Treating Water by Degrading Oxyanions Using Metallic Nanostructures

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Abstract

Consideration of the water-energy-food nexus is critical to sustainable development, as demand continues to grow along with global population growth. Cost-effective, sustainable technologies to clean water of toxic contaminants are needed. Oxyanions comprise one common class of water contaminants, with many species carrying significant human health risks. The United States Environmental Protection Agency (US EPA) regulates the concentration of oxyanion contaminants in drinking water via the National Primary Drinking Water Regulations (NPDWR). Degrading oxyanions into innocuous compounds through catalytic chemistry is a well-studied approach that does not generate additional waste, which is a significant advantage over adsorption and separation methods. Noble metal nanostructures, *e.g.*, Au, Pd and Pt, are particularly effective for degrading certain species, and recent literature indicates there are common features and challenges. In this Perspective, we identify the underlying principles of metal catalytic reduction chemistries, using oxyanions of nitrogen (NO_2^- , NO_3^-), chromium (CrO_4^{2-}), chlorine (ClO_2^- , ClO_3^- , ClO_4^-), and bromine (BrO_3^-) as examples. We provide an assessment of practical implementation issues, and highlight additional opportunities for metal nanostructures to contribute to improved quality and sustainability of water resources.

Keywords: metallic nanostructure, oxyanions, catalyst, contaminants, nitrate, chromate, bromate, chlorite

39 Abstract Graphic

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41 Synopsis

42 The removal of toxic and prevalent oxyanion contaminants from water can be carried out
43 through catalytic degradation using metallic nanostructures. This Perspective highlights
44 the commonalities in reduction chemistry, and the challenges specific to oxyanions and
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Introduction

Sustainability of water

Fresh water is essential for life and is a key element of food and energy production, yet it makes up for only 3% of all earthly water.¹ Roughly ~30% of fresh water is readily usable, with the rest locked in ice caps and glaciers.² In 2014, an estimated 346 billion gallons per day of fresh surface and groundwater were consumed in the U.S. for energy production, agriculture, and other needs.³ As a consequence of anthropogenic activities, millions of tons of toxic chemicals are unfortunately released into the water supply every year, negatively impacting water quality.⁴ Clean fresh water is critical to both human health and industrial development, and proper management is required for its sustainable use.⁵

Toxic oxyanion contamination

When in the water environment, many elements speciate into oxyanions depending on pH and electrochemical potential.^{6,7} Their molecular formulae can be generalized as $A_xO_y^z$, where A represents a chemical element, O represents oxygen, and z is the overall charge of the ion.^{8,9} Oxyanions are highly soluble and mobile in water, and are widespread in drinking water sources such as surface and groundwater.⁸

Figure 1 shows elements that commonly form thermodynamically and/or kinetically stable oxyanions at pH 6.5~8.5 and at electrochemical potential (Eh) values of 0.1~0.4, which are the conditions commonly found in drinking water system.¹⁰ An oxyanion of a given element is considered thermodynamically stable if it is the lowest free energy state compared with other species of the element.¹¹ Pourbaix diagrams map the most thermodynamically stable species for a given element as a function of pH and

electrochemical potential.¹² The sulfate (SO_4^{2-}) anion, for example, is the thermodynamically stable species of sulfur at pH 6.5~8.5 and Eh 0.1~0.4 V as shown in the **Figure 2a**.¹³

H																	He
Li	Be																Ne
Na (Na^+)	Mg (Mg^{2+})																Ar
K	Ca	Sc	Ti	V	Cr (CrO_4^{2-})	Mn (MnO_4^-)	Fe (Fe^{3+})	Co	Ni	Cu (Cu^{2+})	Zn (Zn^{2+})	Ga	Ge	As (AsO_4^{3-})	Se (SeO_4^{2-})	Br (BrO_3^-)	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb (Sb(OH)_6^-)	Te (TeO_4^{2-})	I (IO_3^-)	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb (Pb^{2+})	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 1 Periodic table showing the most common oxyanion and cation species (marked by color) under drinking water conditions (pH 6.5~8.5, Eh 0.1~0.4 V). Thermodynamically stable oxyanions are peach-colored, kinetically stable oxyanions are in red, and cationic elements are in blue.

Oxyanions that exist in the environment but are not at the lowest energy state of the element are kinetically stable.¹⁴ Their conversion to a lower free energy state requires additional energy to overcome an activation barrier.¹⁵ For example, perchlorate (ClO_4^-) is an environmentally stable oxyanion of chlorine in water, but chloride is the lowest energy form of chlorine. Chloride (Cl^-), and not perchlorate, is shown within the water stability range in the Pourbaix diagram for chlorine (**Figure 2b**).¹⁶ While most non-metal elements can form common oxyanions in water at pH 6.5~8.5 and Eh 0.1~0.4 V, metal elements tend to form cations instead of oxyanions, or they precipitate as insoluble oxides. For example, iron forms ferrous cation (Fe^{2+}) in water at pH ~6.5 and Eh~0.1 V (**Figure 2c**).¹⁷

Figure 2 Pourbaix diagram of (a) sulfur (modified from Vermeulen et al.¹³), (b) chlorine (modified from Radepon et al.¹⁶), and (c) iron (modified from Tolouei et al.¹⁷). The blue dashed lines indicate the water electrochemical potential window.

Some oxyanions (e.g. carbonate CO_3^{2-}) and cations (e.g. sodium Na^+) are benign to the environment and human health, and are not subject to guidelines or regulations at either the federal or state level. However, other oxyanions and cations are toxic and can cause severe health problems.¹⁸ Nitrogen (e.g. $\text{NO}_3^-/\text{NO}_2^-$), chromium (e.g. CrO_4^{2-}), bromine (e.g. BrO_3^-), and chlorine (e.g. ClO_2^-) oxyanions as well as certain cations (e.g. Cu^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+}) are regulated by the National Primary Drinking Water Regulations (NPDWRs) with a maximum contaminant level (MCL) as set by the US Environment Protection Agency (EPA).¹⁹ U.S. states often have stricter regulations. For example, the state of California has an MCL of 6 ppb for perchlorate (ClO_4^-) in drinking water, but there is not yet a federal MCL.²⁰

Many technologies have been developed for the removal of oxyanions from water including adsorption,²¹ ion exchange (IX),²² and reverse osmosis (RO).²³ However, these methods and processes do not degrade the compounds, but instead transfer the contaminant into a secondary waste stream requiring disposal. Biological²⁴ and chemical²⁵ treatments of contaminants can be used to transform the contaminants to inert products. Biological processes are sensitive to operational conditions (e.g. pH and

salinity) and require long startup times though, and chemical treatments often require an excess of chemical reagents and can generate toxic byproducts.

