



Novel Method for Activating Klozur Persulfate: Fundamental Science and Key Characteristics

Brant A. Smith P.E., Ph.D.

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Outline

- Klozur Persulfate
- Current Activation Methods
 - Oxidative and Reductive Pathways
- Organic Activation
 - Oxidative Pathways
 - Reductive Pathways
- Summary and Conclusions



KLOZUR PERSULFATE

Introduction to Klozur[®] Persulfate

Klozur[®] Persulfate is:

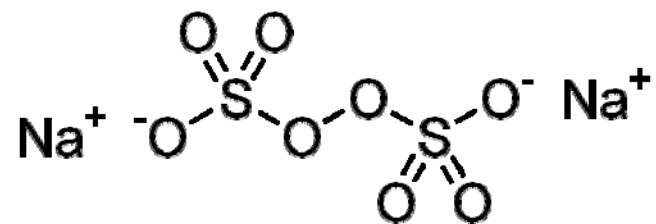
- Based on the sodium persulfate molecule:
 - A strong oxidant used for the destruction of contaminants in soil and groundwater
 - Highly soluble in water (significant oxidant mass is smaller volumes)
- Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution
- Applicable across a broad range of organic contaminants



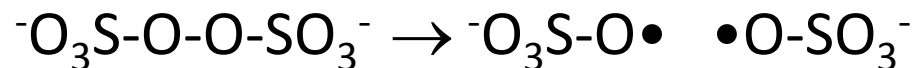
Field solubility of
more than 500 g/L
possible

Fundamental Chemistry

- Klozur[®] Activated Persulfate is based upon the persulfate anion:



- Persulfate is a peroxygen, and similar to hydrogen peroxide, it can be split at the O-O bond forming the sulfate radical:



Why Activate?

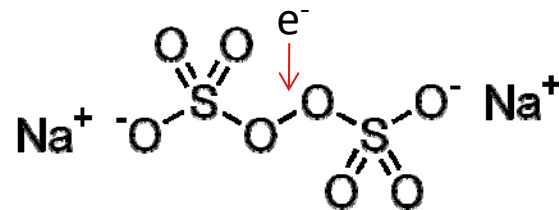
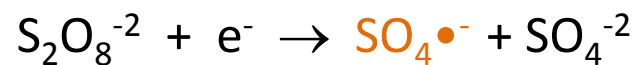
- Formation of radicals that are:
 - More powerful oxidants (SO_4^{\bullet} and OH^{\bullet}) than persulfate itself
 - Reductants ($\text{O}_2^{\bullet-}$)
 - Nucleophiles ($\text{O}_2^{\bullet-}$ and HO_2^-)
 - Kinetically much faster reacting

- Two primary methods of activations:
 - Donation of an electron
 - Reactions with water

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical (OH^{\bullet})	2.59	Siegrist et al.
Sulfate radical ($\text{SO}_4^{\bullet-}$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist et al.
Chlorine (HOCl)	1.48	CRC (76th Ed)
Oxygen	1.23	CRC (76th Ed)
Oxygen	0.82	Eweis (1998)
Fe (III) reduction	0.77	CRC (76th Ed)
Nitrate reduction	0.36	Eweis (1998)
Sulfate reduction	-0.22	Eweis (1998)
Superoxide ($\text{O}_2^{\bullet-}$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

Persulfate Activation: Electron Donation

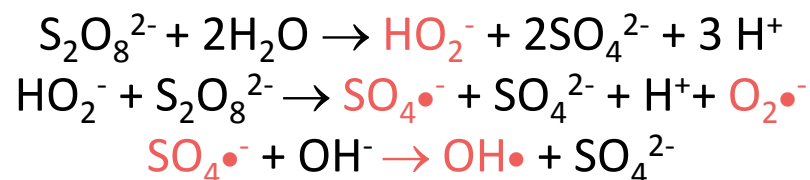
- Similar to Fenton's Reagent:



- Activation methods based on one electron transfer:
 - Reduced metals: Fe (II), Fe (0), etc
 - Organics
 - Hydrogen peroxide

Persulfate Activation: Reactions with Water

- Sodium persulfate is activated when the solution is raised to pH > 10.5
- Alkaline Activation (Furman et al., 2010):

