Molybdenum-Catalyzed Perchlorate Reduction: Robustness, Challenges, and Solutions

Changxu Ren,[1,§] Eric Y. Bi,[1,2,§] Jinyu Gao,[1] and Jinyong Liu[1,*]

[1]Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, United States.
[2]Martin Luther King High School, Riverside, CA 92508, United States.

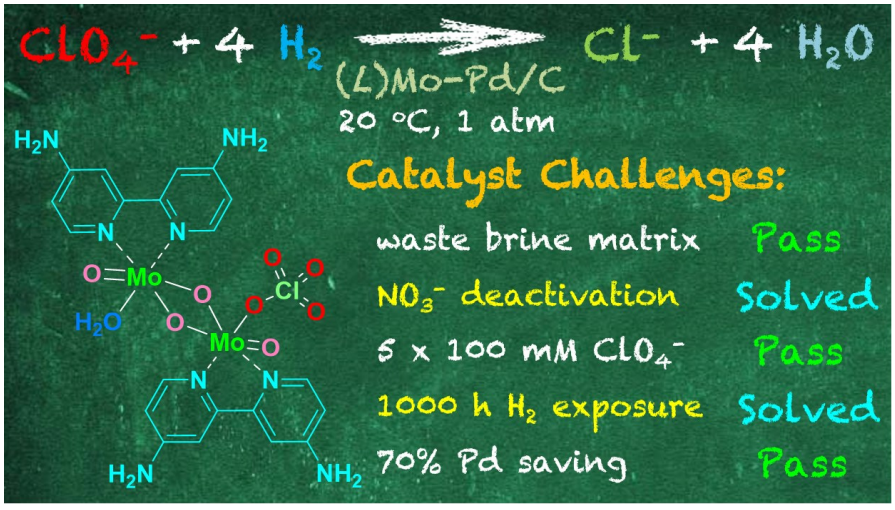
ABSTRACT

We have recently developed a highly active ligand-enabled (*L*)Mo−Pd/C catalyst (*L* = 4,4'-diamino-2,2'-bipyridine) for aqueous perchlorate (ClO_4^-) reduction with 1 atm H_2 at room temperature. This study reports on a series of satisfactory properties of this catalyst closely relevant to ClO_4^- treatment in waste brines resulting from ion-exchange resin regeneration. In the presence of concentrated salts and humic acid, the catalyst experienced limited inhibition but completed ClO_4^- reduction in a few hours with an adjustable loading between 0.2 and 2 g/L. The catalyst was not deactivated by the high oxidative stress from multiple spikes of 100 mM ClO_4^-. The challenge of deactivation by nitrate was solved by pretreating the brine with In−Pd/Al_2O_3. The loss of activity upon ligand hydrogenation was overcome by regenerating the Pd/C at pH 12. We also optimized the catalyst formulation and saved 70% of Pd without sacrificing the activity. The substantially enhanced performance and lowered adverse environmental impacts of (*L*)Mo−Pd/C make the catalytic treatment competitive to microbial reactors for ClO_4^- reduction. We showcase the power of coordination chemistry in environmental technology innovation and expect this catalyst to promote the reuse of ClO_4^--selective resins for sustainable water treatment.

KEYWORDS

palladium; brine; regeneration; deactivation; ion-exchange

TOC



INTRODUCTION

The excess uptake of perchlorate (ClO_4^-) through contaminated water and food can disrupt thyroid hormone production, which is critical for the growth, development, metabolism, and mental function of humans.[1] In the United States, California[2] and Massachusetts[3] set the maximum contamination level for ClO_4^- in drinking water at 6 and 2 μg/L, respectively. In China, the proposed 2021 revision of the National Standards for Drinking Water Quality included ClO_4^- at 70 μg/L.[4] With the improved understanding of ClO_4^- toxicity[5] and the discovery of ClO_4^- on Mars,[6] the remediation of ClO_4^- contamination is an imperative research topic for environmental engineering[7-9] and space explorations.[10-11]

Although ion-exchange (IX) resins can readily remove ClO_4^- from water,[12] achieving a rapid reduction of enriched ClO_4^- has been a challenge for over two decades. Microbial reactors can take days to weeks to stabilize the function of ClO_4^- reduction,[13-14] and most abiotic methods require harsh conditions and a large excess of reducing agents.[15-19] The use of rhenium (Re) for ClO_4^- activation together with palladium (Pd) for H_2 activation (Re−Pd/C) realized rapid and complete reduction of ClO_4^- into Cl^- at ambient conditions.[20-25] Recently, we have replaced Re with a highly reactive molybdenum (Mo) species, which was formed *in situ* from a common fertilizer, Na_2MoO_4, and a common bipyridine ligand (*L*) (Figure 1).[26] In comparison to Re−Pd/C catalysts, the new (*L*)Mo−Pd/C shows even higher activity, does not involve specialized preparation procedures and is not deactivated by air exposure.[26] Spectroscopic evidence suggested a dimeric structure of the surface-immobilized Mo site, with each Mo coordinating with an *N,N*-bidentate ligand.[26] The coordination of Mo with the electron-rich ligand enables the rapid reaction with highly inert ClO_4^- via oxygen atom transfer to the reduced Mo^{IV} site:

$$ClO_x^- + (L)Mo^{IV}(O) \rightarrow (L)Mo^{VI}(O)_2 + ClO_{x-1}^-$$

The oxidized Mo^{VI} is then reduced back to Mo^{IV} by Pd-catalyzed hydrogenation:

$$(L)Mo^{VI}(O)_2 + H_2 \rightarrow (L)Mo^{IV}(O) + H_2O$$

The overall reaction is the complete and clean reduction of ClO_4^- :

$$ClO_4^- + 4\ H_2 \rightarrow\ Cl^- + 4\ H_2O$$

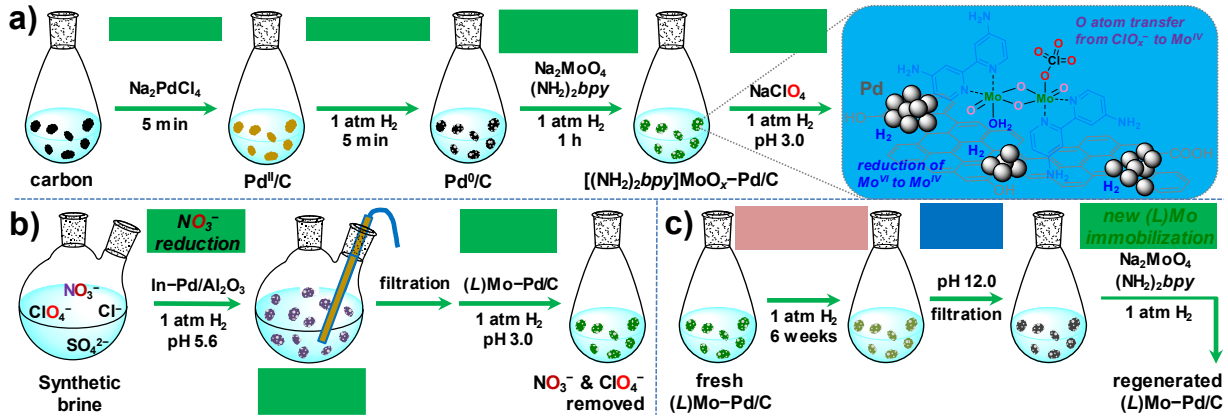


Figure 1. Illustrated experimental procedures for **(a)** preparation of (*L*)Mo−Pd/C with adjustable Pd and Mo contents, **(b)** sequential reduction of NO_3^- by In−Pd/Al_2O_3 and ClO_4^- by (*L*)Mo−Pd/C, and **(c)** hydrogenation deactivation and regeneration of (*L*)Mo−Pd/C.

To promptly transfer the exciting invention into engineering solutions, herein we report on systematic evaluation and improvement of the (*L*)Mo−Pd/C catalyst in terms of various conventional and novel properties closely relevant to practical applications, including i) performance in water matrices of concentrated salts and natural organics, ii) longevity in challenging and continuous oxidative and reducing environments, and iii) cost-effectiveness optimized through catalyst formulation. In particular, we provide viable solutions to catalyst deactivation challenges. The results will guide the application of this catalyst and exemplify lab-scale evaluations of new water treatment catalysts.

MATERIALS AND METHODS

Chemicals and Materials. Na_2MoO_4•$2H_2O$ (≥99%), Na_2PdCl_4 (98%), and humic acid were purchased from Sigma−Aldrich. The ligand 4,4'-diamino-2,2'-bipyridine ($(NH_2)_2$*bpy*, >98%) was purchased from TCI America. $NaClO_4$, NaCl, Na_2SO_4, NaH_2PO_4, $NaNO_3$, NH_4Cl, and NaOH in ≥99% purities were purchased from Fisher Chemical. Ultrahigh purity (99.999%) H_2 gas was purchased from Airgas. The standard 2 N sulfuric acid solution was purchase from Alfa Aesar. All chemicals were used as received. Aqueous solutions were prepared with deionized (DI) water (resistivity >18.2 MΩ cm). The carbon support was purchased from Alfa Aesar (Norit GSX; steam activated and acid-washed; surface area 1300 m^2/g) and used as received.

Preparation and Use of (*L*)Mo−Pd/C Catalyst. In this study, we prepared the catalyst with various formulations from pristine activated carbon, Pd^{II} and Mo^{VI} precursors, and free ligand (Figure 1a). The first step followed our previously developed *in situ* method to prepare Pd/C.[27] The amounts of carbon and Pd are adjustable based on the specific catalyst powder loading in water (0.2−2.0 g/L) and the specific Pd content in the catalyst (0.1−5.0 wt%). In a 50-mL flask, activated carbon powder was added to 50 mL of DI water. The flask was capped with a rubber stopper, and the mixture was sonicated for 1 min. Under magnetic stirring, Na_2PdCl_4 solution was added dropwise into the carbon suspension. Stirring for another 5 min was sufficient for Pd^{II} immobilization onto carbon support. H_2 gas was supplied through a 16-gauge stainless steel needle. Another needle was used as the gas outlet so that the H_2 pressure in the flask was maintained at 1 atm. The exposure to H_2 for 5 min was sufficient to reduce all Pd^{II} into Pd^0 nanoparticles.[27] The resulting Pd/C catalyst could be either immediately added with Mo or filtered and dried under vacuum for future use. In the second step, stock solutions of Na_2MoO_4 and $(NH_2)_2$*bpy* were sequentially added in the Pd/C suspension. The solution pH was adjusted to 3.0 using 2N H_2SO_4. The amount of Mo is adjustable for specific Mo content in the catalyst (0.5−5.0 wt%), whereas the molar ratio of *L*:Mo was kept at 1:1. The following exposure to 1 atm H_2 for 1 h afforded the final (*L*)Mo−Pd/C catalyst.[26] The addition of $NaClO_4$ (1−100 mM) initiated the catalytic reduction at room temperature (20 °C). Aliquots were collected intermittently from the gas outlet needle and immediately filtered by 0.22-μm cellulose acetate membrane to quench reactions.

Perchlorate Reduction in the Synthetic Brine. After (*L*)Mo−Pd/C was prepared, solid salts were added to the catalyst suspension following the composition of a previously studied waste brine (Table 1) collected from a Californian water treatment plant using a regenerable ion-exchange system.[21] Because the reduction of NO_3^- consumes H^+:[21]

$$NO_3^- + 2.5\ H_2 + H^+ \rightarrow 0.5\ N_2 + 3\ H_2O$$

$$NO_3^- + 4\ H_2 + 2\ H^+ \rightarrow\ NH_4^+ + 3\ H_2O$$

a 50-mL double-neck flask was used to monitor and maintain the solution pH during the reaction. Both necks were capped with rubber stoppers, one of which accommodated a Fisherbrand accumet gel-filled pencil-thin pH combination electrode (Figure 1b). The other stopper accommodated the two stainless needles for H_2 supply and sampling. H_2SO_4 (0.1 M) was added through the sampling needle to adjust the pH back to the working range for the catalyst (3.0 ± 0.1).

Table 1. Composition of the Synthetic IX Regenerant Brine

component[a]	concentration
chloride	0.9 M (32.3 g/L as Cl^-, ~5 wt% NaCl)
perchlorate	1 mM (100 mg/L as ClO_4^-)[b]
nitrate	38 mM (2.36 g/L as NO_3^-)
sulfate	48 mM (4.70 g/L as SO_4^{2-})
phosphate	0.22 mM (20.9 mg/L as PO_4^{3-})

[a] Na^+ was the only cation introduced with the above anionic species because K^+, Ca^{2+}, and Mg^{2+} (taking a small portion of total cations in the real brine) did not significantly impact reaction kinetics.[24] Although present in the real waste brine, carbonate was not added to the synthetic brine because it was fully removed as CO_2 bubbles during pH adjustment to 3.0.[21]

[b] The ClO_4^- concentration in the real brine was 0.02 mM (~2 mg L^{-1} as ClO_4^-) because the IX resin was not perchlorate-selective. We increased the concentration to 1 mM for (i) ensuring the accuracy of ClO_4^- quantitation in the concentrated salt matrix, (ii) comparing the catalyst performance with most experiments that used 1 mM ClO_4^- as the probe. The catalyst is capable of reducing as low as 0.01 mM (~1 mg/L) ClO_4^- by >99% (i.e., <10 μg/L in the treated water).[26]

Preparation and Use of In−Pd/Al_2O_3 Catalyst. A 5 wt % Pd on γ-Al_2O_3 (Pd/Al_2O_3) catalyst and $InCl_3$ (98%) were purchased from Sigma−Aldrich and used as received. The $InCl_3$ was dissolved in ethanol and added in Pd/Al_2O_3 via incipient wetness following a reported method.[28] The solid was dried in air at 120 °C for 4 h and reduced with H_2 for 12 h. Then the catalyst was collected and used at 2 g/L to reduce NO_3^- in the synthetic brine. Due to the scope of this work, the preparation and formulation of In−Pd/Al_2O_3 were not further optimized. The pH monitoring and adjustment during NO_3^- reduction (5.6±0.2) followed the same reactor configuration as described above. After NO_3^- reduction was complete, In−Pd/Al_2O_3 was filtered out, and the treated brine was added with 0.2 g/L of (*L*)Mo−Pd/C to reduce ClO_4^- (Figure 1b).

Aqueous Sample Analysis. The concentrations of ClO_4^- and NO_3^- were measured on an ion chromatography (Dionex ICS-5000) with a conductivity detector and 25 μL sample loop. The best separation of ClO_4^- from other anions was achieved by using a Dionex IonPac AS16 analytical column at 30 °C with 1 mL/min of 65 mM KOH eluent. A Dionex IonPac AS 19 analytical column was used to separate NO_3^-. 20 mM KOH eluent was used to achieve the best separation. The concentration of Mo in aqueous samples was analyzed by inductively coupled plasma−mass spectrometry (ICP−MS, Agilent 7700). The concentration of the free $(NH_2)_2$*bpy* ligand was quantified by high-performance liquid chromatography (Shimadzu Nexera XR) with a photodiode array detector.

Catalyst Collection and Elemental Analyses. The catalyst powders, either freshly prepared or used after reactions, were collected by vacuum filtration through a ceramic funnel covered with Whatman qualitative filter paper. The filter paper was transferred into a 20-mL scintillation vial and dried in an oven at 70 °C to remove moisture. The contents of Mo, Pd, C, H, and N in the catalyst powders were determined by inductively coupled plasma−optical emission spectrometry (ICP−OES, PerkinElmer Optima 8300) after microwave digestion in HNO_3−H_2O_2 (performed by the Microanalysis Laboratory at the University of Illinois at Urbana-Champaign).

Regeneration of (*L*)Mo−Pd/C Catalyst. This set of procedures is illustrated in Figure 1c. After the catalyst was deactivated by hydrogenation, the pH of the water suspension was adjusted to 12.0 with NaOH. The suspension was stirred for 10 min and filtered under vacuum. The collected solid was redispersed in DI water and added with new stock solutions of Na_2MoO_4 and $(NH_2)_2$*bpy* to regenerate the (*L*)Mo−Pd/C following the procedures described above.

RESULTS AND DISCUSSION

Catalyst Performance for Brine Treatment. We prioritize the evaluation of (*L*)Mo−Pd/C by assessing its performance in a practical scenario: ClO_4^- reduction in a waste brine resulting from IX resin regeneration. Further assessment and development will be meaningful only if the catalyst can demonstrate satisfactory activity under challenging conditions. We prepared the synthetic brine containing all anion constituents in a previously studied brine (Table 1). Because early IX resins were not highly selective for ClO_4^-, the waste brines produced from resin regeneration typically contained sulfate, nitrate, and even phosphate at orders of magnitude higher concentrations than ClO_4^-.[21,29-31] We added 1 mM ClO_4^- in the synthetic brine (Table 1, footnote b). The ClO_4^- reduction was conducted at the optimized pH of 3.0, and the complete conversion into Cl^- has been confirmed.[26] Most abiotic ClO_4^- reduction systems require H^+ to enable oxygen atom transfer (OAT) in the aqueous phase.[18,20-26,32-35]

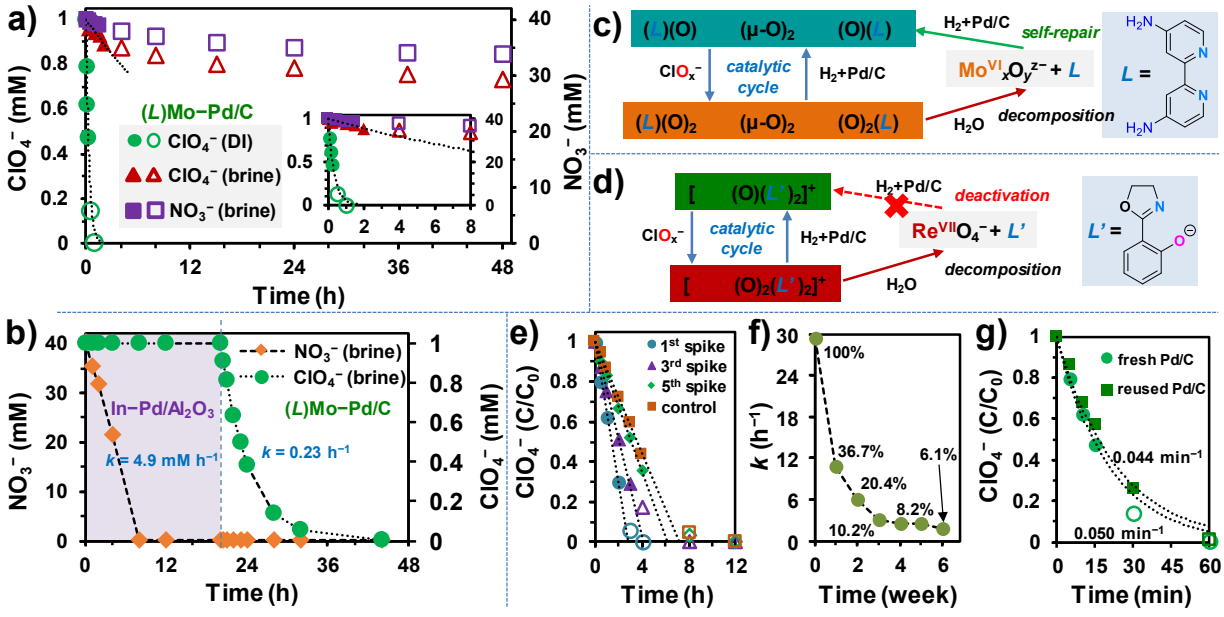


Figure 2. Degradation of ClO_4^- and NO_3^- in the synthetic brine by **(a)** (*L*)Mo−Pd/C only and **(b)** sequential application of In−Pd/Al_2O_3 (2 g/L at pH 5.6) and (*L*)Mo−Pd/C; mechanistic schemes for **(c)** self-repair of (*L*)Mo−Pd/C and **(d)** deactivation of (*L'*)$_2$Re−Pd/C caused by concentrated ClO_4^-; **(e)** reduction of continuous spikes of 100 mM ClO_4^- by 2 g/L of (*L*)Mo−Pd/C; **(f)** the decrease of ClO_4^- reduction rate constants after continuous H_2 exposure; and **(g)** ClO_4^- reduction by (*L*)Mo−Pd/C prepared from reused Pd/C after treatment at pH 12. Default reaction conditions: 0.2 g/L of (*L*)Mo−Pd/C (5 wt% Mo, 5 wt% Pd), pH 3.0, 1 atm H_2, 20 °C. In panels **a**, **e**, and **g**, filled symbols were used to fit the 1st- or 0th-order model, whereas hollow ones were either not appropriate for fitting (i.e., $C/C_0 < 0.2$) or indicating the deviation from models.

In comparison to the performance in deionized (DI) water (i.e., no concentrated brine constituents added), the synthetic brine matrix substantially retarded ClO_4^- reduction (Figure 2a).

During the relatively fast reaction in the first 2 h, the barely fit first-order rate constant was only 1.9% of that observed in DI water (Table 2 entry 5 versus 1). The gradually flattened kinetics suggested catalyst deactivation (i.e., loss of intrinsic activity). The simultaneous reduction of NO_3^- in the synthetic brine followed a similar trend (Figure 2a). To identify the deactivating species, we examined the effect of individual constituents on ClO_4^- reduction. In comparison to the DI water control, the addition of 80 mM $H_2PO_4^-$, 1 M SO_4^{2-}, and 1 M Cl^- lowered the rate constant by 37%, 64%, and 86%, respectively (Table 2 entries 2−4 versus 1). However, these anions merely caused inhibition (i.e., decrease of reaction rate by reaction site competition) rather than deactivation. First, the ClO_4^- reduction followed the 1st-order kinetics well (Figure S1). The most inhibited catalyst in 1 M NaCl still achieved >99.5% ClO_4^- reduction within 15 h (Figure S2). Second, recycling the catalyst from the previous use in 80 mM NaH_2PO_4, 1 M Na_2SO_4, or 1 M NaCl by filtration fully restored the activity (Figure S3). Although the catalyst was significantly inhibited by concentrated Cl^-, increasing the catalyst loading from 0.2 g/L to 2.0 g/L achieved >99.99% ClO_4^- reduction within 1 h (Figure S4). Notably, the activity was >13 times higher than that of the previously developed salt-resistant ReO_x−Pd/C (Table 2 entry 4 versus 8 and 9).[21]

Table 2. Rate Constants for ClO_4^- Reduction by Mo and Re Catalysts

entry	other constituents in the solution	k (L h^{-1} g_{cat}^{-1}) [a]
	[$(NH_2)_2$*bpy*]MoO_x−Pd/C (5 wt% Mo, 5 wt% Pd)	
1	DI [b]	14.83 ± 0.37
2	80 mM NaH_2PO_4	12.26 ± 0.81
3	1 M Na_2SO_4	5.47 ± 0.23
4	1 M NaCl	2.19 ± 0.14
5	synthetic waste brine (see Table 1)	0.25 ± 0.04
6	synthetic waste brine without NO_3^-	2.12 ± 0.16
7	40 mM NH_4Cl	9.88 ± 0.39
	ReO_x−Pd/C (5 wt% Re, 5 wt% Pd)	
8	DI [b]	0.047 ± 0.003 [c]
9	1 M NaCl	0.16 ± 0.01 [c]
10	synthetic waste brine (see Table 1)	0.0079 ± 0.0003 [c]
11	synthetic waste brine without NO_3^-	0.18 ± 0.01 [c]

[a] Apparent first-order rate constants (h^{-1}) for 1 mM ClO_4^- reduction (pH 3.0, 1 atm H_2, 20 °C) normalized by the loading of catalyst powder in water (g_{cat} L^{-1}) to facilitate cross-comparison. The loading of Mo- and Re-based catalysts used in experiments were 0.2 and 2.0 g/L, respectively.

[b] Containing ~1 mM H_2SO_4 (for pH adjustment to 3.0) and cations introduced with Na_2MoO_4 or $KReO_4$ precursor.

[c] Data reported in Ref 21.

Hence, NO_3^- was the only remaining suspect for catalyst deactivation. We prepared a new synthetic brine that only excluded NO_3^-. In this brine, the ClO_4^- reduction profile resembled that in 1 M NaCl (Figure S2, Table 2 entry 4 versus 6), confirming that NO_3^- is responsible for catalyst deactivation. The slight inhibition in the presence of 40 mM NH_4Cl (assuming complete reduction of NO_3^- into NH_4^+)[36] is primarily attributed to Cl^- (Table 2 entry 7 versus 1 and 4) rather than NH_4^+. In a separate experiment, we used (*L*)Mo−Pd/C to first treat 40 mM NO_3^- for 48 h. The water-rinsed catalyst only retained 11% of the original activity for ClO_4^- reduction (Figure S5). Because Pd-based catalysts integrating In, Cu, or Sn as the second metal have shown excellent NO_3^- reduction activities,[37] the severe deactivation of (*L*)Mo−Pd/C is attributed to the reaction

between NO_3^- (or intermediates such as NO_2^-, NO, and N_2O) with the (*L*)Mo site rather than with Pd. Inorganic chemistry studies using molecular Mo species for NO_3^- reduction have observed inhibition by those nitrogen intermediates.[38-39] Similar deactivation of the Re site has been observed from the ReO_x−Pd/C catalyst.[21] While deeper mechanistic insights into the deactivation phenomenon warrant further investigation, in this study, we prioritize the research effort as solving this challenge by preventing NO_3^- from reacting with the Mo catalytic site.

The Solution to Catalyst Deactivation by Nitrate. We proposed a two-stage treatment to protect (*L*)Mo−Pd/C from reacting with NO_3^- (Figure 1b). In the first stage, NO_3^- in the synthetic brine was reduced with a well-established In−Pd/Al_2O_3 catalyst.[40] Similar to the previous report,[21] 2 g/L of In−Pd/Al_2O_3 reduced >99.98% of the 38 mM of NO_3^- within 8 h (Figure 2b) with a <30% product selectivity toward NH_4^+, whereas no ClO_4^- reduction was observed. Then we filtered out In−Pd/Al_2O_3 and added 0.2 g/L of (*L*)Mo−Pd/C into the nitrate-removed brine. As expected, the reduction of 1 mM ClO_4^- proceeded rapidly and achieved 99.9% reduction within 24 h. The (*L*)Mo−Pd/C showed the highest ClO_4^- reduction activity in both DI water and brine among the hydrogenation catalysts studied to date (Table S1).

