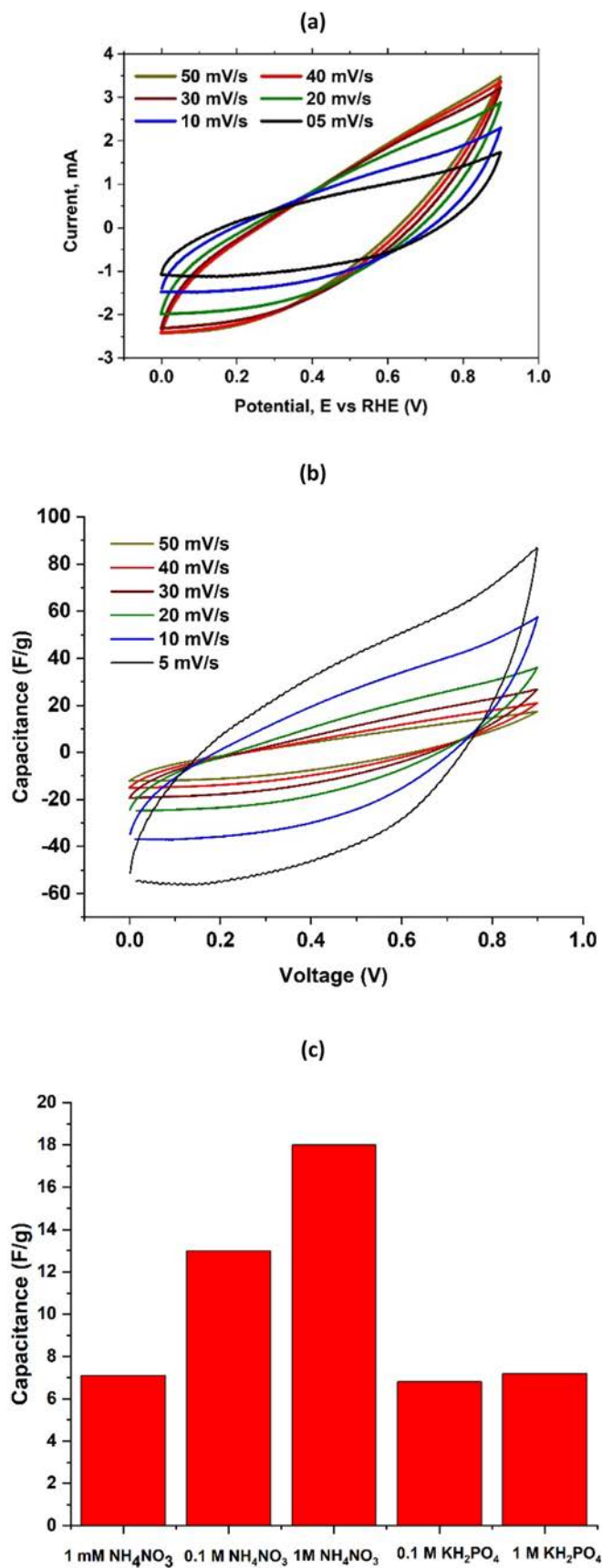


Fig. 2. (a) current vs potential in a cyclic voltammetry experiment (b) capacitance curve at different scanning rates for a 1 mM NH_4NO_3 solution. (c) summary of the capacitance values at different electrolyte concentrations. Nitrates have a higher capacitance than phosphates. For the phosphates, the capacitance values <100 mM were not measured due to high resistances. This figure is reproduced from our previous work [1].

