Synthesis of Chloride-Free Potash Fertilized by Ionic Metathesis Using Four-Compartment Electrodiagnosis Salt Engineering

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ABSTRACT: A sustainable approach for the production of high-purity potash fertilizers devoid of chloride is highly needed. Conventional preparation processes for chloride-free potash fertilizers have certain limitations, such as complicated synthesis procedure, including high-temperature requirement, causing environmental pollution. In this work, a novel approach has been proposed for the production of high-purity potash fertilizer (KNO₃, K₂SO₄, and KH₂PO₄) from KCl by metathesis electrodialysis (MED). Sulfonated poly(ether sulfone)-based cation-exchange membrane and quaternized brominated poly(2,6-dimethyl-1,4-phenylene oxide)-based anion-exchange membranes are used for the MED experiments. The membranes show adequate water uptake, ionic conductivity, and ion-exchange capacity with good mechanical and thermal stabilities. The yields of KNO₃, K₂SO₄, and KH₂PO₄ are found to be 90, 86, and 90%, respectively. The power consumptions during MED experiment for KNO₃, K₂SO₄, and KH₂PO₄ are calculated to 0.94, 0.89, and 1.04 kWh/kg, respectively. The purity of products is confirmed by inductively coupled plasma and X-ray diffraction analysis and by measuring ionic contents. The process provides an energy-intensive way for high-purity synthesis of KNO₃, K₂SO₄, and KH₂PO₄.

INTRODUCTION

Potassium is one of the essential macronutrients like nitrogen and phosphorous, which is consumed by plants.1,2 Interestingly, potassium is responsible for more than 60 enzymatic systems in plants that are essentially required for the synthesis of proteins, vitamins, starch, and cellulose. It plays a vital role in photosynthesis, through which plants get energy and control opening and closing of stomata and thus it is required for tissue water balance in plants. However, a deficiency of potassium is recorded in most of the soil, so one can supply potassium to plants as fertilizers. Potash consumption in 2009–2010 in India was 3.33 million tonnes; the demand of fertilizers is ever increasing. In 1971–1972, potash consumption in India was 1.90 kg/ha, which surged to 17.1 kg/ha in 2008–2009, a 9-fold increase.3 It is essential to produce highly soluble, chloride-free potassic fertilizers. Potassic fertilizers are mainly categorized into two types: chlorine-containing fertilizers, viz., KCl, and chloride-free fertilizers, such as KNO₃, K₂SO₄, K₂HPO₄, K₂CO₃, etc. The most common potassic fertilizer is potassium chloride (KCl), readily recovered from naturally occurring raw materials of potash, which constitutes 90% of potassic fertilizers.4 The use of potassium chloride leads to increase in the chloride content of the soil, excess concentration of which causes toxicity in the crops grown and higher salinity and acidity of the soil.5 The disadvantage of the presence of chloride in soil is the formation of hazardous compounds by reaction with ammonium nitrate, the most common nitrogenous fertilizer.6 Chloride-free potash fertilizers, such as monopotassium phosphate (KH₂PO₄), potassium sulfate (K₂SO₄), potassium nitrate (KNO₃), etc., are preferred for chloride-sensitive crops. These potassium salts are rare, usually produced when KCl reacts with nitrate, sulfate, and monobasic phosphate source.7