Catalyst Stability against Oxidative Stress. After solving the nitrate deactivation challenge, we evaluated the stability of (*L*)Mo−Pd/C during the treatment of concentrated ClO_4^-. The regeneration of ClO_4^--selective resins can produce highly concentrated ClO_4^- up to 10 g/L (~100 mM) within one bed volume of waste brine.[12,15] Although ClO_4^- is highly inert, the ClO_x^- intermediates are much more reactive with the (*L*)Mo site,[34] where the ligand carries two strong electron-donating $-NH_2$ groups. For Re−Pd/C catalysts prepared from presynthesized $[Re^{V}(O)(L')_2]^+$ (*L'*=various oxazoline-phenolate ligands) as the active site, concentrated ClO_x^- could cause the accumulation of $[Re^{VII}(O)_2(L')_2]^+$ and irreversible decomposition into ReO_4^- and free *L'* (i.e., deactivation, Figure 2d).[24-25] In contrast, the active $[(L)(O)Mo^{IV}]_2(\mu\text{-}O)_2$ site in (*L*)Mo−Pd/C is prepared *in situ* from inorganic molybdate and free $(NH_2)_2$*bpy* ligand. If similar hydrolysis of oxidized $[(L)(O)Mo^{VI}]_2(\mu\text{-}O)_2$ occurs, the products would be the starting materials, allowing the active site to form again (i.e., self-repair, Figure 2c). To verify this hypothesis, we challenged (*L*)Mo−Pd/C with five spikes of 100 mM ClO_4^-. The reduction of the fifth ClO_4^- spike was not slower than the control, where the fresh (*L*)Mo−Pd/C reduced 100 mM ClO_4^- in the presence of 400 mM Cl^- (Figure 2e and Table S2). Therefore, the gradual activity loss is attributed to the accumulation of Cl^- from ClO_4^- reduction. After five spikes, each (*L*)Mo site had undergone 1,920 redox turnovers without deactivation. Notably, the removal of 100 mM ClO_4^- reached >99.99%, more effective than the previously reported thermal treatment (92−98%).[12]

Catalyst Longevity under Reducing Atmosphere. It has been well documented that pyridine structures are susceptible to Pd^0-catalyzed hydrogenation, and those with electron-donating substitutions (e.g., $-NH_2$) have the lowest reactivity.[41-42] To evaluate the catalyst longevity under extended hydrogenating conditions, we exposed the water suspension of (*L*)Mo−Pd/C to 1 atm H_2 atmosphere for up to 1000 h (6 weeks, Figure 1c). The rate constants for ClO_4^- reduction decreased exponentially by 90% in the first three weeks (0.113 day^{-1}, Figure 2f and Figure S6). The activity loss in weeks 4−6 was less pronounced and remained at 6% of the original activity after 1000 h. We attribute the rapid activity decrease to the hydrogenation of pyridyl rings in Mo-coordinated $(NH_2)_2$*bpy*. After that, the hydrogenation product still coordinated with Mo and enabled ClO_4^- reduction to a limited extent. This interpretation is supported by the limited ClO_4^- reduction activity using selected aliphatic diamine ligands and no activity without using any organic ligand.[26]

Elemental analyses of solid catalysts found that long-term exposure to H_2 caused roughly 20% and 50% loss of Mo and N, respectively (Table 3 entry 4 versus 2). In comparison, the redox transformation during ClO_4^- reduction is not the cause for the leaching (Table 3 entry 3). In general, aliphatic amines have 5−6 units higher p*K*a values than pyridines (i.e., much more prone to be protonated). The hydrogenation of pyridyl structures might also eliminate the π-π stacking interaction with carbon support and thus enhance dissolution. The original $(NH_2)_2$*bpy* ligand was not detected in the water. In contrast, the Pd content did not significantly change in the solid, and ICP−MS analysis detected up to 0.01% of the total Pd dissolved in various water samples. Such stability is as expected because solid-state Pd^0 can be readily maintained under H_2 atmosphere.[27]

Table 3. Elemental Analyses of Solid Catalysts (Unit: Weight Percentage, wt%)

entry	Sample	Pd	Mo	Pd:Mo[b]	C	H	N
1	Pd/C without Mo[a]	3.86	0.01	-	83.61	1.14	0.52
2	fresh (*L*)Mo−Pd/C[a]	3.25	3.58	0.91:1	77.92	1.24	2.82
3	used (*L*)Mo−Pd/C after 1 mM ClO_4^- treatment	3.09	3.23	0.96:1	77.30	1.24	2.74
4	after 6-week exposure under 1 atm H_2	3.30	2.95	1.12:1	79.14	1.03	1.37
5	after regeneration at pH 12	3.53[c]	0.03	-	83.41	1.29	2.04

[a]Pd/C and (*L*)Mo−Pd/C had the nominal 5 wt% loadings for both Pd and Mo.

[b]Because elemental analyses of solid samples always have deviations and can be significantly impacted by the addition of other constituents in the solid, the ratio between the two metals is a more meaningful indicator of metal leaching than the absolute weight percentage of each metal. Recall that Pd leaching is minimal under the H_2 atmosphere.[27]

[c]For the same reason as footnote b, this value is slightly lower than that in the original Pd/C (3.86% for Pd and 0.52 for % N) because of the residual N (2.04%).

Catalyst Regeneration after Ligand Hydrogenation. The above findings suggest that the loss of the most precious component, Pd, is minimal. To restore the catalyst activity, we investigated the regeneration of Pd/C platform by removing Mo and hydrogenated ligand residues. Inspired by an early study on molybdate desorption from carbon,[43] we elevated the pH to 12 under air and achieved quantitative dissolution of Mo within 10 min (Figure S7). Elemental analysis of the solid confirmed the complete removal of Mo but incomplete removal of N-containing residues (Table 3 entry 5 versus 1). After adding fresh Na_2MoO_4 and $(NH_2)_2$*bpy* to the regenerated Pd/C (Figure 1c), the "refurbished" (*L*)Mo−Pd/C showed only slightly diminished activity (Figure 2g), probably due to the N-containing residues left on the carbon support. Hence, after several rounds of such regeneration, a complete recovery of Pd via chemical extractions[44-46] could be necessary.