Metallic nanostructure based catalytic water treatment as a sustainable process

Commonly used water treatment technologies based on IX and reverse osmosis not only generate concentrated waste streams but they also require large energy input.²⁶ Catalysis offers the desirable advantages of less energy usage and no waste generation, though it is not yet a common treatment approach. As one of the principles of green chemistry in reducing and eliminating the formation of hazardous compounds,²⁷ catalysis can also play an enabling role in their degradation and removal from the water environment, once formed. Any chemicals needed for catalysis should also be sustainably produced. For reduction reactions, for example, hydrogen gas can be obtained through water electrolysis (with electricity generated from solar panels or wind turbines) and formic acid can be obtained from biomass conversion.^{28,29}

The most studied materials are metal-based catalysts due to their outstanding catalytic properties, with regard to activity, selectivity, and/or stability.^{30,31} Metallic nanostructures are defined as metallic objects with at least one dimension in the range of one to a few hundred of nanometers, for example, spherical nanoparticles, nanorods, nanosheets, and nanocubes.^{32,33} The occupancy of d-bands of metal atoms allows reversible bonding to reactants via electron transfer, initiating surface reactions and affording them their catalytic activity.³² Metal catalysts generally contain nanoparticles (zero-dimensional metallic nanostructures) attached to a porous support, and have been used for both oxidative and reductive catalytic processes to convert contaminants in water to environmentally inert compounds.³⁴ Oxyanions (e.g. nitrite,³⁵ nitrate,³⁶ bromate,³⁷ and

perchlorate^{3,5}) and organohalides (e.g. trichloroethene³⁹ and chloroform⁴⁰) have been widely studied as target contaminants for catalytic reduction.

A 2012 review by Werth and coworkers assessed the state of knowledge concerning palladium-based catalysts for water remediation³⁴ of several contaminants (halogen and nitrogen containing organic compounds), and briefly addressed the catalytic reduction of oxyanions. In this contribution, we focus on oxyanions (**Table 1**) and the current state of understanding of their catalytic chemistry and prospects of catalytic water treatment.

Table 1 Concentration level and health effect of common toxic oxyanions

Contaminant	Regulated concentration level (ppm)	Potential health effects
Nitrate	10 (measured as nitrogen, US EPA)	Infant methemoglobinemia (blue-baby syndrome); probable carcinogen
Nitrite	1 (measured as nitrogen, US EPA)	Infant methemoglobinemia (blue-baby syndrome), probable carcinogen
Chromium(VI)	0.1 (measured as total chromium, US EPA)	Probable carcinogen
Bromate	0.01 (measured as bromate, US EPA)	Probable carcinogen
Chlorite	1 (measured as chlorite, US EPA)	Anemia; nervous system effects
[Chlorate]	[Not regulated]	Thyroid dysfunction
Perchlorate	0.002 (measured as perchlorate, Massachusetts state level) 0.006 (measured as perchlorate, California state level)	Thyroid dysfunction
Arsenic (as arsenate and arsenite)	0.01 (measured as total arsenic, US EPA)	Probable carcinogen
Selenium (as selenate and selenite)	0.05 (measured as total selenium, US EPA)	Circulatory system dysfunction

Catalytic Detoxification of Oxyanions Using Metallic Nanostructures

Monometallic nanostructures can function as a materials platform for catalytic reduction to 1) adsorb and dissociate reducing agents (e.g. H_2 to surface adsorbed hydrogen atom), 2) adsorb oxyanion contaminants on the surface of catalyst, 3) abstract oxygen from oxyanions by reacting with hydrogen adatoms, and 4) desorb the deoxygenated products from the surface of catalyst.³⁴ Monometallic compositions are sufficient to convert nitrite,⁴¹ bromate,⁴² and chromate⁴³ to inert species. However, some oxyanions like nitrate⁴⁴ and perchlorate⁴⁵ require a second metal as a promoter. The promoter metals are typically more oxophilic and can more efficiently abstract oxygen from oxyanion contaminants.⁴⁶ The promoter metal would then be re-reduced by hydrogen adatoms generated on the primary metal.³⁶

Nitrogen oxyanions

Occurrence and health effects

Nitrogen oxyanions like nitrate (NO_3^-) and nitrite (NO_2^-) are widespread contaminants of surface water and groundwater.^{47,48} The sources of these nitrogen oxyanions mainly come from chemical fertilizers and industrial waste.⁴⁹ A number of medical issues are associated with NO_3^-/NO_2^- intake, such as damage to the nervous system, spleen, and kidneys. Evidence is building that nitrogen oxyanions are carcinogenic and that they have a strong correlation with high cancer levels.⁵⁰ Nitrogen oxyanions can cause the *in-situ* formation of cancerous nitrosoamines in the body, and ingestion of nitrates during pregnancy can also cause infant methemoglobinemia (i.e. “blue baby syndrome”).⁵¹ The US EPA has placed a MCL of 10 ppm and 1 ppm (measured as nitrogen) in drinking

water for NO_3^- and NO_2^- , respectively.¹⁹

Current technology

Ion exchange (IX), reverse osmosis (RO), and electrodialysis reversal (EDR) are the only methods accepted by the US EPA for $\text{NO}_3^-/\text{NO}_2^-$ removal from water.^{52–54} IX is the most widespread technology used in for removing $\text{NO}_3^-/\text{NO}_2^-$ from drinking water sources, and has proven very effective in small to medium sized treatment plants, while RO is the second most common $\text{NO}_3^-/\text{NO}_2^-$ treatment alternative.⁵⁵ The most significant drawback of IX is the cost for disposal of the brine waste (which contains concentrated $\text{NO}_3^-/\text{NO}_2^-$ after IX regeneration), especially for inland communities.⁵⁶ For RO, key drawbacks include pretreatment requirements, power consumption, the management of waste concentrate, and higher electricity costs relative to IX.⁵⁷ The use of EDR in potable water treatment has increased in recent years, offering the potential for lower residual volumes through improved water recovery, the ability to selectively remove nitrate ions, and the minimization of chemical and energy requirements.⁵⁸

Catalytic chemistry

Catalytic nitrate/nitrite reduction using metallic nanostructures is a promising method for direct drinking water treatment and IX waste brine treatment. **Scheme 1** shows the Gibbs free energy (ΔG) values for nitrate/nitrite reduction to dinitrogen and ammonia using hydrogen at standard conditions are -229 kJ/mol and -530 kJ/mol, respectively.⁵⁹ For nitrate reduction to dinitrogen and ammonia, the free energy values are -835 and -733 kJ/mol, respectively.⁵⁹ Under laboratory conditions (1 mM nitrate $\sim$ 14 ppm-N, pH 7, 25 °C, 1 atm), the calculated corresponding free energy values decrease to -778 and -653 kJ/mol. Since ΔG is negative (exergonic reaction), the reduction of nitrate (and nitrite) to

the two end-products is thermodynamically favorable at room temperature. These reactions do not proceed without catalysts that lower the activation barriers for the respective reactions.

