Research Objectives:

The primary objectives of the proposed research are to investigate the details of an environmentally attractive process which will very efficiently remove temporary hardness without requiring any chemicals for regeneration or production of sludge. According to information available in the open literature, the proposed process will be the first one to utilize rainwater or snowmelt as an efficient regenerant.

Potential Relevance and Future Applications:

Removal of temporary hardness from water is a treatment or pre-treatment practiced in a wide variety of drinking water plants. With the recent growth in pressure-driven membrane processes (e.g., reverse osmosis, nanofiltration), removal of hardness through pre-treatment has attained special significance for the protection of the relatively delicate membranes. The two universally practiced processes in this regard are lime softening and ion exchange. While lime softening produces voluminous sludge to be disposed of, ion exchange process generates highly concentrated brine or acid as a waste regenerant stream. Residuals management will continue to be a major concern with these processes.

Underlying process chemistry:

Ion-exchange fiber with carboxylate functionality (-COOH) forms the heart of the process. The fibers are essentially hard long cylinders with diameter about 20 µm. Like spherical ion-exchange resin beads, the fibers can be used in fixed-bed column and the following constitute the two primary steps of the process:
Step 1. Hardness Removal by the Ion Exchange Fibers

\[ 2 \text{F-COOH} + \text{Ca(HCO}_3\text{)} \rightarrow (\text{F-COO})_2\text{Ca} + 2\text{H}_2\text{CO}_3 \]

Step 2. Regeneration with Carbon Dioxide Sarged Rainwater/Snowmelt

\[ 2\text{CO}_3\text{H}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{C}_2\text{O}_4\text{H}_2 \]
\[ 2\text{H}_2\text{C}_2\text{O}_4\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{HCO}_3^- \]
\[ (\text{F-COO})_2\text{Ca} + 2\text{H}^+ \rightarrow 2\text{F-COOH} + \text{Ca}^{2+} \]
Overall: \[ (\text{F-COO})_2\text{Ca} + 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O} \rightarrow 2\text{F-COOH} + \text{Ca}^{2+} + 2\text{HCO}_3^- \]

Note: From a mass balance perspective, no additional chemicals/additives are present in the regeneration waste.

Figure 1. Effluent histories for Ca\(^{2+}\) for fixed bed column run using cation exchange resin beads and fiber. (EBCT = Empty bed contact time, SLV = Superficial liquid velocity)

Originality and Innovation:

One of the generic goals in every segment of the water industry is to reduce or eliminate "residuals" without compromising with the treated water quality. Figure 1 demonstrates Ca\(^{2+}\) effluent history for fixed bed column run using cation exchange resin beads and fibers. The chemical composition of functional group and hardness removal mechanism were identical in both the cases. A 24 hour interruption test during column run with both type of exchangers, reveals a faster kinetics for Ca\(^{2+}\) removal through ion-exchange fiber. In this regard, the process offers unique opportunities to achieve complete and fast removal of hardness without producing any residual waste as evident from reactions described in "process chemistry". The key features which make the process very distinct from the existing technologies are as follows:
The process takes advantage of the unique properties of the ion exchanger fibers in a way that CO$_2$ sparged rainwater or snowmelt can be used as the sole regenerant, thus producing virtually no waste. Figure 2A demonstrates an efficient regeneration of ion exchange fiber using CO$_2$ sparged snow-melt. With higher partial pressure of CO$_2$, better regeneration is achieved. As opposed, almost negligible regeneration is possible for resin beads with CO$_2$ sparged snow-melt irrespective of inlet CO$_2$ partial pressure (figure 2B). The complete absence of alkalinity in rainwater or snowmelt makes them ideally suited as a regenerant. If necessary, the harvested rain water or snowmelt can be chlorinated prior to long-term storage without any adverse effect on the process.

The physical configuration of the process is exactly the same as that of any fixed-bed adsorption process. The proposed process, does not, therefore, introduce any operational complexity.

Scientically, the proposed process takes advantage of the fast kinetics of ion-exchange fibers unattainable with more popular resin beads. The sizes (i.e., foot prints) of the units may very likely be smaller than conventional treatment units.

According to information available in the open literature, use of rainwater or snowmelt has never been practiced as a regeneration ingredient to date. Volume of regenerant needed is less than ten percent compared to the volume of hard water treated for softening.

A host of water industries may benefit from the outcome of the proposed softening process. The current research thrusts of AWWARF do not address the specific performance enhancement in regard to the elimination of residuals for softening processes.

![Figure 2. Effluent concentration profiles for (A) Ion-exchange fibers and (B) resin beads during CO$_2$ sparged snow-melt regeneration at different CO$_2$ partial pressure.](image-url)
Publication:

