Anion Exchange Resins as Sources of Nitrosamines and Nitrosamine Precursors [Project #4295]

ORDER NUMBER: 4295

DATE AVAILABLE: December 2012

PRINCIPAL INVESTIGATORS:
Philip C. Singer and Riley C. Flowers

OBJECTIVES:
The overall objective of this research was to investigate the potential relationship between the use of anion exchange resins in drinking water treatment and the presence of nitrosamines and nitrosamine precursors in finished drinking water, employing a large number of resins representing the array of anion exchange resins used in drinking water treatment practice.

BACKGROUND:
Nitrosamines are a family of potent chemical carcinogens including, among others, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), and N-nitrosodi-n-butylamine (NDBA). NDMA and other nitrosamines have been identified as disinfection byproducts. They are regulated in the states of California and Massachusetts and are candidates for federal regulation.

Anion exchange resins, used for the removal of anionic contaminants such as arsenic, nitrate, and perchlorate from drinking water, consist of polymer networks with positively charged amine groups. Resins are often synthesized using trimethylamine (TMA), triethylamine (TEA), tri-n-propylamine (TPA), or tri-n-butylamine (TBA), which are known precursors of NDMA, NDEA, NDPA, and NDBA, respectively. Drinking water treatment plants using anion exchange resins have been found to have higher levels of NDMA in their finished waters.

APPROACH:
The study was conducted in three distinct phases: controlled bench-scale batch experiments, continuous-flow bench-scale column studies, and an analysis of samples collected from a number of full-scale treatment plants using anion exchange. The objective of the batch contact studies was to investigate the release of NDMA, NDEA, NDPA, and NDBA and their precursors by a large, representative group of anion exchange resins employed for the treatment of drinking water. Sixteen strong base anion exchange resins were obtained from four different manufacturers. Immediately prior to use, each resin was cleaned using a uniform cleaning procedure. The cleaned resins were contacted with laboratory-grade water (LGW) buffered at pH 7.0. After 1 hour of contact, the resins were separated from solution and the solutions were analyzed for nitrosamines and nitrosamine formation potential.
The objective of the continuous-flow column studies was to investigate the release of nitrosamines and nitrosamine precursors under simulated treatment plant operating conditions, including regeneration, periodic down-time, and the introduction of low levels of oxidant. Samples of a representative collection of resins, including resins found to release high levels of nitrosamines and nitrosamine precursors during the batch contact studies, were packed untreated (as received) into glass chromatographic columns, and LGW buffered at pH 7 was passed through the columns at an empty bed contact time (EBCT) of 3 min., representative of flow conditions in water treatment practice. Effluent samples were collected immediately after introducing the feed water to the columns, and at various times thereafter. The columns were regenerated periodically with NaCl solution. Additionally, column flow was interrupted and the resins were stored submerged in the columns for 12–14 hours. Feed water containing free chlorine or preformed monochloramine was introduced at the end of each experiment. Effluent samples were collected immediately before and after regenerations, flow interruptions, and the introduction of oxidant. All influent and effluent samples were analyzed for nitrosamines and nitrosamine precursors.

Ten full-scale drinking water treatment plants using resins found to release high levels of nitrosamines or nitrosamine precursors during the batch and column contact studies were identified for sampling. Sample sites were selected to assess the impact of resin age, i.e., how long the resins had been in place since they were first installed. Additionally, in selecting sampling sites, consideration was given to geographical diversity, i.e., eastern United States, Midwest, and west coast. Grab samples of anion exchange process influent and effluent were collected at each site and shipped to the University of North Carolina where they were analyzed for NDMA, NDEA, and NDBA and their corresponding precursors.

RESULTS/CONCLUSIONS:
In the 1-hour batch contact experiments at pH 7.0, 6 of the 16 resins tested released nitrosamines at concentrations as high as 974 ng/L, and 10 of the 16 released nitrosamine precursors with concentrations reaching above 2000 ng/L. TMA resins were found to release NDMA and NDMA precursors, while the TEA, TPA, and TBA resins were found to release their corresponding nitrosamines and precursors. Resins manufactured with TEA or TBA functional groups were also found to release NDMA precursors in addition to NDEA or NDBA precursors.

In the continuous-flow column experiments, resins released high levels of nitrosamines and nitrosamine precursors (up to >2000 ng/L) in the first 10 bed volumes (BV) of flow, with concentrations decreasing with continued column flow. Regeneration of the resins with NaCl resulted in a spike in nitrosamine precursors, as did 12–14 hour flow interruptions. These elevated concentrations were washed away within 20 BV of continued flow. The introduction of chlorine or preformed monochloramine resulted in increases in nitrosamine concentrations. The nitrosamine precursors released are believed to be present as unreacted residual materials from resin synthesis, and explanations for the increased precursor releases during regeneration and flow interruption are offered. No
clear differences were observed between nitrosamine and precursor releases from resins with gel or macroporous structures.

The study of 10 full-scale treatment plants using anion exchange resins found that 3 plants contained appreciable levels of nitrosamines in their anion exchange effluent, and 5 plants contained nitrosamine precursors in their anion exchange effluent. The effects of resin regeneration and resin downtime shown in laboratory studies were observed at some of the treatment plants, but not all of the plants.

This research clearly demonstrates that strong base anion exchange resins can serve as sources of nitrosamines and nitrosamine precursors in drinking water, most likely due to the presence of residual tri- and dialklyamines remaining from resin synthesis. Resin regeneration and downtime were found in laboratory experiments and field observations to be important factors leading to an increase in nitrosamine contamination. Laboratory experiments suggested that resins can be washed clean of any residual nitrosamines and precursors, and field observations confirmed that resins that have been in place for longer periods of time tend to release lower levels of nitrosamine precursors.

APPLICATIONS/RECOMMENDATIONS:
The research findings suggest that nitrosamine and nitrosamine precursor levels will be different at each plant using anion exchange technology, and that utilities should be attentive to the potential for high levels of nitrosamines and their precursors, especially when new resins are installed, after regeneration, and after extended periods of downtime. More research is needed to fully determine the extent and the persistence of nitrosamine contamination at anion exchange plants and to develop a treatment protocol that can effectively minimize the addition of nitrosamines and nitrosamine precursors to water treated by anion exchange resins.

While the use of anion exchange indicates that nitrosamines may be a problem in water treatment practice, it does not follow that every treatment plant that uses anion exchange will have elevated nitrosamine levels. The potential for the occurrence of nitrosamines and nitrosamine precursors in the finished water at full-scale anion exchange facilities must be evaluated on a plant-by-plant basis.

An important implication of these findings is that new resins need to be rinsed or cleaned effectively before being placed into service. This may require multiple regenerations or extended rinsing. Utilities should analyze for nitrosamines and nitrosamine formation potential before placing resin beds into service. Additionally, resin suppliers need to take care in providing contaminant-free resins for use in drinking water treatment.