Scheme 1 Reduction reaction of nitrite and nitrate, to nitrogen gas and ammonia with corresponding standard Gibbs free energy values (25 °C, 1 atm, 1 M reactant concentrations, pH 0)

Generally, noble metallic nanostructures (i.e. Pd, Pt) adsorb and dissociate reducing agents (e.g. H₂) into reactive species (e.g. surface-adsorbed hydrogen atoms), and also adsorb NO₂⁻ onto the surface. Oxygen is then abstracted from the NO₂⁻, and the formed N-species further react together to form dinitrogen gas, or hydrogenate completely to form ammonium species. Pd is the most studied monometallic catalytic nanostructure for nitrite reduction,^{60–64} ever since the initial metal screening work of Vorlop and co-workers. They showed Pd to be the most active towards dinitrogen, compared to Pt, Rh and other metals.^{65,66}

The most commonly accepted catalytic reduction pathway of nitrite on the Pd surface is illustrated in **Scheme 2**. The surface adsorbed hydrogen atoms can go on to react with co-adsorbed nitrite to form NO_(ads) on the surface. NO_(ads) is a key intermediate in the nitrite reduction pathway which can lead to both dinitrogen and ammonia.^{41,67}

Scheme 2 Nitrite catalytic reduction pathway on Pd surface with hydrogen gas as a reducing agent (modified from Martínez et al.⁶⁸). The DFT calculated pathway is kinetically unlikely to occur.

In the formation of dinitrogen, $\text{NO}_{(\text{ads})}$ can dissociate to allow for dinitrogen formation through the direct coupling of $\text{N}_{(\text{ads})}$ species.⁴¹ Dinitrogen can also be formed through a mechanism where $\text{NO}_{(\text{ads})}$ is converted through the intermediate N_2O . In the formation of ammonia, $\text{NO}_{(\text{ads})}$ can lead to NH_4^+ through the stepwise hydrogenation of a presumed $\text{N}_{(\text{ads})}$ species. Werth and coworkers showed, using isotopically labeled N species that N_2O forms N_2 exclusively, while NO forms both N_2 and ammonium.⁶⁷

Direct $\text{NO}_{(\text{ads})}$ hydrogenation has been proposed for NH_4^+ formation via $\text{HNO}_{(\text{ads})}$, $\text{H}_2\text{NO}_{(\text{ads})}$, and $\text{H}_2\text{NOH}_{(\text{ads})}$ intermediates,⁶⁸ though we are doubtful of this pathway. While $\text{NO}_{(\text{ads})}$ hydrogenation has been demonstrated experimentally over Pt, this pathway was ruled out experimentally for Pd, and was determined computationally to be more unlikely to occur compared to $\text{N}_{(\text{ads})}$ formation and hydrogenation.^{41,60}

Improving the activity of Pd-based catalysts has been a main focus of many studies (**Table 2**). Various catalyst structures, support and compositions with addition of secondary metal have been studied in catalytic nitrite reduction.^{61,69,70} Seraj *et al.* synthesized Pd-Au alloy catalysts and found that the addition of Au improves the nitrite reduction activity, and the alloy structure showed reduced loss of catalytic activity in sulfide fouling tests.⁷¹ Their DFT (density functional theory) calculations indicated that

Au enhanced the activity of Pd through electronic effects, and reduced sulfur poisoning by weakening the sulfide bonding at the Pd-Au surface. Wong and coworkers synthesized Au nanoparticles (NPs) covered with submonolayer amounts of Pd, and observed improved nitrite reduction activity by an order of magnitude.³⁵ The enhancement effect of Au on Pd catalysis of nitrite reduction was attributed to the creation of zerovalent two-dimensional Pd ensembles and high Pd dispersion.

Table 2 Performance of metallic nanostructures in the catalytic reduction of nitrite

Catalyst	k_{cat}^* (L/ g metal/min)	Hydrogen donor	Initial pH	Reaction temperature	Ref.
5wt% Pd/Al ₂ O ₃	-	H ₂	5.2	Room temperature	60
5wt% Pt/Al ₂ O ₃	-				
Pd ₈₀ Cu ₂₀ /PVP	1.67	H ₂	5.5-7.5	Room temperature	46
5wt%Pd/Al ₂ O ₃	4	H ₂	5	Room temperature	70
5%Pd 0.5%In/Al ₂ O ₃	6.9				
5.42%Pd 0.86%In/Al ₂ O ₃	17.43	H ₂	7	Room temperature	67
2.8nmPd/PVP	1.53	H ₂	8.5	Room temperature	62
3.2nmPd/PVA	1.47				
1wt%Pd/Al ₂ O ₃	76				
Pd NPs	40	H ₂	5-7	Room temperature	35
Pd-on-Au NPs	576				
1wt% Pt/Al ₂ O ₃	0.6	H ₂	5.5	10 °C	72
1wt% Pt Cu/Al ₂ O ₃	0.7				
0.25wt%Pd/ACC	7.06	H ₂	4.5	25 °C	69
5wt%Pd/CNF	2.44	H ₂	5	21 °C	64
PdAu alloy	5	H ₂	6.4	22 °C	71

* Re-calculated k_{cat} normalized by total metal amount based on the published data.

Researchers have also focused on enhancing the nitrite reduction selectivity to nontoxic N₂. Higher N₂ selectivity was found to relate to large catalyst particle sizes,⁶⁴ specific shapes (e.g. Pd rods and cubes),³¹ type of stabilizing surfactants,⁷³ and especially reaction conditions. An increase in pH generally decreased both the activity of nitrogen oxyanion reduction and the selectivity to N₂, though the mechanistic reason is still not completely understood.⁴⁴ Lefferts and co-workers reported surface coverage changes of

the reaction intermediates at different pH values using attenuated total reflectance infrared spectroscopy, which could be the source of reactivity and selectivity differences.⁶⁰ Reactant concentration has little effect on the normalized activity (in unit of liter per gram-catalyst per min) if the reaction is in the kinetically-controlled region, while it has strong effect on the selectivity of nitrogen oxyanion reduction. Shin *et al.* showed that an increased initial nitrite concentration or lower H₂ flow rate both enhanced N₂ selectivity, and concluded that surface adsorbed nitrogen reacts with NO₂⁻ in solution to form dinitrogen.⁴¹

While effective for nitrite, monometallic Pd (or Pt) nanostructures show little activity for nitrate reduction,⁷⁴ and require a secondary promoter metal, such as copper (Cu), tin (Sn), or indium (In) (**Table 3**).^{75–78} The secondary metal is thought to be oxidized after abstracting the oxygen from nitrate, and converting it to nitrite. The oxidized secondary metal is then re-reduced by hydrogen atoms adsorbed on the Pd or Pt surface. The nitrate-to-nitrite catalytic cycle is shown in the **Scheme 3**. The nitrite presumably reduces to dinitrogen or ammonia via **Scheme 2**.