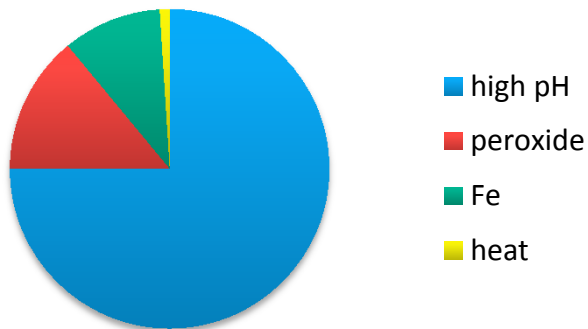


(note: $\text{H}_2\text{O}_2 \leftrightarrow \text{HO}_2^- + \text{H}^+$ $\text{pK}_a = 11.7$)

- Forms:
 - Oxidative radical: $\text{SO}_4^{\bullet-}$, and $\text{OH}\bullet$
 - Reductive radical: $\text{O}_2^{\bullet-}$
 - Nucleophiles: $\text{O}_2^{\bullet-}$ and HO_2^-
- Analogous to the chemistry that has been studied with catalyzed hydrogen peroxide (CHP)

Current Activators

Estimated Activator Usage

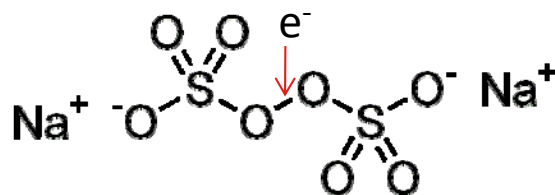


- Alkaline Activated Persulfate
 - High pH
 - Well suited for suited for most applications
 - Reductants, oxidants and nucleophiles
- Iron-Chelate Activated Persulfate
 - Chlorinated ethenes and hydrocarbons
 - Less contaminant mass
- Heat
 - Complex sites
 - Polishing step after thermal treatment
- Hydrogen Peroxide
 - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate

ORGANIC ACTIVATION

Organic Activation

- Organic molecules are thought to donate electron to persulfate



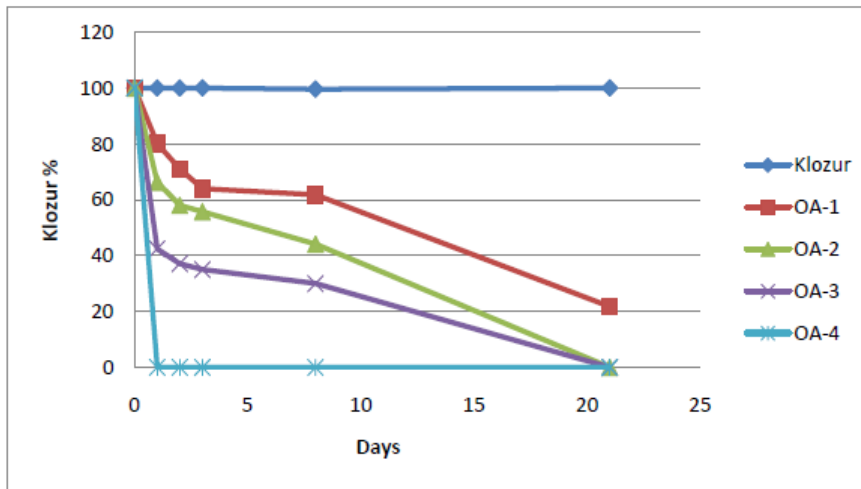
- Not all organics well suited to this task
 - Persulfate anion without activation will react very slowly or not at all with many organics
- On surface, very similar to iron-chelate activation
 - One electron transfer mechanism
 - Typically only sulfate radical
 - Little to mitigate acid formation

Patent Pending Technology:
US 2014/0116960 (WSU)
and US 2013/0248458
(PeroxyChem)