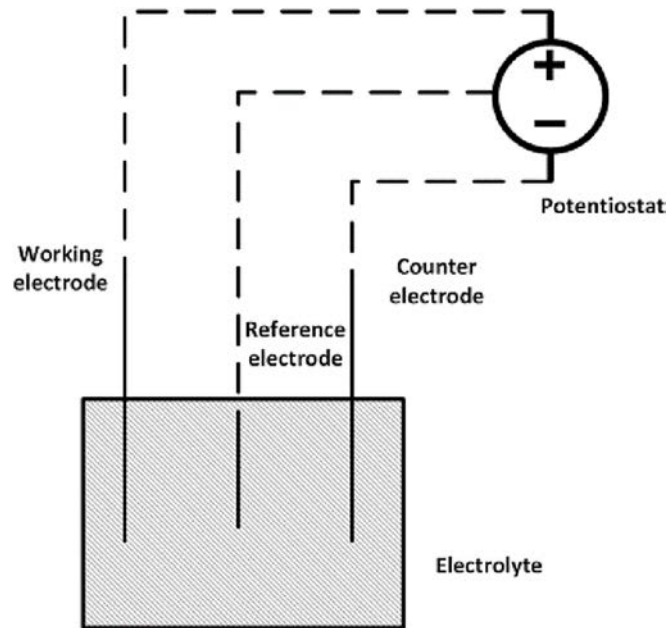


Fig. 3. Schematic of the batch test set up used for this work. It consists of a beaker with the electrolyte in which the working electrode, counter-electrode and reference electrode are immersed and they are connected to a potentiostat. The working and the counter electrodes are the carbon-SS electrodes. Adsorption takes place when the potential is supplied across the electrodes and desorption is carried out by stopping the current (0 V) or changing the polarity (-1 V).