Scheme 3 Nitrate catalytic reaction pathway to nitrite on Pd surface with M (Cu, Sn, or In) as a secondary metal promoter and hydrogen gas as a reducing agent (modified from Guo et al.³⁶)

Among the Pd-based bimetallic catalysts, Pd-Cu is the most studied, even though Cu is not the best promoter choice. Vorlop and coworkers originally reported that Pd-Sn and Pd-In catalysts were more active for nitrate reduction and more N₂ selective than Pd-Cu.⁷⁹ Chaplin and coworkers reported Pd-In was more stable than Pd-Cu with regard to metal leaching during catalyst regeneration.⁸⁰ When sulfide-poisoned Pd-Cu and Pd-In catalysts were treated with a dilute bleach solution, 11% of the total Cu leached into solution while no In leaching was detected. Thus, In is more appropriate for water treatment.

Recently, Wong and coworkers studied the role of In using In-on-Pd nanoparticle catalysts in kinetic testing, *in-situ* x-ray absorption spectroscopy, and DFT simulations.³⁶ They experimentally observed the *in situ* oxidation of In upon exposure to NO₃⁻ solution, providing experimental evidence for In as a redox site for the nitrate-to-nitrate step (**Scheme 3**). The material exhibited nitrate reduction volcano dependence on In surface coverage, with 40% Pd surface coverage (40 sc%) by In that was 50% higher than that of a sequentially impregnated InPd/Al₂O₃ catalyst (with >95% selectivity to dinitrogen).³⁶ DFT calculations indicated In ensembles containing 4 to 6 atoms provide the strongest binding sites for nitrate oxyanions and lead to smaller activation barriers for the nitrate-to-nitrite step.³⁶ Lumped kinetic modeling implicated both factors for the observed volcano peak near 40 sc%.

Table 3 Performance of metallic nanostructures in the catalytic reduction of nitrate

Catalyst	k_{cat}^* (L/ g metal/min)	Hydrogen donor	Initial pH	Reaction temperature	Ref.
1.6% Pd/CeO ₂	2.06	H ₂	-	25 °C	74
40 sc% In-on-Pd NPs	2.15	H ₂	5.5	Room temperature	36
5%Pd 5%In/Al ₂ O ₃	2.23	H ₂			
5%Pd 1.25%In/Al ₂ O ₃	3.86	H ₂	5	Room temperature	81
5%Pd 0.625%In/Al ₂ O ₃	2.02	H ₂			
5%Pd 1%In/Al ₂ O ₃	0.084	H ₂			79
	0.012	HCOOH	6	Room temperature	
5%Pd 2%In/Al ₂ O ₃	0.0628				
5%Pd 4%Sn/Sty-DVB	0.51	H ₂	5	25 °C	82
5%Pd 4%In/Sty-DVB	0.19				
2%Pd 0.5%Cu/Al ₂ O ₃	0.59	H ₂	5	Room temperature	83
1%Pd 0.25%In/SiO ₂	0.65	H ₂			
1%Pd 0.25%In/Al ₂ O ₃	2.8	H ₂	5	Room temperature	84
5%Pd 2%In/ SiO ₂	0.57	H ₂			
5%Pd 2%In/ Al ₂ O ₃	0.214	H ₂	5	Room temperature	76
5%Pd 2%In/ TiO ₂	0.236	H ₂			
5%Pd 1.25% In/AC	6.08	H ₂	5	Room temperature	85
1.6%Pd 2.2%Sn/ZSM-5	1.73	H ₂	5	Room temperature	77
0.1%Pd 0.01%In/Al ₂ O ₃	0.12	H ₂	5	Room temperature	86
1.6%Pd 2.2%Cu/NBeta	0.33	H ₂			
1.6%Pd 2.2%Sn/NBeta	2.8	H ₂	4.5-5	Room temperature	87
1.6%Pd 2.2%In/NBeta	0.42	H ₂			
5%Pd 1.5%Cu/Al ₂ O ₃	3.88	H ₂	5	Room temperature	88
2.5%Pd 0.25%In/C	0.0088	H ₂	5	Room temperature	89
1%Pd 0.25%In/Al ₂ O ₃	3.1	H ₂	5	Room temperature	90
1%Pd 0.25%In/Al ₂ O ₃	5.16	H ₂			
1%Pd 1%In/SiO ₂	0.3	H ₂			
1%Pt 0.25%In/Al ₂ O ₃	2.02	H ₂	5	Room temperature	91
1%Pt 1.2%In/SiO ₂	0.24	H ₂			
0.92%Pd 0.32%In/Al ₂ O ₃	0.049	H ₂	6	Room temperature	92
0.75%Pt 0.25%Cu/Al ₂ O ₃	1.1	H ₂	6.5	10 °C	93
4.7%Pd 1.5%Sn/Al ₂ O ₃	0.3	HCOOH	5	Room temperature	94
1.6%Pt 0.8%Cu/Al ₂ O ₃	0.5	H ₂			
1.6%Pd 0.5%Cu/Al ₂ O ₃	0.39	H ₂			
1.6%Pt 0.8%Ag/Al ₂ O ₃	0.39	H ₂	-	10 °C	95
1.6%Pd 0.8%Ag/Al ₂ O ₃	0.44	H ₂			
1.5%Pd 0.5%Cu/Al ₂ O ₃	0.28	H ₂			
1.5%Pd 0.5%Co/Al ₂ O ₃	0.048	H ₂	5	-	96
1.5%Pd 0.9%In/Al ₂ O ₃	0.12	H ₂			
2%Pd 0.6%Cu/ACC	0.08	H ₂	5.5	25 °C	97
5%Pd 0.5%Sn/PPy	1.7	H ₂	3.5	25 °C	98
Pd ₆₀ Cu ₄₀ /PVP	0.08	H ₂	5.5-7.5	Room temperature	46
0.75%Pt 0.25%Cu/Al ₂ O ₃	1.1	H ₂	5.5	10 °C	72
5%Pd 0.86Cu/ASA	1.09	H ₂	5.4	25 °C	99

0.13%Pd 0.03%Cu/GFC	0.96	H ₂	5.1	25 °C	¹⁰⁰
5%Pd 1.5%Cu/SnO ₂	0.089	H ₂	4	25 °C	¹⁰¹
4.9%Pd 1.5%Cu/ZrO ₂	3.92				

* Re-calculated k_{cat} normalized by total metal amount based on the published data.