Optimization of Catalyst Formulation. To further reduce the use of Pd and maximize cost-effectiveness, we examined the effect of variable Pd and Mo contents on ClO_4^- reduction activity. Our recently developed method enables "instant" preparation of Pd/C with any metal content and significantly reduces the technical efforts for fine-tuning the metal contents.[27] With the Mo content fixed at 5 wt%, the decrease of Pd content by 90% (i.e., from 5 to 0.5 wt%) only lowered the rate constant by 71% (Figure 3a and Figure S8a), suggesting the feasibility of using less Pd to achieve the same catalytic activity at an increased loading of catalyst.[27] However, if the Mo content is kept at 5 wt%, the increased catalyst loading will involve more Mo and ligand. Interestingly, after the Pd content was lowered to 0.5 wt%, the initially optimized 5 wt% of Mo (using 5 wt% Pd/C)[26] became excessive, and 3 wt% was found to be the optimal content (Figure 3b and Figure S8b). The tripled loading of 3 wt% Mo−0.5 wt% Pd/C exhibited the same rate of ClO_4^- reduction as the original 5 wt% Mo−5 wt% Pd/C (Figure 3c). Hence, the new formulation

involved a tripled amount of carbon and 80% more (*L*)Mo but saved 70% of Pd, the most expensive component.

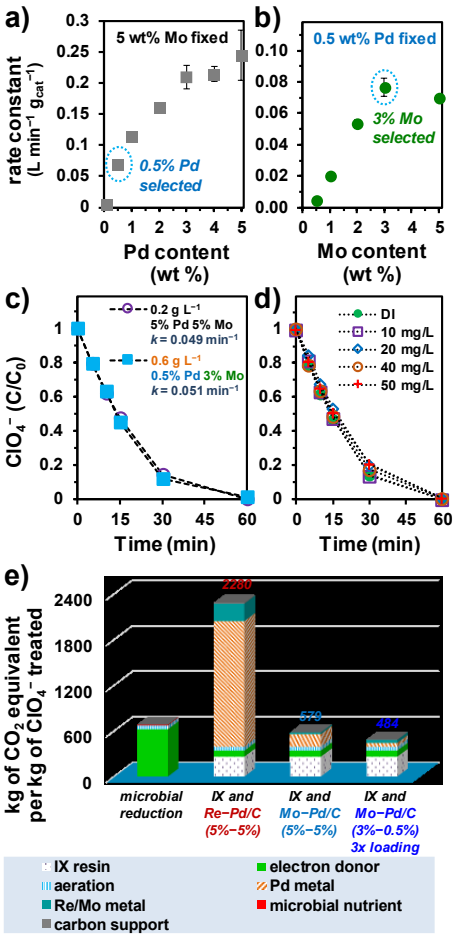


Figure 3. Optimization of **(a)** Pd and **(b)** Mo content in the (*L*)Mo−Pd/C catalyst, and the ClO_4^- reduction performance **(c)** with two catalyst formulations and **(d)** in the presence of 10−50 mg/L humic acid (0.2 g/L, 5 wt% Mo and 5 wt% Pd). Common reaction conditions: 1 mM ClO_4^-, pH 3.0, 1 atm H_2, and 20 °C. Panel **e** shows the comparison of "global warming" impacts by microbial reduction and sequential IX-catalysis treatment based on the data in a previous LCA study.[47]

A life cycle assessment (LCA) study comparing microbial and catalytic (using ReO_x−Pd/C) reduction of ClO_4^- found that the mining and refining of Pd and Re contributed to the majority of adverse environmental impacts.[47] Because Re is a minor component in Mo minerals, we assume that the adverse impacts from Mo are not higher than from Re. The activity of (*L*)Mo−Pd/C is 290- and 10-fold higher than ReO_x−Pd/C in DI water and NO_3^--free synthetic brine, respectively (Table 2). Furthermore, catalyst optimization has saved 70% Pd to achieve the same activity. Based on all of these advancements, the environmental impacts from Pd can be reduced by at least 970 and 33 folds for use in DI water and brine, respectively. With the same LCA metrics and 33-fold decrease of Pd consumption, the new catalytic ClO_4^- reduction module using (*L*)Mo−Pd/C coupled with ion-exchange resin has become comparable to microbial reduction (Figure 3e and Text S1).

Implications to Perchlorate Treatment. The above results showcase a highly active, robust, and cost-effective heterogeneous catalyst for ClO_4^- reduction. Regarding practical

