



PERMANGANATE PRE-OXIDATION FOR CYANOTOXIN CONTROL: FREQUENTLY ASKED QUESTIONS

Can I use permanganate to remove cyanotoxins in my raw water supply?

Yes, as the first treatment chemical applied to raw water in a multi-step treatment system, permanganate is particularly well-positioned to begin the process of improving the quality of your water.

Permanganate reduces the concentration of extracellular cyanotoxins, such as the microcystin variants, -LR, -RR, and -LA, as well as anatoxin-a. Additional studies must be completed for cylindrospermopsin, but it appears to be a very slow reaction under typical drinking water treatment conditions. There is no oxidation reaction with saxitoxin.

What is a multi-step or multi-barrier treatment system?

Multi-barrier treatment refers to surface water treatment plant designs that use many different processes for the removal of dissolved substances and insoluble suspended solids.

These processes typically include:

1. source water quality control and treatment, including watershed control to minimize nutrient loading, mixing and destratification of the raw water, algacide application, and other treatment techniques;
2. pre-coagulation treatment of raw water, such as oxidation with permanganate, natural organic matter (NOM) adsorption with powdered activated carbon (PAC), or pre-sedimentation for solids separation;
3. coagulation-flocculation-sedimentation for turbidity and suspended solids removal, with or without PAC addition;
4. treatment of clarified water, including such processes as ozonation, chlorination, pH adjustment, and recarbonation;
5. filtration, including granular activated carbon contactors;
6. post-filtration treatment, including pH adjustment, disinfection, and distribution system protection (phosphates for corrosion control).

How much permanganate should I add?

As in any permanganate application, the correct amount to add will depend on the characteristics of your raw water. The critical parameters are available reaction time, water temperature, pH, reduced inorganic content, such as iron, manganese, and sulfides, plus total organic carbon (TOC), including taste and odor compounds, disinfection by-products (DBP) precursors, and color compounds. Minerals and soils in the form of turbidity may also contribute to the permanganate demand of a raw water.

Conduct a simple permanganate demand test to determine the amount of permanganate that will react within set time periods: 5 minutes, 15 minutes, 30 minutes, 60 minutes or longer. Match the permanganate dosage to the available reaction time in your plant.

For more information on conducting a permanganate demand test, contact us and request Analytical Method 104 – “Determination of CAIROX® Potassium Permanganate Value (PVt) for Drinking Water Applications.”

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How do I determine the available reaction time in my plant?

The reaction time depends on the water flow rate and the volume of the pipelines and basins from the point of permanganate injection (typically the raw water intake) to the point where all permanganate is gone and the manganese dioxide solids have formed (precipitated). In most cases, the goal is to have all of the permanganate completely reacted within the flocculators.

Selecting the point in the process where all permanganate must be reacted will vary from plant to plant and is impacted by the efficiency of the coagulation-flocculation process and the raw water characteristics, such as hardness.

If a Harmful Algal Bloom (HAB) occurs in my raw water supply, should I turn-off the permanganate feed?

No. Permanganate is added for many important reasons. Permanganate protects the beginning of your treatment process and improves the quality of the raw water. It oxidizes and removes unwanted inorganic contaminants, such as dissolved iron and, especially, dissolved manganese. Easy-to-oxidize NOM, including some taste and odor compounds, are also eliminated. Some NOM constituents that contribute to DBP formation are removed, lowering the DBP formation potential and improving the performance of down-stream coagulation and carbon treatment.

Freshly precipitated manganese oxides adsorb and remove some hazardous monovalent and divalent metals, such as radium. These oxides also help to coagulate colloidal solids.

Will permanganate lyse (break open) blue-green algae cells and release toxins into the water column?

For permanganate dosages that are typically used in water treatment, 1-3 mg/L, research reports and treatment plant data show that cell lysis does not occur. The reactions with iron, manganese, sulfides and easily oxidized NOM will occur before cell lysis.

If permanganate is dosed at very high amounts, 5 mg/L, 10 mg/L, 20 mg/L and higher, lysis may occur. If algal cells are already compromised and leaking, permanganate may contribute to further disintegration of the cell, releasing cyanotoxins into the water. When a permanganate residual concentration is still present in the water, it will oxidize microcystin variants and anatoxin-a. The plant's other down-stream processes will remove toxin components not oxidized by permanganate.

Will the permanganate's reaction with microcystin produce toxic by-products?

No. Research demonstrates that permanganate oxidation of microcystin LR results in products that are no longer toxic. Mouse bioassay has been used to demonstrate toxin destruction (Rositano, 1996). In studies with microcystin LR and RR, protein phosphatase I inhibition assay (PPIA) also confirms permanganate's removal of the toxicity (Rodriguez, 2007). Further, permanganate oxidation does not generate chlorinated disinfection by-products and it will lower the DBP formation potential of the raw water.

In the same study, applying free chlorine to the raw water to control cyanotoxins formed chlorinated by-products.

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Will permanganate pre-oxidation positively impact the coagulation-flocculation processes in my plant?

Yes, permanganate pre-oxidation improves coagulation-flocculation of raw water colloidal particles and organics, including cyanobacteria and algal cells. In a 2013 study, J. Fan reported that pre-oxidation with 0.5 mg/L KMnO_4 and alum increased algae cell removal by 12% over alum alone. Also, when 1.0 mg/L KMnO_4 was dosed with alum, algae cell removal was increased by 20% over alum alone.

Does permanganate treatment interfere with the cyanotoxin test methods?

Water that has been treated with permanganate can be monitored for cyanotoxin using liquid chromatography/mass spectrometry (LC/MS/MS) instrumentation with no interference. However, there is some anecdotal evidence that, when using the enzyme-linked immunosorbent assay (ELISA) test, the cyanotoxin reading may be artificially high. The exact mechanism for this possible effect has not yet been identified.

Are there literature references that I can review?

Yes. Here are several studies that report on permanganate's positive contribution to the removal of cyanotoxins in drinking water.

Request our Cyanobacteria/Cyanotoxin Literature Packet for additional information.

Carus Corporation, Analytical Method 104 – “Determination of CAIROX® Potassium Permanganate Value (PVt) for Drinking Water Applications.”

Carus Corporation, “A Vital Component of Any Microcystin Risk Reduction Strategy”, Technical Brief (2016)

Carus Corporation, “CAIROX® Potassium Permanganate & CARUSOL® Liquid Permanganate: An Initial Barrier for Extracellular Cyanotoxins”, Technical Brief (2016)

Fan, J., “Evaluating the Effectiveness of Copper Sulfate, Chlorine, Potassium Permanganate, Hydrogen Peroxide, and Ozone on Cyanobacterial Cell Integrity,” *Water Research*, 47:53-5164 (2013)

Fan, J., “The Effects of Various Control and Water Treatment Processes on the Membrane Integrity and Toxin Fate of Cyanobacteria”, *Journal of Hazardous Materials*, 264:313-322 (2014)

Karner, D., et. al., “Microcystin Algal Toxins in Source and Finished Drinking Water”, *Journal AWWA*, 72-81 (2001)

Rositano, J., “The Destruction of Cyanobacterial Peptide Toxins by Oxidants Used in Drinking Water Treatment”, Research Report No. 110, Urban Water Research Association of Australia Inc., (UWRAA) (1996)

Rodriguez, E., et. al., “Oxidation of Microcystins by Permanganate: Reaction Kinetics and Implications for Water Treatment”, *IWA, Water Research* 41 (2007)