Assessment of technology readiness

Attempts have been made to scale-up the catalytic reduction process for nitrate treatment.^{69,100,102,103} For example, a company has developed a catalytic unit based on Pd-Cu supported on activated carbon cloth, and is conducting pilot tests with the Southern Nevada Water Authority to treat 90-ppm nitrate-containing water at a throughput of 2-8 m³/h.¹⁰²

Werth and co-workers have worked on developing Pd-In catalyst-based trickle-bed flow reactors (TBR) for nitrate treatment of drinking water and IX waste brine.^{86,89,104} Gas and liquid flow rates, catalyst metal loading, and catalyst pellet size were varied to optimize TBR performance. Catalytic activity in the flow reactor was ~18% that of the same catalyst tested in batch mode, which was attributed to H₂ mass transfer limitations. Catalytic activity was lower by ~50% in the IX waste brine treatment compared to drinking water treatment, which was caused by competitive adsorption between the chloride and sulfate anions with the nitrate reactant.

Chromium Oxyanions

Occurrence and health effects

In the US, chromium is the second most common inorganic contaminant, after lead.^{105,106} The most common forms of chromium are trivalent chromium (Cr(III)) and hexavalent chromium ("chromium-6", Cr(VI)). Chromium oxyanions (e.g. chromate CrO₄²⁻) are frequently used in metallurgy, pigment manufacturing, and wood treatment processes.¹⁰⁷

Inappropriate disposal of industrial wastewater results in chromium contamination. Chromium oxyanions have cytotoxic and carcinogenic properties.¹⁰⁸ The US EPA set a MCL of total chromium (Cr(III) + Cr(VI)) to 0.1 ppm for drinking water.¹⁹ California has a more restrictive MCL of 0.05 ppm for total chromium.^{109,110} The World Health Organization (WHO) provides a drinking water guideline value of 0.05 ppm for Cr(VI).¹¹¹

Current technologies

Numerous removal methods, including chemical reduction,¹¹² IX,¹¹³ adsorption,¹¹⁴ biodegradation,¹¹⁵ and membrane filtration¹¹⁶ have been studied for Cr(VI) (in the form of CrO_4^{2-}). Barrera-Díaz and coworkers reviewed chemical, electrochemical and biological methods for aqueous chromate reduction.¹¹⁷ Some of the most common remediation strategies use redox reactions to convert chromate to a chromium oxide solid by adding Fe(II) as the electron donor ($6 \text{Fe}^{2+}_{(\text{aq})} + 2 \text{CrO}_4^{2-}_{(\text{aq})} + 13 \text{H}_2\text{O} \rightarrow 6 \text{Fe}(\text{OH})_3 (\text{s}) + \text{Cr}_2\text{O}_3 (\text{s}) + 8 \text{H}^+$).¹¹⁸ IX is used on a large scale to remove chromate (e.g., Cal Water in California).

Catalytic chemistry

While Cr(VI) is highly toxic and carcinogenic, Cr(III) is non-toxic and an essential trace element for humans.¹¹⁹ Cr(III) is in a soluble cation form (Cr^{3+}) under acidic conditions and readily precipitates as a $\text{Cr}(\text{OH})_3$ solid at neutral pH condition. The catalysis strategy is to 1) reduce CrO_4^{2-} to Cr^{3+} under acidic conditions, and 2) raise the pH to convert Cr^{3+} to insoluble $\text{Cr}(\text{OH})_3$. Formic acid is widely used as a reducing agent because it also provides the low pH condition. Reduction of chromate using hydrogen generated from

the decomposition of formic acid¹²⁰ and the formation of Cr(OH)₃ precipitate¹²¹ are thermodynamically favorable (**Scheme 4**).

Scheme 4 Formic acid (HCOOH) decomposition to hydrogen and carbon dioxide, reduction reaction of chromium oxyanion, and formation of chromium hydroxide with their corresponding standard Gibbs free energy values (25 °C, 1 atm, 1 M reactant concentrations, pH 0)

The Cr(VI) reduction reaction is slow and requires a catalyst, but the formed Cr(III) rapidly forms Cr(OH)₃ without one. Noble metallic nanostructures (e.g. Pd, Pt, Au, Ag) have been investigated for the former reaction.

Sadik's group first reported the reduction of chromate to Cr³⁺ over colloidal Pd NP catalysts using formic acid.⁴³ The reaction likely follows a Langmuir-Hinshelwood surface reaction mechanism, involving H adatom formed from the dehydrogenation of formic acid on the metal surface.¹²² Surface adsorbed hydrogen then reduce the co-adsorbed chromate/dichromate to Cr³⁺ via a hydrogen transfer pathway.¹²² Although formic acid has been the most commonly studied, other reducing agents, such as hydrogen gas,^{43,123} sulfur,¹²⁴ and poly(amic acids)¹²⁵ have also been studied.

Other noble metallic nanostructures, such as Pt,^{126–128} Ag^{102,103} and Au^{126,129}, as well as their bimetallic forms, such as PdAu and AuAg^{129,131} have also been investigated for chromate reduction (**Table 4**). Yadav et al. compared Pt, Pd, and Au nanoparticles immobilized in a metal-organic framework, and found that Pt was the most active while

Au was inactive.¹²⁶ The reason for Pt as the most active catalyst is not clear. Bimetallic NPs (e.g. AuAg and PdAu) were found to have enhanced catalytic activities compared with their monometallic forms in the chromate reduction reactions.¹²⁹ The relative importance of electronic, geometric and bifunctional effects on Cr(VI) reduction using bimetallic nanostructures is not known at this point.

To understand the structure-property relationships of monometallic catalysts, Pd-based materials with different shapes were synthesized and studied for catalytic chromate reduction (**Table 4**). Zhang et al. found Pd icosahedron-shaped NPs to be the most active among other shaped studied (spheres, rods, spindles, cubes and wires).¹³² They attributed its reduction ability to the icosahedron having a greater fraction of surface Pd atoms exposed on {111} facets. We recommend normalizing measured reaction rate constants to surface Pd atoms (calculated or experimentally titrated) as a more quantitative way to compare shape effects.¹³³

Support effects are have been studied extensively also (**Table 4**).^{134–136} The metal-normalized reaction rate constants (re-calculated from published values) span two orders of magnitude. This wide activity range suggests the presence of intraparticle mass transfer effects on observed reaction rates, interfering with any potential compositional effect of the support on Cr(VI) reduction. Mass transfer effects can be assessed (and corrected for) if rigorous experimentation is carried out.¹³⁷

Table 4 Performance of metallic nanostructures in the catalytic reduction of chromate