Potassium nitrate is a highly soluble source, which contains two most common elements, potassium and nitrate, essential for the growth of plants. KNO₃ is commonly used in fields where chloride-free potash is required to fulfill the requirement of potash along with nitrate without any further action and other transformation. KNO₃ is mainly produced by the reaction of KCl with a nitrate source like sodium nitrate, nitric acid, or ammonium nitrate according to availability and requirement. Industrial production of KNO₃ is based on the reaction of KCl and HNO₃ in the presence of pentanol.8 Three-fourths of potassium sulfate was also produced by the reaction of KCl and dissolved sulfates or sulfuric acid. Traditional methods for K₂SO₄ production are the Mannheim method, association—displacement method, and double decomposition method.9,10 The Mannheim method is quite
simple with good product yield and quality, but there are several drawbacks, such as strong corrosiveness and abrasiveness of raw materials, high reaction temperature, high energy consumption, and so on. K$_2$SO$_4$ is produced when KCl reacts with ammonium sulfate, and it has high impurity. Zisner et al. also reported the production of K$_2$SO$_4$ by differential contacting process.$^5$ Potassium phosphate is also a highly soluble salt commonly used as fungicide, food additive, and fertilizer. Traditionally, KH$_2$PO$_4$ is produced from phosphoric acid, potassium hydroxide, and water. The reaction between phosphoric acid and potassium hydroxide is highly exothermic. In 1989, Haifa Chemicals Ltd. prepared KH$_2$PO$_4$ using phosphoric acid and potassium hydroxide in the presence of organic solvent with a long-chain primary amine. Monopotassium phosphate produced by acidulation of phosphoric acid solution and amines is regenerated by calcium oxide or calcium carbonate, but the overall process is not economically viable.$^{11}$ So, there is a need of a simple and cheap method to produce chloride-free potash.

Electrodialysis (ED) is found to be a potential-driven process used for the separation and recovery of valuable ionic species from aqueous solution without waste generation.$^{12-16}$ Metathesis electrodialysis (MED) is a modified electrodialysis process that can convert one salt into another by double-ion-exchange reaction. The MED process has many advantages over traditional metathesis reaction, including high purity of product. MED has a great impact where traditional processes are not applicable due to high solubility of both substrate and product. The aim of this work was to prepare chloride-free potassic fertilizers by an economically viable and eco-friendly process. Different phosphate, sulfate, and nitrate sources were used along with low-cost potassic fertilizer (KCl) to produce high-value potassium dihydrogen phosphate, potassium sulfate, and potassium nitrate, which are rich sources of potash, nitrogen, sulfur, and phosphorus.

# **EXPERIMENTAL SECTION**

**Materials.** Poly(ether sulfone), obtained from Solvay Chemicals Pvt Ltd., India, was used after drying. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), N-bromosuccinimide, and N-methylmorpholine were purchased from Sigma-Aldrich. N,N-Dimethyl acetamide, N-methyl-2-pyrrolidone, KCl, NaH$_2$PO$_4$, Na$_2$SO$_4$, and NaNO$_3$ were supplied by S D Fine-Chem Ltd. Double-distilled water was used throughout the experiment.

**Methods.** Sulfonated poly(ether sulfone) (SPES)-based cation-exchange membrane of thickness 190 μm and quaternized brominated poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO)-based anion-exchange membranes of thickness 160 μm were prepared for MED experiment by previously reported methods.$^{16,18}$

**Chemical, Thermal, Mechanical, and Physicochemical Characterization of Cation Exchange Membranes (CEM) and Anion Exchange Membranes (AEM).** Synthesized CEMs and AEMs were characterized for their chemical, thermal, and mechanical behaviors by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and universal testing machine, respectively. Membranes were physicochemically characterized with their ion-exchange capacity (IEC), ionic conductivity (IC), water uptake, number of water molecules per ionic site (λ), and dimensional stability. Details are given in the Supporting Information section.

**Metathesis Electrodialysis (MED) Process for Synthesis of Chloride-Free Potash.** Metathesis electrodialysis (MED) experiments were performed an in-house-made electrodialysis (ED) system having an effective area of 200 cm$^2$, as described in [Scheme 1](https://doi.org/10.1021/acsomega.8b01005). ED stack contains an alternate arrangement of CEMs and AEMs based on SPES and QPPO, respectively. In ED stack, precious metal-oxide-coated titanium-based electrodes were used. ED has four different compartments, as illustrated in a stack configuration: two feed compartments and two product compartments. The first and third compartments were charged with the feed solution in recirculation mode of 3 L/h, whereas double-distilled water was used in the second and fourth compartments. The turbulence of solutions was maintained at the same flow rate by peristaltic pumps. Na$_2$SO$_4$ solution (0.02 M) was recirculated to avoid electrode reaction. The experiment was conducted with 10 cell pairs of CEMs and AEMs at a constant direct current electrical potential of 2 V/cell pair applied potential. Inductively coupled plasma (ICP) and IC analyses were used for the determination of ionic concentration in the product compartment at a regular interval. I–V curve of CEM and AEM in the MED process was also recorded in.
equilibration with 0.10 M KCl solution by varying the applied potential from 0 to 5 V/cell pair with the interval of 0.5 V. The specific energy consumption (P) and current efficiency (CE) for production of potassic fertilizers were calculated by standard formula, and the details are given in the Supporting Information section.