Organic Activation

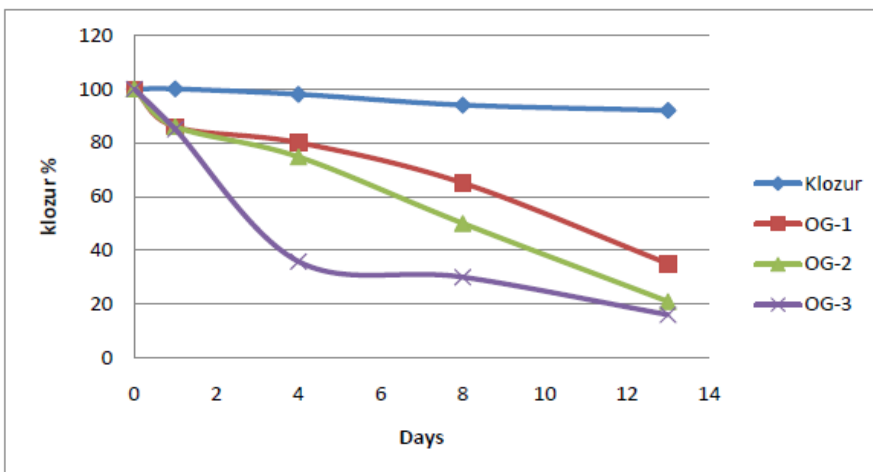
- More detailed analysis
 - May allow for better control over rate of activation
 - Potential to completely consume persulfate in given time frame
 - Help in creation of biogeochemical conditions
 - Reductant pathway under increasingly alkaline conditions
 - Allows for treatment of contaminants such as 1,1,1-TCA and Carbon Tetrachloride
 - May help in difficult to treat compounds
 - Ease of use benefits

Rate of Reaction with Persulfate



- Residual persulfate concentrations over time at room temperature (~25°C)

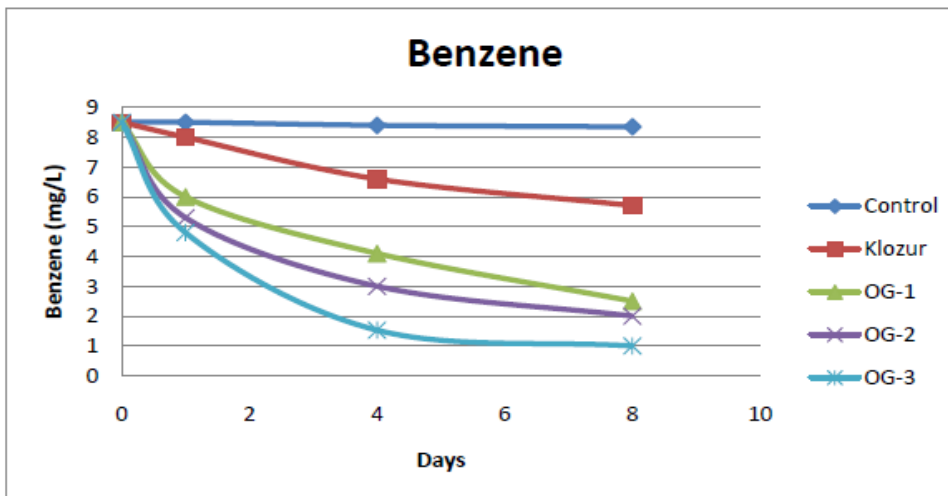
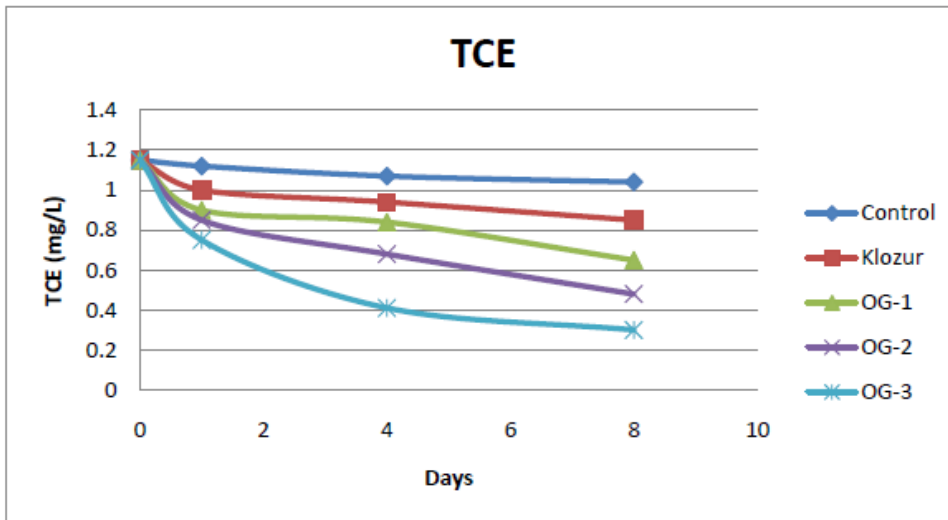
- OA 1 = 0.1:1
- OA 2 = 0.25:1
- OA 3 = 0.5:1
- OA 4 = 1:1