Catalyst	k_{cat}^* (L/ g metal/min)	Hydrogen donor	Initial pH	Temperature	Ref
Pd colloid	28.97	HCOOH	2	45 °C	43
Pd tetrapod	0.14	HCOOH	-	50 °C	138
Pd nanowire	0.07	HCOOH	-	Room temperature	135
Urchin-like Pd	0.01	HCOOH	-	Room temperature	139
Pd icosahedron	0.03	HCOOH	1.5	Room temperature	132
AuPd@Pd	24.04	HCOOH	-	50 °C	131
2.93% Pd/TiO ₂ nanotube	62.23	H ₂	2	25 °C	140
Pd/ γ -Al ₂ O ₃ film	-	HCOOH	-	30 °C	141
13.1% Pd/PEI/PVA nanofibers	65.07	HCOOH	-	50 °C	134
1.13% Pd/Fe ₃ O ₄	-	HCOOH	4	45 °C	142
1.2% Pd/Amine-functionalized SiO ₂	14.14	HCOOH	-	25 °C	143
22.4% Pd/ZIF-67	8.47	HCOOH	-	-	144
2% Pd/MIL-101	0.15	HCOOH	-	50 °C	126
5.66% Pd/Eggshell membrane	1.85	HCOOH	-	43 °C	127
Pd/Tobacco mosaic virus	345.88	HCOOH	3	Room temperature	145
2% Pt/MIL-101	0.56	HCOOH	-	50 °C	126
5.91% Pt/Eggshell membrane	2.61	HCOOH	-	43 °C	127
10.38% Pt/Magnetic mesoporous silica	20.00	HCOOH	-	25 °C	128
2.7% Ag/Biochar	5.54	HCOOH	-	50 °C	130
3.05% AgAu/Ruduced graphene oxide	253.70	HCOOH	-	Room temperature	129
2% Au/MIL-101	0	HCOOH	-	50 °C	126

* Re-calculated k_{cat} normalized by total metal amount based on the published data.

Assessment of technology readiness

Currently, all studies on chromate reduction have been conducted in batch reactors. We are not aware of any pilot-scale catalytic systems to treat Cr(VI). Most batch studies assessed catalyst performance based on Cr(VI) disappearance; they did not quantify the chromium end-products of the reaction. The Cr(OH)₃ precipitate would likely foul any catalyst during flow operation if low pH is not maintained, which would be problematic for long-term performance and regeneration. Further, the performance of these catalysts in the presence of real waters (i.e. in the presence of other ions and chemical species present in complex water matrices) has not been studied.

Halogen oxyanions

Of the six halogen elements (e.g. F, Cl, Br, I, At and Ts) in the periodic table, the oxyanions of chlorine, bromine and iodine are the most common. Different anionic species can exist depending on halogen oxidation state.¹⁴⁶ For example, chlorine can exist as hypochlorite (ClO^- , Cl oxidation state of +1), chlorite (ClO_2^- , +3), chlorate (ClO_3^- , +5) and perchlorate (ClO_4^- , +7) anions.¹⁴⁶ Chlorite (ClO_2^-), perchlorate (ClO_4^-), as well as bromate (BrO_3^-), are regulated drinking water contaminants.

Occurrence and health effects

In drinking water treatment plants, bromate (BrO_3^-) can be found as a disinfection by-product (DBP) arising from the ozonation of bromide-containing source waters ($\text{O}_3 + \text{Br}^- \rightarrow \text{O}_2 + \text{BrO}^-$; $2 \text{O}_3 + \text{BrO}^- \rightarrow 2 \text{O}_2 + \text{BrO}_3^-$).¹⁴⁷ A suspected carcinogen, the US EPA has set a MCL of 0.01 ppm for bromate in drinking water.¹⁹

Chlorite (ClO_2^-) and chlorate (ClO_3^-) are also DBPs in drinking water caused by the decomposition of chlorine dioxide, another strong oxidizing agent used in water treatment.¹⁴⁸ Chlorite can cause anemia and affect the human nervous system; it has a MCL of 1 ppm.¹⁹ Chlorate was evaluated under the US EPA 2012-2016 Unregulated Contaminant Monitoring Rule (UCMR-3) and is on the 2016 Contaminant Candidate List (CCL-4), indicating it can potentially be regulated in the future.¹⁴⁹

Perchlorate (ClO_4^-) occurs naturally in arid regions and in potash ore.¹⁵⁰ It also used in the manufacture of rocket propellant, explosives, and fireworks, and contamination of water resources arises from improper disposal of these materials.^{20,151} Perchlorate can cause dysfunction of the human thyroid, leading to metabolic problems, such as heart rate, blood pressure and body temperature regulation.¹⁵¹ It was evaluated

under the US EPA 2001-2005 Unregulated Contaminant Monitoring Rule (UCMR-1) and is on the 2009 Contaminant Candidate List (CCL-3), suggesting a federally mandated MCL is possible. Several states have set drinking water standards for perchlorate, e.g. Massachusetts has an MCL of 0.002 ppm and California an MCL of 0.006 ppm.¹⁵²

Current technologies

Numerous treatment methods have been explored to remove bromate in water, including IX, activated carbon adsorption, membrane filtration, biodegradation, chemical reduction, and photocatalysis.^{153–157} Although many of these technologies are still in the laboratory evaluation and development stages, some have been tested in the pilot scale.¹⁵⁸ Perchlorate can be removed from contaminated water through similar means.¹⁵² A full-scale IX treatment system was successfully operated in California to lower perchlorate concentration from 10-200 ppb to <4 ppb.¹⁶¹ The disposal of the IX waste brine is a costly concern. Chlorite removal is comparatively less studied, and done only at the laboratory scale.^{159,160}

Catalytic chemistry for bromine oxyanion

Thermodynamically, the reduction of bromate (BrO_3^-), chlorite (ClO_2^-), chlorate (ClO_3^-), and perchlorate (ClO_4^-) are energetically favorable (**Scheme 5**), but the kinetics for these transformations are slow.

Scheme 5 Reduction reactions of bromate, chlorite, chlorate and perchlorate with the corresponding standard Gibbs free energy values (25 °C, 1 atm, 1 M reactant concentrations, pH 0)

Chen et al. reported that bromate (BrO_3^-) could be directly reduced over Pd and Pt catalysts using hydrogen.³⁷ The role of metallic nanostructures (e.g. Pd, Pt) is to adsorb and dissociate hydrogen which subsequently reacts with adsorbed BrO_3^- .⁴² This reaction leads to the formation of the reduced product Br^- and water. The oxidized metal is then reduced by hydrogen, thus closing the catalytic cycle.⁴² Subsequent studies focused on improving the catalytic activity of monometallic nanoparticles, in particular Pd, as well as catalyst stability by using different supports including metal oxides,^{37,162–164} silica,^{37,165} carbon based materials,^{37,42,163,166–171} and zeolites (**Table 5**).^{172,173}

Table 5 Performance of metallic nanostructures in the catalytic reduction of bromate