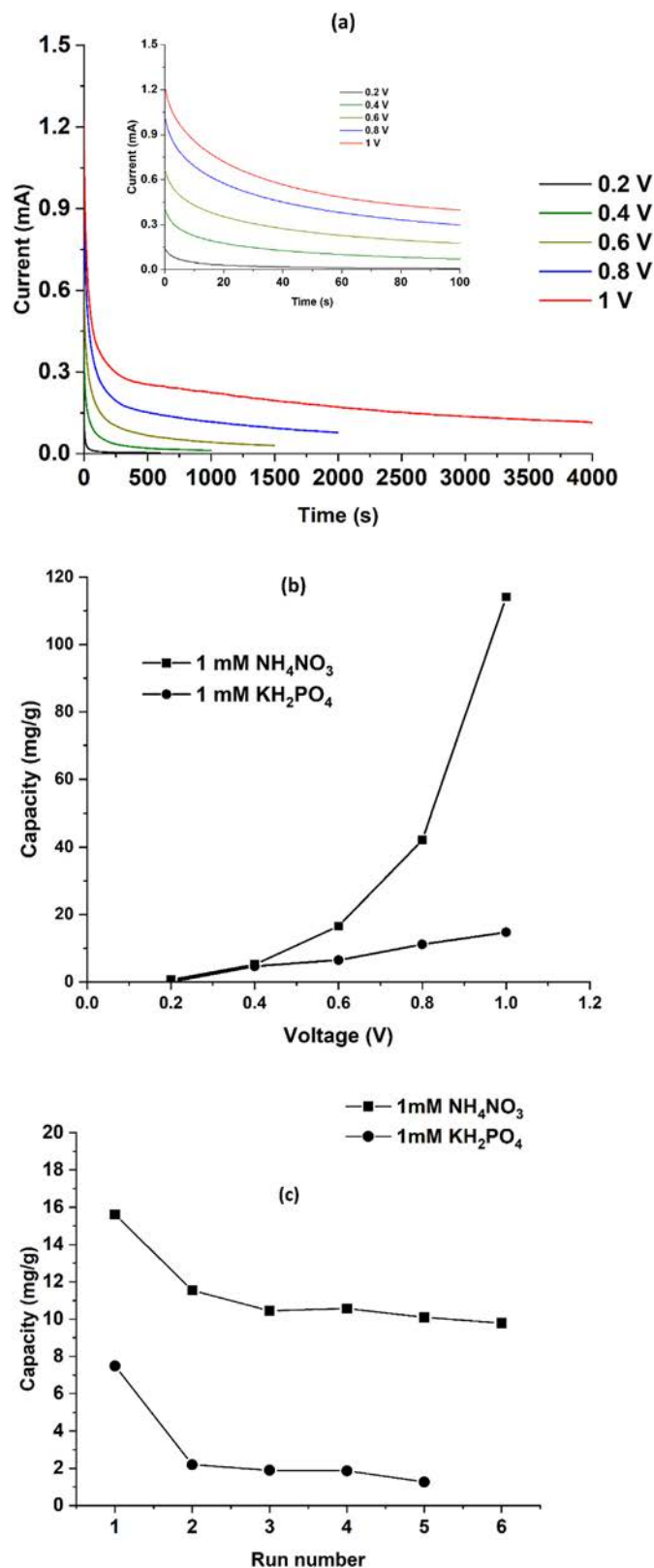


Fig. 4. (a) transient current responses in working electrode at different voltages. The capacity is obtained by integrating the area under the curve (b) Capacity vs voltage for 1 mM solutions of NH_4NO_3 and KH_2PO_4 . The adsorption capacity increases with increasing voltage due to more migration of the ions and is consistent with the recent study [2]. The adsorption capacity of the nitrates (NO_3^-) was higher than that of the phosphate ions (H_2PO_4^-) and this is consistent with the findings of Macias et al. [3]. This is due to the smaller ionic radii of the nitrate ion. The values of capacities are higher than the ones reported in literature [2,4,5] possibly due to the differences in the type of carbon and in this work, the total capacity rather than the capacity due to the electroadsorption effect alone is reported. (c) Phosphates show a bigger loss in capacity with respect to cyclic adsorption-desorption studies probably due to incomplete removal. These results are discussed in our earlier publication [1].

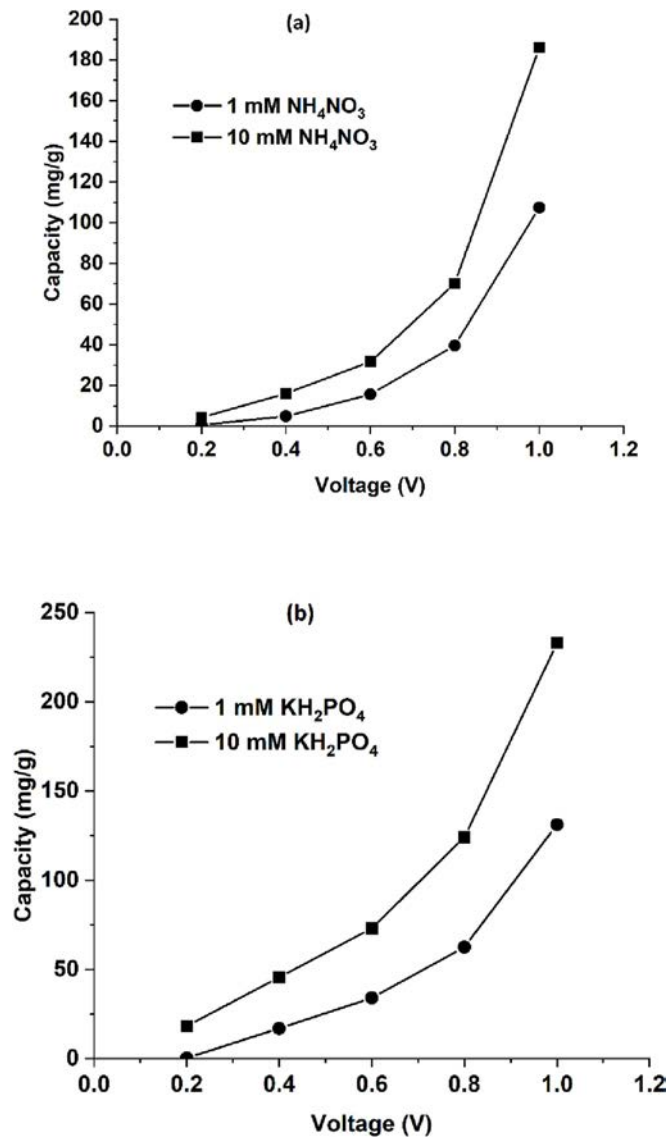


Fig. 5. (a) and (b) Capacity vs voltage for higher concentrations of nitrates and phosphates. As concentration increases, more ions are present which show an increase in the current, thereby an increase in capacity is observed.