RESULTS AND DISCUSSION

Functional group determination in CEM and AEM was conducted by FTIR spectroscopy, and the corresponding spectra are shown in Figure 1. In spectrum of CEM, the broad absorption band was observed between 3300 and 3500 cm$^{-1}$ associated with $-\text{OH}$ stretching vibrations of water molecules present in association with ionic sites. The absorption band at 1585 cm$^{-1}$ attributed to the $-\text{C}≡\text{C}$ stretching vibrations of aromatic skeleton of polymer. The two absorption peaks at 1160 and 1103 cm$^{-1}$ are characteristic of aromatic SO$_3^{-}$ stretching vibrations. The peak for aryl oxide appears at 1239 cm$^{-1}$. Figure 1 shows the FTIR spectra of AEM; a sharp peak at 1114 cm$^{-1}$ confirms the quaternization reaction between brominated PPO and $\text{N}$-methylmorpholine. The absorption band at 1600 cm$^{-1}$ is assigned to the stretching vibration of $-\text{C}≡\text{C}$ in the phenyl ring present in the polymer backbone. A dominant peak at 1185 cm$^{-1}$ indicates the stretching of $-\text{C}≡\text{O}≡\text{C}$ bond between the phenyl ring. The absorption band at 1470 cm$^{-1}$ arises due to symmetric and asymmetric stretching vibrations of the phenyl group.$^{20}$

Thermal stabilities of AEM and CEM were analyzed by TGA, and the corresponding thermograph is presented in Figure 2. Both the membranes have weight losses of 4.39 and 5.83%, respectively, in the temperature range of 80–120 $^\circ$C due to the presence of water molecules as bound water. Thereafter, weight losses in the temperature range of 200–430 $^\circ$C for AEM and CEM were found to be 12.48 and 9.58%, respectively, due to degradation of the functional group present as ion-exchange moiety in membranes. The major weight loss was recorded above 450 $^\circ$C due to degradation of the polymer backbone. The above discussion shows that both AEM and CEM are thermally stable.

Both membranes showed higher tensile strength and elastic modulus in dry condition compared to the wet condition. The measured tensile strength was almost double, and the elastic modulus was 3 times higher than that in the wet condition for both CEM and AEM. The elongation at break in the wet state is found to be higher as water molecules associated with an ionic group present in the membrane matrix show plasticizing behavior in the wet state. The results show that CEM and AEM used were mechanically stable and flexible in nature.

Table 1 shows the physicochemical and electrochemical properties of IEMs. IEMs should possess a moderate amount of water uptake, high ion-exchange capacity, and high ionic conductivity for efficiency and viability of electromembrane processes.
process. Both CEM and AEM show an appreciable amount of mass gain when equilibrated with water, with values of 12.12 and 27.7%, respectively. Water uptake by IEMs determines the movement of counterion and mechanical stability of membranes. Higher water uptake leads to poor mechanical stability of IEM, whereas moderate amount of water in the membrane retains the stability along with high transport of ions. Ion-exchange capacity (IEC) represents the number of ion-exchange groups present in IEMs. IECs for CEM and AEM were calculated to be 1.40 and 2.15 meq/g, respectively. With the boost of ion-exchangeable groups, water molecules per unit ionic site also increases. Water molecules present in matrix interconnect the ionic channels, which enhances the transport of counterions. The ionic conductivity (IC) of IEMs determines the feasibility of membrane under electromembrane process. Higher ionic conductivity results in the lower power consumption, which favors product formation. The calculated IC values for both CEM and AEM are 3.15 × 10⁻² and 1.30 × 10⁻² S/cm, respectively, which well matched the values reported in the literature.¹⁶,¹⁸