Catalyst	k_{cat}^* (L/ g metal/min)	Hydrogen donor	Initial pH	Temperature (°C)	Ref.
1.93% Pd/ Al_2O_3	0.69	H_2	5.6	Room temperature	³⁷
2% Pd/ SiO_2	0.004	H_2	5.6	Room temperature	³⁷
2% Pd/Activated carbon	0.04	H_2	5.6	Room temperature	³⁷
2% Pt/ Al_2O_3	0.27	H_2	5.6	Room temperature	³⁷
0.3% Pd/5% CNF/SMF	0.15	H_2	6.5	25 °C	¹⁶⁶
2.2% Pd/Mesoporous carbon nitride	4.07	H_2	5.6	25 °C	¹⁶⁸
0.1% Pd/ Fe_3O_4	0.69	H_2	6	27 °C	¹⁷⁴
2% Pd/Magnetic MCM-41	0.55	H_2	5.6	25 °C	¹⁷⁵
1.3% Pd/Core-shell silica	1.1	H_2	7	20 °C	¹⁶⁵
0.86% Pd/ $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$	4.16	H_2	5.6	25 °C	¹⁶²
1.5% Pd/ZSM-5	0.10	H_2	-	25 °C	¹⁷²
1.4% Pd 1% Cu/ZSM-5	0.92	H_2	-	25 °C	¹⁷²
0.92% Pd/Faujasite zeolite Y	0.07	H_2	-	Room temperature	¹⁷³
1.6% Pd 0.84% Cu/Faujasite zeolite Y	0.92	H_2	-	Room temperature	¹⁷³

*Re-calculated k_{cat} normalized by total metal amount based on the published data.

The support composition significantly increases reduction activity, which appears to relate to the isoelectric point (IEP) of support.³⁷ It was explained that Pd/Al₂O₃ (IEP ~8.0) is more active than the Pd/SiO₂ (IEP ~2.0) and Pd/C (IEP <2.0), because the Al₂O₃ is positively charged at the reaction pH of 5.6, thereby electrostatically increasing the local oxyanion concentration near the Pd domains.³⁷ Incorporating a second metal, such as Cu, appears to increase bromate reduction activity.^{171,173} The catalytic behavior of bimetallic nanostructures for this reaction may be similar to that for other oxyanions, but this has not been established yet.

Catalytic chemistry for chlorine oxyanions

Few have studied chlorite and chlorate reduction. As early as 1995, patent literature disclosed the use of monometallic Pd and other precious metals for the catalytic reduction of chlorite/chlorate, as well as bromate anions.¹⁷⁶ Perchlorate catalytic reduction is difficult to achieve using monometallic Pd, requiring a second metal (in this case, rhenium, **Table 6**).^{45,177–180} Pd adsorbs and dissociates hydrogen to reactive species (e.g. surface-adsorbed hydrogen atoms) which go on to reduce the oxidized Re.¹⁷⁸ The role of Re, an oxophilic metal, is to adsorb chlorine oxyanions and abstract an oxygen atom from perchlorate to form chlorate.¹⁸¹ Chlorate can undergo the same process to be reduced to lower-valent chlorine oxyanion. The reaction pathway follows $\text{ClO}_4^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_2^- \rightarrow \text{Cl}^-$.⁴⁵ Using *ex-situ* X-ray photoelectron spectroscopy (XPS), Choe et al. concluded that Re likely cycled between a higher oxidation state (+7) and lower oxidation states (+5/+4 and +1) during perchlorate reduction.¹⁷⁸

Table 6 Performance of metallic nanostructures in the catalytic reduction of perchlorate

Catalyst	k_{cat}^* (L/ g metal/min)	Hydrogen donor	Initial pH	Temperature	Ref.
5%Re 5%Pd/C	0.03	H ₂	2.9	25 °C	180
1%Re 5%Pd/C	0.04				
13%Re 4.71%Pd/C	0.04	H ₂	3	23 °C	45
9.4%Re 5%Pd/C	0.034				
2.9%Re 5%Pd/C	0.007				
5%Pd 5.5%Re	0.24	H ₂	2.7	23 °C	179
	0.098		3.8		
12%Re 5%Pd/C	0.009	H ₂	2.7	21°C	178
7%Re 5%Pd/C	0.3	H ₂	3	Room temperature	182
10%Pd/C	0.012	H ₂	7	20°C	177

* Re-calculated k_{cat} normalized by total metal amount based on the published data.

Assessment of the technology readiness

Continuous-flow fixed-bed reactors have been studied for the reduction of halogen oxyanions under simulated conditions.^{163,164,166,167,169,170} A life cycle assessment (LCA) was performed by Yaseneva et al. to assess the potential application of a carbon nanofiber supported Pd catalyst for bromate removal from industrial wastewater and natural waters in a plug flow reactor (5 mL water/min).¹⁷⁰ The bromate reduction activity in industrial wastewater samples was lower than that in the natural water sample due to the presence of other anions (e.g. Cl⁻, SO₄²⁻ and dissolved organic compounds) which competed for the active sites on the catalyst surface. The treatment process using carbon nanofiber supported Pd catalyst was more efficient in terms of activity and less costly and environmentally impactful, compared with the process based on a conventional Pd/Al₂O₃ catalyst.

Liu et al. investigated the impact of water composition on the activity of perchlorate reduction using Re-Pd/C.¹⁸⁰ The perchlorate reduction activity was higher in

simulated brine than that in real IX waste brine. Nitrate in the IX waste brine was found to deactivate the Re-Pd/C, but the deactivation mechanism is not known.¹⁸⁰ Choe et al. assessed the environmental sustainability of perchlorate treatment technologies including IX, bioremediation, and catalytic reduction.¹⁸³ They found the environmental impact of catalytic treatments to be 0.9~30x higher compared to conventional IX, which could be mitigated with increased catalytic activity and increased H₂ mass transfer.¹⁸³ To date, there is no published work on catalytic treatment of chlorite/chlorate oxyanions at the testbed level.

Perspective and Research Opportunities

Comparison of reduction catalytic activity for the different oxyanions

Based on the re-calculated values compiled in **Tables 2-6**, we found that the reaction rate constants for NO₂⁻, NO₃⁻, CrO₄²⁻, BrO₃⁻, and ClO₄⁻ reduction using monometallic Pd catalyst were roughly 1, 0, 10, 0.1 and 0.01 liter per gram metal per min, respectively. In terms of their reactivity on Pd, the oxyanions were ordered in the following way: CrO₄²⁻ > NO₂⁻ > BrO₃⁻ >> ClO₄⁻ > NO₃⁻. These oxyanions are broadly less reactive compared to halogenated organic compounds like trichloroethene, due to the latter's ability to bind more readily to metal surfaces.³⁹

Chaplin et al. compared rate constants for several oxyanion contaminants over mono- and bi-metallic Pd catalysts and suggested that the X-O bond strength was one factor in determining reaction rates.³⁴ Another factor is molecular geometry, which can affect the adsorption and activation of the oxyanion to the catalyst surface. NO₂⁻ has a bent shape, different from the trigonal planar shape of NO₃⁻. CrO₄⁻ and ClO₄⁻ are

tetrahedral in shape, and BrO_3^- is trigonal pyramidal. Tetrahedral molecules tend to be more stable and are more difficult to adsorb, which could be a reason for the low reactivity of ClO_4^- compared with BrO_3^- , even though the Cl-O bond (197 kJ/mol) is weaker than the Br-O bond (242 kJ/mol). Considering CrO_4^{2-} and ClO_4^- have the same geometry, their bond strengths appear correlated to their relative reactivity. DFT calculations can provide insights to the effects of bond strength, molecular shape, and metal-adsorbate interactions on oxyanion reactivity differences.