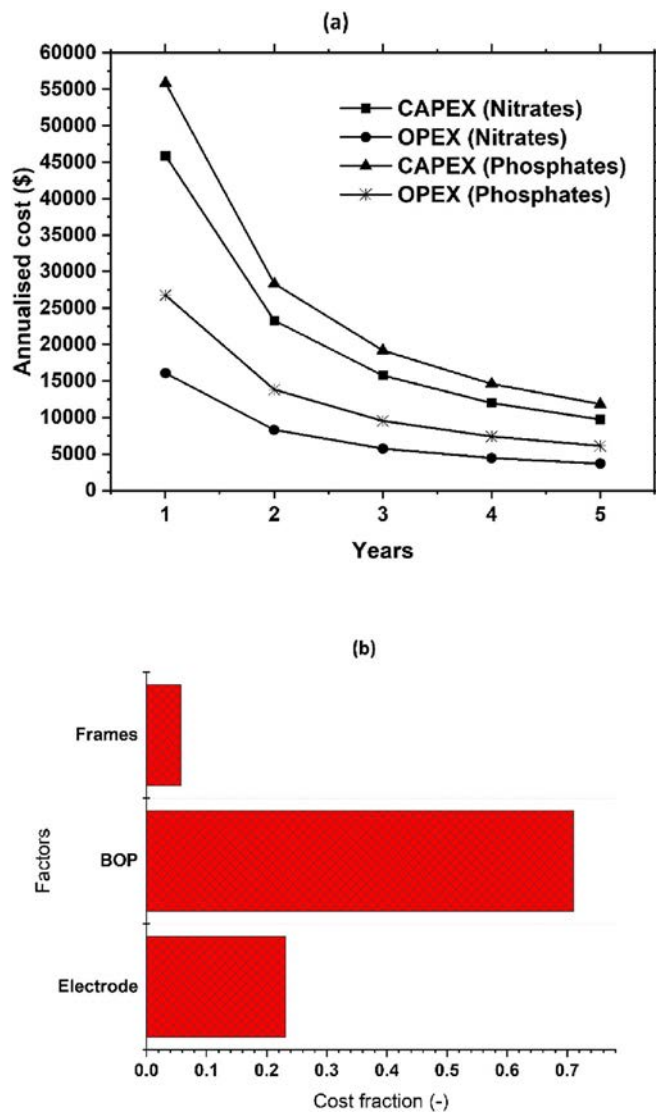


Fig. 6. (a) Capital and operating expenditure (CAPEX and OPEX) for the removal of nitrates and phosphates. The inlet and outlet concentrations to the CDI unit are 1 mM and 0.1 mM respectively. The cost functions were taken from the work of Hand et al. [6]., The capital expenditure is a function of the amount of carbon, stainless steel, binder material and the frames along with the balance of plant. The operating expenditure is the sum of the energy and the labor costs. The higher CAPEX and OPEX for the phosphate solution is due to the lower capacitance (b). Bulk of the cost is from the balance of plant while the electrode and the frames come to about 30%. The work of Hand et al., [6] calculates cost values based on the assumption of an ideal capacitor. Detailed cost values can only be obtained by solving a full model that is available in literature, which considers axial and or traverse transport of ions [7–9].