Current—voltage characteristic of IEMs are taken from 0.5 to 4.5 V/cell pair after equilibrating the IEMs in 0.1 M salt solution and are presented in Figure 4. Three characteristic regions are found, viz, ohmic, plateau, and nonohmic. These regions represent the characteristics of IEMs in terms of ion-transport mechanism and concentration polarization phenomenon. From the figure, it is clear that current is directly proportional to applied voltage and thus obeys Ohm’s law in the ohmic region due to the presence of a large number of ions in solution, whereas in the plateau region, current becomes almost constant, which shows concentration polarization. Thereafter, in the nonohmic region, current rises steeply due to dissociation of water molecules at higher applied potential. It was concluded that our region of interest is the plateau region and that whole MED experiments were carried out in this region.

K₂SO₄ is produced during MED using KCl and Na₂SO₄ reactants at 2 V/cell pair applied potential across the electrodes. During the conversion process, a 2:1 stoichiometric ratio of KCl and Na₂SO₄ was used. The overall stoichiometric equation for K₂SO₄ synthesis is given below

\[ 2\text{KCl} + \text{Na}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{NaCl} \]

Figure 5 shows the current density value vs time for different feed concentrations. The current density value first increases and then decreases with time due to the higher concentration gradient between feed and product compartments. However, over time, concentration of ions gradually decreases and maintains equilibrium in both the compartments, which leads to decrease in the current density. From the graph, it can be seen that the current density value is higher for feed with 1.0 M concentration than for feed with 0.2 M concentration. Figure 6 shows the conversion of K₂SO₄ from KCl with respect to time during MED. Herein, K₂SO₄ is a product formed by the ion-displacement reaction of KCl and Na₂SO₄. The concentrations of Na₂SO₄ and KCl as well as the applied voltage for the migration of ions have been optimized during the whole process. The feed was filled in compartments 1 and 3 (KCl and Na₂SO₄), while deionized water was filled in compartments 2 and 4. Double-displacement reaction takes place between KCl and Na₂SO₄, and the formation of products K₂SO₄ and NaCl occur in compartments 2 and 4, respectively. The migration of K⁺ and SO₄²⁻ starts from compartments 1 and 3, respectively, to compartment 2 as we apply potential. From the graph, it can be easily seen that the concentration of KCl decreases with time; on the other hand, the concentration of K₂SO₄ increases. The initial concentration of KCl in the first compartment was 0.99 M, but as a result of migration of ions, this concentration was reduced to 0.69 M after 30 min. Simultaneously, the concentration of K₂SO₄ (0.15 M) in compartment 3 revealed the formation of product. The runtime of the experiment was 5 h, where the concentration of the product was found to be about 0.43 M. In the same time, migration of Na⁺ and Cl⁻ occurs from compartments 3 and 1, respectively, to compartment 4 to form NaCl (Scheme 1). Figure 7 shows the formation of NaCl during MED. The formation of K₂SO₄ as a product takes place in the second compartment, whereas the
formation of NaCl takes place in the fourth compartment. The formation of NaCl enhances the product formation due to the higher depletion of ions from their respective reactant compartments, so the respective product shall increase. Figure 7 (inset) focuses on the effect of optimized voltage on the product conversion. It is clear from the graph that the formation of product is higher when applied voltage is 2.5 V/cell pair compared to 2 V/cell pair. Solid K₂SO₄ crystals were obtained by evaporating the water from the product compartment solution obtained by the MED process. Figure 8 shows the X-ray diffraction (XRD) pattern of synthesized K₂SO₄ by metathesis electrodialysis (MED) process.