Applicability of catalytic remediation to other oxyanions

The soluble forms of As (arsenate and arsenite) and Se (selenate and selenite) are toxic,¹⁸⁴ making the metal form desirable as the reduced end-product. The reduction of As and Se oxyanions can be achieved using bacteria,^{185,186} but this has not been reported using heterogeneous catalysts. Thermodynamically, it is favorable to reduce arsenate (AsO_4^{3-}) to arsenite (AsO_3^{3-}) to elemental arsenic using hydrogen as a reducing agent (**Scheme 6**).¹²⁰ The reduction of selenate (SeO_4^{2-}) to elemental selenium using hydrogen is also thermodynamically favored. Catalytic reduction is possible, but fouling due to solids formation would make this approach problematic with regard to long-term performance stability and regeneration.

Scheme 6 Reduction reaction of arsenate/arsenite to arsenic metal, and selenate to selenium metal with corresponding standard Gibbs free energy values (25 °C, 1 atm, 1 M reactant concentrations, pH 0)

Possible catalytic water treatment scenarios using metallic nanostructures

We highlight several opportunities for the use of metallic nanostructure enabled catalytic systems. A passive in-situ groundwater treatment could be envisioned using permeable reactive barriers or horizontal-flow treatment wells filled with catalytic material and supplied with reductant (e.g. formic acid).¹⁸⁷ Pilot scale tests have been carried out in both US and Europe.^{188,189} Although the studies focused on halogenated organic compounds, the approach and associated reactor design can be applied to treat oxyanion contaminants as well. For the latter, bench scale and pilot scale studies have been carried out successfully for nitrate and perchlorate.^{89,104,180}

Catalysis is an exciting concept to address the issue of spent IX brine, especially if the metal catalysts can be designed to be more active in high-salinity water.¹⁰⁴ Researchers have shown that nitrate brine treatment is feasible using a combined IX-catalytic treatment system, and can have a lower environmental impact than IX alone.⁸⁹ Current technical challenges of this system include the depressed activity of the catalyst (due to the high concentrations of salt species), and possible, unquantified metal loss during operation. Metal nanostructures that can operate at high-salinity conditions durably are desired.

Catalytic processes could also potentially be used at a consumer, point-of-use level. A major concern would be the safe use and storage of hydrogen. Alternative safe and inexpensive reductants (e.g. formic acid) could be used instead of hydrogen gas; a water electrolysis (as part of an under-the-sink treatment unit) could be used to produce the required amounts of hydrogen on-demand. Catalysis could also be useful in the

treatment of decentralized water supplies at the community level, if hydrogen can be sustainably supplied on a larger scale, e.g., using wind energy¹⁹⁰ or photovoltaics.

Roadmap for deployment of catalysts for oxyanion treatments

The progress of technology of catalytic reduction of oxyanions can be roughly assessed using technology readiness level (TRL) values, as introduced by the National Aeronautics and Space Administration (NASA) in the 1970s (**Scheme 7**).¹⁹¹ Most academic laboratory studies are at the TRL 1 (e.g. batch reactors), with fewer at TRL 2 (e.g, flow reactors, LCA and techno-economic analysis, TEA). Of the oxyanions, nitrate treatment by catalysis is the furthest along with respect to technology development. IX-brine and fresh water treatments described in previous sections can be characterized to be at least at TRL 4. There is much room to develop catalyst technologies for the other oxyanions, which can be enabled by university-industry partnerships.¹⁹²

Scheme 7 Technology readiness level (TRL) for catalytic reduction of oxyanion contaminants. The colored boxes represent current and past activities in research and development.

Practical implementation issues of catalytic water treatment

Strong progress has been made in developing new catalysts and catalytic reduction processes for oxyanions in drinking water and waste brine treatment. However, practical application requires the sufficient and low-cost supply of reducing agents, usually

hydrogen. As mentioned earlier, catalytic treatment unit using stored H₂ gas will likely not be adopted for home use, but its electrolytic production is appropriate. The estimated amount of H₂ needed to treat one cubic meter of nitrate-contaminated water (from 100 to 9 mg-N/L) is 0.33 kg H₂, assuming 100% selectivity to dinitrogen and 10% H₂ utilization efficiency. Its production would cost ~\$1.65 based on electricity priced at ~\$0.08/kWh.¹⁹³ In comparison, a small IX system (serving a community of <500 people) would cost ~\$2.70 to treat the same water to the same treatment goal.⁵² The H₂ production cost is lower than the IX cost, indicating the margin for cost competitiveness for a catalytic water treatment, which would need to accommodate other operations and maintenance costs and capital costs. To further reduce the hydrogen cost, future research should focus on ways to increase hydrogen utilization efficiency, for example, improving hydrogen mass transfer.

The high per-mass cost of the precious metals used in the catalyst material could be of some concern. However, the catalyst itself accounts for only a small fraction of the overall capital cost. A study by Reinhard and co-workers found that the catalyst was ~10% of the total cost of a treatment unit they designed and constructed, which was designed to remove trichloroethene from groundwater using Pd/Al₂O₃.¹⁸⁹ Lowering the metal content or replacing with an earth-abundant catalyst are helpful, though not critical, research goals. Instead, the more important opportunity is to design metal catalysts that perform stably under realistic water conditions and that require less downtime for regeneration. Long-term studies on the operation and effective regeneration of the catalyst are lacking.

To make more informed decisions on whether catalysis could be competitive against the available technologies, catalytic treatment approaches need to incorporate a technoeconomic analysis of capital and operational costs, and a LCA to address their environmental footprint. The LCA work on the combined IX-catalyst nitrate system⁸⁹ and a catalytic perchlorate system¹⁸³ are a promising start.

Conclusions

Metal nanostructures can degrade toxic water-borne oxyanions at ambient conditions in the form of supported precious metal reduction catalysts. The hydrogenation of oxyanions (nitrite/nitrate, chromate, bromate, chlorite and perchlorate) is exergonic ($\Delta G < 0$), but the reaction can be slow without combining the primary metal with a second one. An understanding of the surface reaction mechanisms continues to be needed, especially in water systems (*e.g.*, a drinking water source or spent IX brine) that contain other chemical species besides the target oxyanion. It can lead to more active, selective, and durable catalysts (*e.g.*, what are the appropriate metal particle size and shape, and support composition). Scale-up of catalytic systems will require attention to mass transfer effects associated with the imposition of intraparticle and interparticle transport rules, and engineering and reactor design issues associated with hydrogen gas as the reducing agent.

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