- OG -1= 0.1:1
- OG-2 = 0.25:1
- OG-3 = 0.5:1

ORGANIC ACTIVATION:
OXIDATIVE PATHWAY

Contaminant Treatment



- Contaminant concentrations at 2°C

– OG- 1 = 0.1:1

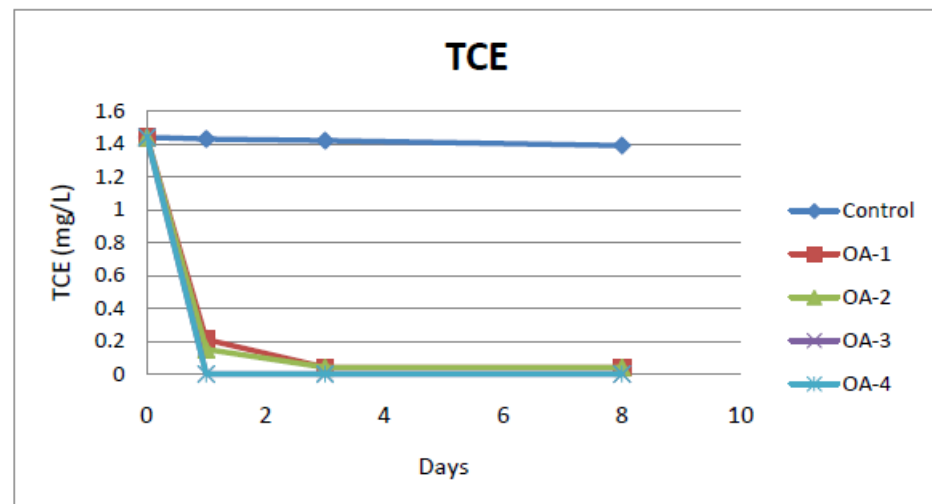
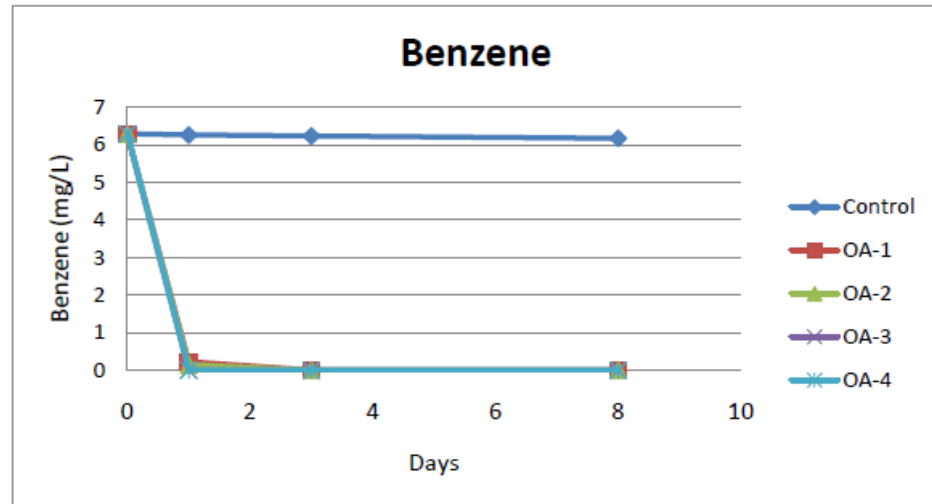
– OG- 2 = 0.25:1