Highly valuable potassium nitrate was synthesized by MED experiment using 0.6 M K₂SO₄ and 1.2 M NaNO₃ as feed solutions for compartments 1 and 3, respectively, whereas DI water was used in the other two compartments (Scheme 1). The experiments were carried out at applied voltages of 1.5 and 2 V/cell pair. K⁺ from feed 1 migrated to compartment 2, and NO₃⁻ migrated from feed 3 to compartment 2, leading to dilution of feed 1 and feed 3, whereas concentrating compartment 2 with KNO₃. Similarly, Na⁺ migrated from feed 2 to compartment 4 and SO₄²⁻ migrated from feed 1 to compartment 4, concentrating with Na₂SO₄. The overall equation for the production of KNO₃ using MED process is shown below

\[ K_2SO_4 + 2NaNO_3 \rightarrow 2KNO_3 + Na_2SO_4 \]

respectively. Initially, after 2 h at 1.5 V/cell pair, the concentration of KNO₃ in compartment 2 was 0.57 M, whereas the concentration of K₂SO₄ in compartment 1 reduced to 0.21 M. Initially, ion migration was quick because of higher concentration of ions in compartments 1 and 3 and hence the formation of KNO₃ in compartment 2 was higher, and after 2 h of experiment, no significant change was observed in the concentration of KNO₃. Over time, the concentration difference of ions in both the compartments decreased so that migration of ions became slow. At 2.0 V/cell pair applied potential (Figure 9B), the overall production of KNO₃ increased. The concentration of KNO₃ increased efficiently to 0.65 mol/L in the small interval of 2 h, which was quite higher than that during the production at 1.5 V/cell pair. Over time, ion migration from feed compartment to product compartment was rapid, and finally, the concentration of KNO₃ in product compartment was found to be 0.97 M, whereas the concentration of K₂SO₄ decreased from 0.6 to 0.066 M. Figure 10 presents the concentration of Na₂SO₄ in the fourth compartment at applied voltages of 1.5 and 2 V/cell pair. From the figure, it is clear that 2 V/cell pair applied
voltage is more effective in production of KNO₃ and Na₂SO₄ as byproduct. The Na₂SO₄ produced in this process was used in the former process for the synthesis of K₂SO₄. To check the purity of KNO₃, XRD analysis was carried out and the result is presented in Figure 11. Crystalline KNO₃ was obtained by evaporating water from product compartment solution produced during MED experiment. Diffraction peaks at 27.8, 32.37, 34.43, and 47.55 were found to be associated with the crystal structure of KNO₃. The purity of the product was also checked by ICP analysis of the dried solid material. This shows the production of high-purity KNO₃ during MED without impurity.

KH₂PO₄ from KCl and NaH₂PO₄ was also synthesized by MED, with NaCl formed as byproduct, as presented in the following equation

\[ \text{KCl} + \text{NaH}_2\text{PO}_4 \rightarrow \text{KH}_2\text{PO}_4 + \text{NaCl} \]