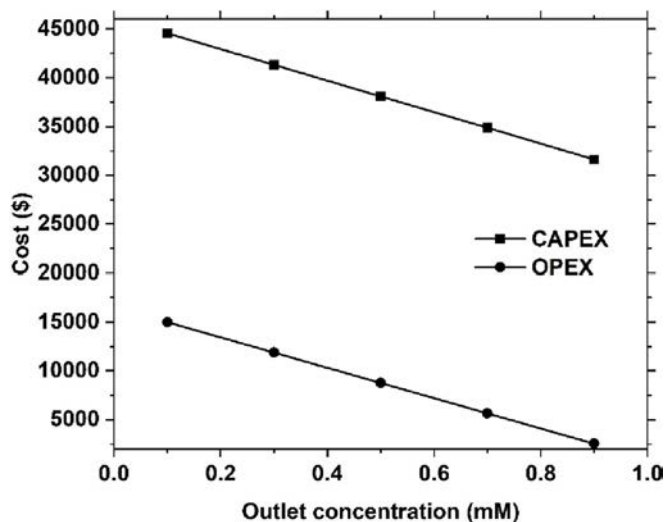


Fig. 7. The effect of outlet concentration on the CAPEX and OPEX are shown here. A higher outlet concentration means poorer separation and a lower number of electrode pairs are required. The number of electrode pairs drops from 40,236 for 0.1 mM to 4400 for 0.9 mM. Overall energy consumption drops from 3.9 MJ to 0.44 MJ. The capacitance value is fixed to 8 F/g and one electrode replacement is considered for every five years.

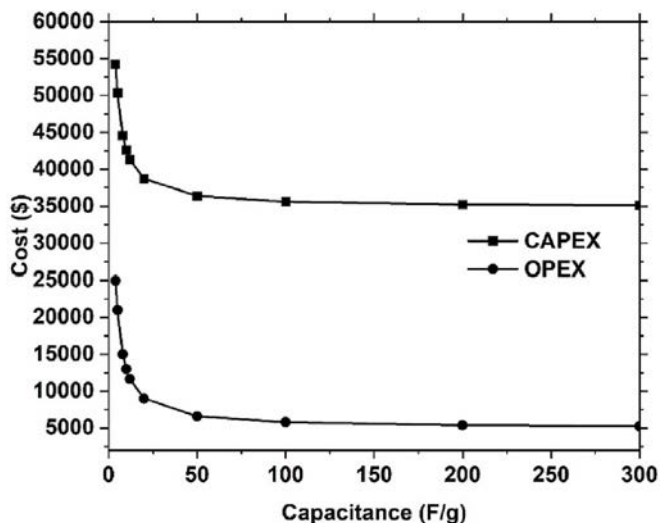


Fig. 8. The effect of capacitance on the costs is shown here. Here the outlet concentration and the electrode replacement frequency are fixed to 0.1 mM and 1 replacement for 5 years. Higher capacitance results in lower mass of electrodes, thereby lowering the costs. Mass of carbon drops from 800 kg to 11 kg (the electrodes become thinner). A capacitance value of >50 does not seem to have any significant effects on costs.

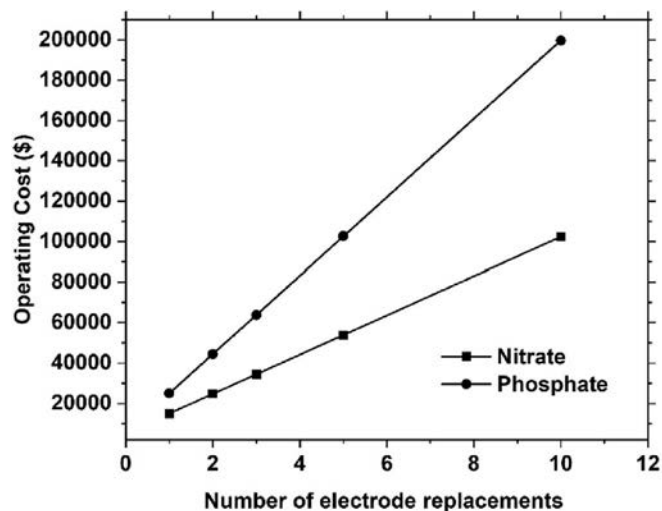


Fig. 9. The effect of electrode replacement frequency on the operating expenditure is shown. The fixed values are capacitance (8 F/g: Nitrate and 4 F/g Phosphate) and the outlet concentration to 0.1 mM. The frequency of electrode replacement has a significant effect on phosphate removal due to the lower capacitance. Operating expenses varied from 15,000–102,000 \$ for Nitrate removal and 25,000–199,000 \$ for Phosphate removal. The work does not consider competing ions [2,5] which may have some effect on the adsorption of the nitrates and thereby affecting the process performance.