– OG- 3 = 0.5:1

Contaminant Treatment

- Contaminant concentrations over time at $\sim 2^{\circ}\text{C}$

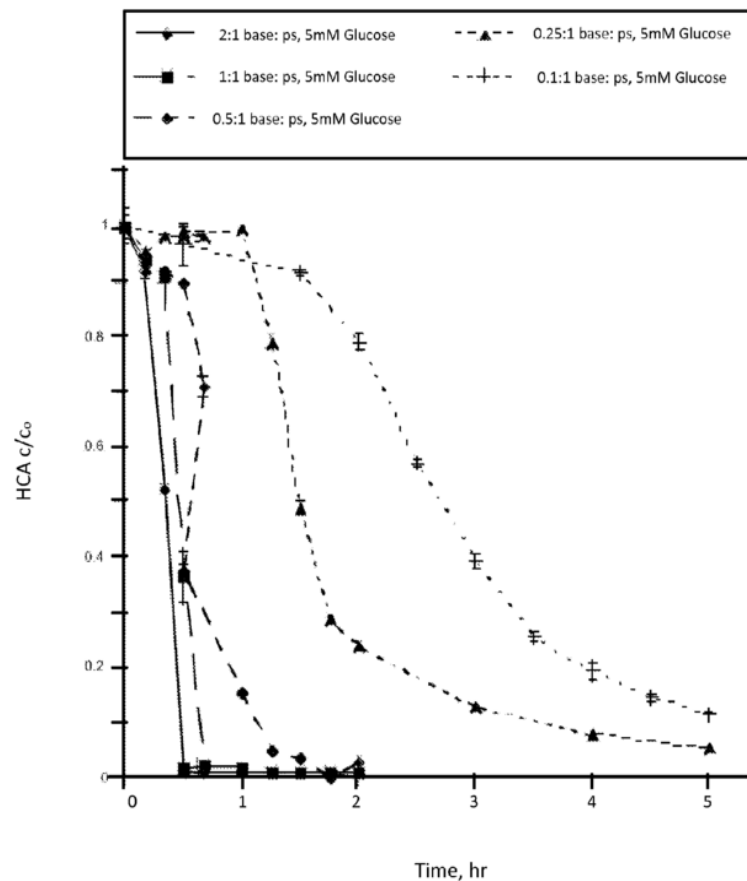
- OA- 1 = 0.1:1
- OA-2 = 0.25:1
- OA- 3 = 0.5:1
- OA- 4 = 1:1



ORGANIC ACTIVATION:
REDUCTIVE PATHWAY

Enhanced Reductive Ability with Increasing pH

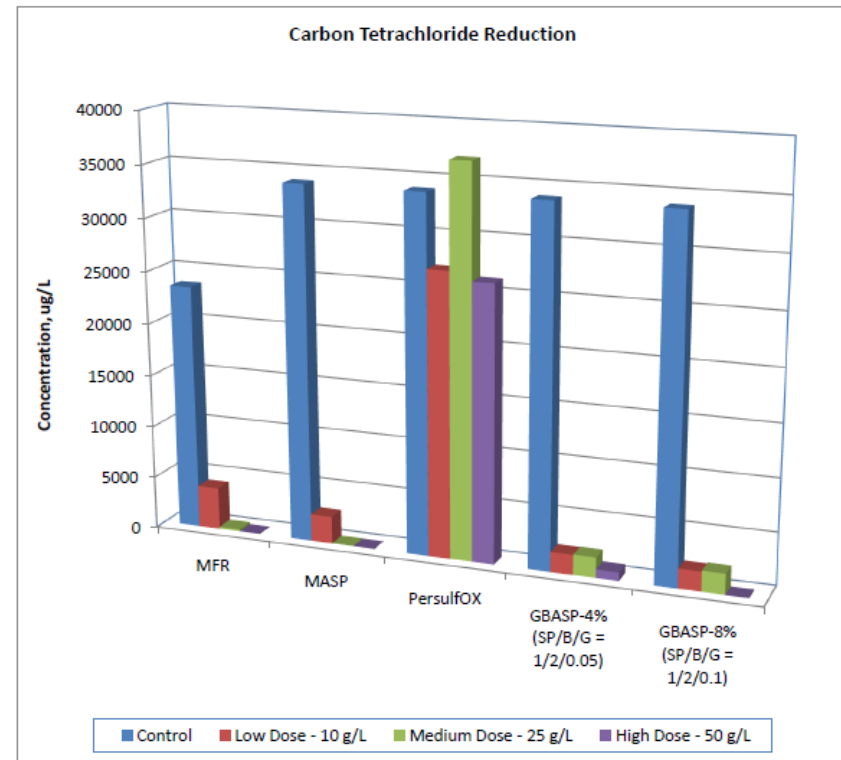
- Treatment of reductant probe (Hexachloroethane) with increasing concentrations of sodium hydroxide



Courtesy of Washington State University

Third Party Bench Test Looking at Treating Carbon Tetrachloride Site

- Treatment of Carbon Tetrachloride by different technologies:
 - MFR = Modified Fenton's Reagent
 - MASP = MFR Persulfate
 - PersulfOX = Product Name
 - GBASP = Organic with Base Activated Persulfate



Courtesy of ISOTEC

Conclusions

- New method of activation that will provide ease of use and treatment benefits
- Certain organics can be used to activate persulfate forming oxidative and reductive treatment pathways
 - Oxidative with activation by organic
 - Oxidative and reductive under alkaline conditions
- Potential to add organic with persulfate to be delivered to site as an activator/persulfate blend

Questions

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Brant Smith, P.E., Ph.D
Brant.Smith@peroxychem.com