From the above equation, it is clear that 1:1 molar ratio is required for completion of reaction. Different feed concentrations of KCl were used to evaluate the quantitative yield of KH₂PO₄. During MED process, 0.1, 0.2, and 0.5 M KCl and NaH₂PO₄ were used as feed solution in compartments 1 and 3, respectively, whereas DI water was used in compartments 2 and 4 (Scheme 1). Scheme 1 shows the arrangement of ion-exchange membranes and different compartments during MED process; for applied voltage, K⁺ ion migrated from feed compartment 1 to product compartment 2, whereas H₂PO₄⁻ migrated from compartment 3 to compartment 2, leading to the formation of KH₂PO₄ in the product compartment. Similarly, in the fourth compartment, the concentrations of Cl⁻ and Na⁺ increased over time, forming NaCl as byproduct. Figure 12 (inset) shows the decrease of KCl concentration with time. On applying a constant potential of 2 V/cell pair, for different feed concentrations of 0.1, 0.2, and 0.5 M KCl, the concentration of KCl decreased from the initial value to 0.007, 0.05, and 0.16 M, respectively, after 2 h. Figure 12 shows the concentrations of KH₂PO₄ for different feed concentrations after 2 h of MED process as 0.061, 0.11, and 0.24 M for feed solutions of 0.1, 0.2, and 0.5 M, respectively, whereas after 4 h, the concentrations reached 0.095, 0.16, and 0.36 M, respectively. Nearly 90% conversion in the experiment was completed in a span of 4 h. Figure 13 (inset) shows the reduction in the concentration of NaH₂PO₄ with time for different feed concentrations of 0.1, 0.2, and 0.5 M. From the figure, it is clear that reduction is very fast at higher concentration than at lower concentrations. After 4 h of experiment, the concentrations of NaH₂PO₄ in compartment 3 were 0.0015, 0.0038, and 0.086 for feed concentrations of 0.1,
0.2, and 0.5 M, respectively. Figure 13 shows the production of NaCl as byproduct in the fourth compartment for 0.1, 0.2, and 0.5 M concentrations of NaH₂PO₄; the yield of byproduct in the fourth compartment was higher than 90%. It was observed from Figures 12 and 13 that 0.1 M feed concentrations of KCl and NaH₂PO₄ required relatively less time for conversion to KH₂PO₄ and NaCl, whereas higher feed concentration of 0.5 M required more time for the conversion. The number of co-ions increases in the solution at higher concentration, which is responsible for the sluggish movement of ions. Co-ion transport across the membrane during the MED process regulates the quality of product, but no co-ion transport was observed throughout the process.

Energy consumption and current efficiency data were evaluated for the performance of MED experiment during conversion of K₂SO₄, KNO₃, and KH₂PO₄ with 2 V/cell pair applied potential, and the results are presented in Table 3. The CE and P at 2 V potential are found to be 82% and 0.94 kWh/kg, respectively, for K₂SO₄ production, whereas 87.0% and 0.89 kWh/kg, respectively, for KNO₃. The lowest CE and higher power consumption were calculated for the KH₂PO₄ synthesis, which were 81% and 1.04 kWh/kg, respectively. The 2 V/cell pair applied potential was found to be most suitable for the production of chloride-free potash by MED experiment.

Table 3. Energy Consumption (P) and Current Efficiency (CE %) for Production of Chloride-Free Potash at 2 V/Cell Pair Applied Potential

| Salt Produced | P (kWh/kg) | CE % |
|---------------|------------|------|
| K₂SO₄        | 0.94       | 82   |
| KNO₃         | 0.89       | 87   |
| KH₂PO₄       | 1.04       | 81   |

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**CONCLUSIONS**

A novel synthesis approach, metathesis electrodialysis, is developed to obtain high-value potassic fertilizers (K₂SO₄, KNO₃, and KH₂PO₄) with high purity to overcome the limitations of conventional approaches. Quaternized poly(2,6-dimethyl-1,4-phenylene oxide)-based AEM and sulfonated poly(ether sulfone)-based CEM at an applied voltage of 2 V/cell pair were used for the MED process. AEM and CEM show good physicochemical and electrochemical properties with good thermal and mechanical stabilities and are found to be suitable for MED process due to their low electro-osmotic drag. Stoichiometric ratios of the reactant of 2:1, 2:1, and 1:1 for the production of K₂SO₄, KNO₃, and KH₂PO₄ respectively, provide optimum results. MED shows low power consumption and good current efficiency of the order of 1 kWh/kg and 80%, respectively, for the production of potassic fertilizer. The obtained product is confirmed to be of high purity by XRD. The byproduct formed during the synthesis of KNO₃ (Na₂SO₄) is utilized for the formation of K₂SO₄ by MED. In brief, MED is an environmentally friendly and less expensive process to produce high-purity potassic fertilizers.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01005.

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Notes

The authors declare no competing financial interest.

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