Table 1

Summary of the electrosorption experiments. The table is reproduced from our previous work [1].

Electrolyte	Concentration	Capacity (mol/kg)	Capacity (mg/g)
NH ₄ NO ₃	0.4 mM	0.28	22.25
	1 mM	1.43	114.14
	10 mM	2.02	161.6
	100 mM	3.76	301.14
	1 M	5.43	434.35
KH ₂ PO ₄	0.2 mM	0.08	11.09
	1 mM	0.11	14.7
	10 mM	0.14	18.4

Table 2

Summary of the cost estimation for nitrate and phosphate removal. The calculations are based on the work of Hand et al., [6]. The number of the stage is the same for the nitrates and phosphates since it is a function of the exit concentration.

Indicator	Units	NH ₄ NO ₃	KH ₂ PO ₄
CAPEX	US\$	44,546.5	54,252.6
OPEX	US\$	15,003	25,000
Annualised CAPEX	US\$	9726.3	11,846.3
Annualised OPEX	US\$	3659.1	6097.3
Labour cost	US\$	1336.4	1627.6
Cost of electrodes	US\$	8621.9	17,244
Cost of other materials	US\$	5925.1	7279
Balance of plant	US\$	30,000	30,000
Energy consumption	MJ	3.98	3.98
Number of electrode pairs		40,236	40,326

CRediT authorship contribution statement

Shreenath Krishnamurthy: Conceptualization, Methodology, Project administration. **Kaushik Jayasayee:** Conceptualization, Methodology. **Tom-Andre Enebakk Eide:** Investigation. **Ruth Elisabeth Stensrød:** Investigation.

Data availability

Data will be made available on request.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Shreenath Krishnamurthy works at the Process chemistry and Functional materials group in SINTEF Industry's process technology department. Originally from India, Dr. Krishnamurthy obtained his bachelor's degree from Anna University. He then obtained his PhD from the National University of Singapore, where he had worked on a pilot scale demonstration of carbon capture processes using adsorption technology. After 4 years as a post-doc at the University of Edinburgh, he moved to SINTEF in 2018. At the University of Edinburgh, his work was about CO₂ capture using metal organic frameworks. His research focus at SINTEF is on pressure and temperature swing adsorption processes for gas separation applications as well as electrosorption processes for wastewater treatment.



Kaushik Jayasayee has over 15 years of experience in various electrochemical technologies; specifically, hydrogen and batteries. Currently he is holding the position of Senior Technology Advisor at Norwegian Hydrogen AS, Ålesund, Norway, where his role is to advise the projects and customers on hydrogen technology matters. Prior to joining Norwegian Hydrogen in he was working as a Senior Research Scientist at SINTEF AS in Trondheim, Norway. Kaushik has extensive experience in coordinating and leading several national and international SINTEF projects. Kaushik was responsible for leading SINTEF's activities at the Norwegian Center of Excellence in Hydrogen-India (CoE-H India) to establish a sustained cooperation between Norway and India in hydrogen. He holds a PhD from Eindhoven University of Technology, Netherlands, and has worked as a post-

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Ruth Elisabeth Stensrød is working in the process Technology department at SINTEF as a senior engineer and her work deals with characterization of materials by using different techniques as TGA-MS, BET, XRD, chromatography, titration. She has a Bachelor in Engineering, Chemistry and Biotechnology, and a Certificate of apprenticeship in laboratory subjects.

Further reading

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