Simultaneous CO₂ capture and reactive nitrogen removal with a continuous-flow one-step supercritical water reactor

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ABSTRACT
- Carbon dioxide and reactive nitrogen emission from nitrogen-containing wastes are part of the global environmental issues.
- An advanced supercritical water oxidation (SCWO) process has been developed to simultaneously reduce the discharge of carbon dioxide and reactive nitrogen during the treatment of nitrogen-containing wastewater.
- By introducing Ca(NO₃)₂ to the reactor inlet and Ca(OH)₂ to the reactor outlet, 94% of the carbon and 95% of the reactive nitrogen in acrylonitrile (C₂H₃N) were simultaneously converted to solid CaCO₃ and innocuous nitrogen gas at 250 bar and 420 °C.
- In situ formed CaCO₃ in the reactor acted as a catalyst for the decomposition of acrylonitrile.
- The obtained CaCO₃ with average particle size of 1.72 μm can either be used for industrial applications or reconverted to Ca(NO₃)₂, which can be recycled to the reactor, and carbon dioxide, which can be injected into deep geological formations.
- This novel method provides an inherently cleaner SCWO process which offers an attractive solution for the capture of carbon dioxide and reduction of total nitrogen (TN) from nitrogen-containing wastewater, as well as the removal of total organic carbon (TOC).

REMOVAL OF REACTIVE NITROGEN
- The conventional SCWO of acrylonitrile in the absence of Ca(NO₃)₂ resulted in the removal of 94% of the TOC under the following conditions: 250 bar, 481 °C and 10 sec reaction time with a 1.5:1 stoichiometric ratio of oxygen to acrylonitrile (Fig. 3A).
- With respect to TN, only 14% removal was achieved under the same conditions due to the fact that the ammonium generated from acrylonitrile is relatively unreactive under the conventional SCWO.
- On the other hand, the direct introduction of Ca(NO₃)₂ to the reactor resulted in the removal of 95% of the TOC and 85% of the TN even at a lower reaction temperature of 423 °C with all other variables held constant (Fig. 3B).
- TOC in the liquid effluent was dramatically reduced due to catalytic effect of CaCO₃.

CO₂ CAPTURE
- It is suggested that Ca(NO₃)₂ is hydrolyzed to Ca(OH)₂, followed by reaction of Ca(OH)₂ with carbon dioxide generated by the SCWO of acrylonitrile to produce CaCO₃.
- This in situ formed CaCO₃ acts as an effective oxidation catalyst for the decomposition of acrylonitrile in supercritical water.
- Fig. 4A demonstrates that the particles collected from the reactor effluent were CaCO₃, as confirmed by X-ray diffraction analysis.
- The number-weighted average particle size of the obtained CaCO₃ was 1.72 μm.
- Nitrate from Ca(NO₃)₂ reacted with ammonium, generated by the SCWO of acrylonitrile to produce benign nitrogen gas.

CONCLUSIONS
- 94% carbon of acrylonitrile feed was captured as CaCO₃ by introducing Ca(NO₃)₂ to the reactor inlet and Ca(OH)₂ to the reactor outlet.
- Simultaneously, 85% reactive nitrogen was reduced by the reaction of nitrate from Ca(NO₃)₂ with ammonium from acrylonitrile at 420 °C.
- The developed novel process provides a flexible platform for wastewater treatment which simultaneously reduces the discharge of TOC, reactive nitrogen, and CO₂.

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