



Sustainable recovery of ammonium sulfate from saline wastewater using eutectic freeze crystallization: Crystallization kinetics and thermodynamics

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ABSTRACT

This work explored the application of eutectic freeze crystallization (EFC) process as a sustainable desalination approach for recovery of ammonium sulfate (AS) salt from highly saline solution. Batch mode EFC experiments were conducted using jacketed crystallizer to investigate the influence of AS feed concentration (35–42 wt%) and agitation speed (100–400 rpm) on the AS crystallization kinetics and thermodynamic behaviour. Higher AS concentration increased the supersaturation level which enhanced both the nucleation and growth rates. Prolonged freezing duration resulted in solute depletion and a shift to growth-dominated kinetics. Increased agitation speed improved the mass and heat transfer which accelerated crystal formation. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis confirmed the formation of high-purity orthorhombic AS crystals with larger crystal size achieved at higher feed concentration and longer freezing time. Energy analysis showed that the EFC process required 0.4826 kWh/kg AS recovered, representing approximately 75% lower energy consumption as compared to the conventional evaporative crystallization process. Overall, this study demonstrated that effective control of the EFC operating conditions improved the separation efficiency and product quality, highlighting the viability of EFC process for achieving both water reclamation and resource recovery which aligned with circular economy and zero liquid discharge strategies.

1. Introduction

Due to global population growth and industrialization, the increasing generation of saline wastewater from industrial activities such as chemical manufacturing, mining, agriculture, food processing and municipal wastewater presents significant environmental and operational challenges (Dai et al., 2023; Raketh et al., 2021). Ammonium and sulfate are commonly present in such saline effluents, and the high concentrations of ammonium and sulfate ions in discharged effluents without proper treatment contribute to serious environmental impacts such as eutrophication, salinity imbalance in freshwater systems and potential health risks for human consumption (Sahu et al., 2021; Zhao et al., 2023). The significant volume of ammonium and sulfate-rich

wastewater generated from various industrial processes cannot be overlooked. Undeniably, there is an urgent need for advancements in wastewater treatment technologies which not only achieve regulatory compliance through contaminant removal, but also allow for efficient water reclamation and resource recovery. Therefore, a shift in perspective is required at which wastewater should no longer be viewed solely as a source of pollution, but rather as a potential resource containing valuable materials such as nutrients, salts and even metals (John, 2020). This aligns with the objectives outlined in the World Water Assessment Programme of the United Nations' 2030 Agenda for Sustainable Development which emphasizes the development of technologies that facilitate the recovery of valuable by-products from wastewater to achieve the goal of zero liquid discharge.

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