application, it is essential to highlight four technical points. First, the treatment of resin regeneration waste is separated from the drinking water treatment loop. Any concern of the non-neutral pH and minimal leaching of Mo and ligand in the treated brine can be further addressed if necessary. More importantly, cost-effective degradation of concentrated pollutants will advance drinking water treatment technologies by allowing sustainable reuse of ClO_4^--selective IX resins instead of incineration.[12,48-49] Highly selective resins do not require frequent regeneration; thus, a continuous operation for ClO_4^- reduction may not be needed, alleviating catalyst deactivation caused by ligand hydrogenation and allowing the use of a batch reactor configuration. In such cases, abiotic catalysts also have unique advantages over microbial reactors, which usually require continuous operation. The U.S. EPA has included Mo on the Third Unregulated Contaminant Monitoring Rule (UCMR-3) with the minimum reporting level of 1 μg/L in drinking water.[50] If the treated brine is recycled for resin regeneration, further studies are warranted to evaluate the potential transfer of leached Mo from waste brine treatment to drinking water. Second, the use of H_2 gas for reductive pollutant degradation has been widely adopted in environmental engineering projects.[51-56] Third, inorganic sulfide, a potent Pd poison that may be present in the wastes, can be instantly oxidized into inert SO_4^{2-} using common oxidants[57] to avoid catalyst fouling. Fourth, although dissolved organics might not be significant constituents in the waste brine,[21] our data show that 10−50 mg/L of humic acid did not inhibit the (*L*)Mo−Pd/C catalyst (Figure 3d). Although humic acid is a well-known inhibitor to Pd catalysts,[37] it appears that the $(NH_2)_2$*bpy*-coordinated Mo sites are not sensitive to external ligands (e.g., the carboxylate groups in humic acid) and thus preserved the overall activity of (*L*)Mo−Pd/C. We will continue the study on the treatment of waste brines from the regeneration of perchlorate-selective resins. The brine has been reported to contain concentrated ClO_4^- (~100 mM) and $[FeCl_4]^-$ (from 1 M $FeCl_3$ and 4 M HCl).[12] Natural organic matters released from the resin are also expected to be abundant due to the long enrichment for six months. We will report unexpected case-specific challenges and technical solutions from pilot-scale testings of the (*L*)Mo−Pd/C catalyst used for the regeneration of perchlorate-selective resins.

Implications to Catalyst Development. The (*L*)Mo site is generated *in situ* via non-covalent Mo−N bonding and immobilized on carbon support via non-covalent interactions. The structure is also subject to decomposition upon dissolution[26] or significant pH adjustment from 3 to 12. However, under optimized conditions, the (*L*)Mo−Pd/C catalyst exhibits satisfactory performance in various parameters regarding practical applications, including unprecedentedly high activity for ClO_4^- reduction and resistance to oxidative stress. Moreover, the dynamic property of the (*L*)Mo complex also enables facile catalyst regeneration. Besides our continuous research efforts for Re-based catalysts,[25,58-60] this study highlights the value of coordination metal complexes for environmental technology innovation aiming at practical engineering treatment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsestengg.xxxxxxx.

Kinetic profiles of perchlorate and nitrate reduction under various conditions; the comparison with Re-based catalysts; details for the estimation of environmental impact values.

AUTHOR INFORMATION

[§]These authors contributed equally.

Corresponding Author
*(J.L.) E-mail: jyliu@engr.ucr.edu; jinyong.liu101@gmail.com.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support was provided by the National Science Foundation (Award No. CBET-1932942).

REFERENCES

1. Greer, M. A.; Goodman, G.; Pleus, R. C.; Greer, S. E. Health effects assessment for environmental perchlorate contamination: The dose response for inhibition of thyroidal radioiodine uptake in humans. *Environ. Health Perspect.* **2002**, *110*, 927-937.

2. California State Water Resources Control Board: Perchlorate in Drinking Water. https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.html (accessed 2021-09-29).

3. Massachusetts Department of Environmental Protection: Perchlorate Background Information and Standards. https://www.mass.gov/lists/perchlorate-background-information-and-standards#perchlorate---final-standards- (accessed 2021-09-29).

4. National Standard of the People's Republic of China: GB 5749-XXXX (to replace GB 5749-2006) Standards for Drinking Water Quality. **2021**, http://www.cuwa.org.cn/Uploads/file/20210715/20210715225950_71443.pdf (accessed 2021-09-29).

5. Llorente-Esteban, A.; Manville, R. W.; Reyna-Neyra, A.; Abbott, G. W.; Amzel, L. M.; Carrasco, N. Allosteric regulation of mammalian Na^+/I^- symporter activity by perchlorate. *Nat. Struct. Mol. Biol.* **2020**, 27, 533-539.

6. Hecht, M.; Kounaves, S.; Quinn, R.; West, S.; Young, S.; Ming, D.; Catling, D.; Clark, B.; Boynton, W. V.; Hoffman, J. Detection of perchlorate and the soluble chemistry of martian soil at the Phoenix lander site. *Science* **2009**, *325*, 64-67.

7. Hatzinger, P. B. Perchlorate biodegradation for water treatment. *Environ. Sci. Technol.* **2005**, *39*, 239A-247A.

8. Khera, R.; Ransom, P.; Guttridge, M.; Speth, T. F. Estimating costs for nitrate and perchlorate treatment for small drinking water systems. *AWWA Water Sci.* **2021**, *3*, e1224.

9. United States Environmental Protection Agency: Perchlorate in Drinking Water. https://www.epa.gov/sdwa/perchlorate-drinking-water (accessed 2021-08-01).

10. Davila, A. F.; Willson, D.; Coates, J. D.; McKay, C. P. Perchlorate on Mars: A chemical hazard and a resource for humans. *Int. J. Astrobiol.* **2013**, *12*, 321-325..

11. Schuttlefield, J. D.; Sambur, J. B.; Gelwicks, M.; Eggleston, C. M.; Parkinson, B. Photooxidation of chloride by oxide minerals: Implications for perchlorate on Mars. *J. Am. Chem. Soc.* **2011**, *133*, 17521-17523.

12. Gu, B.; Brown, G. M.; Chiang, C.-C. Treatment of perchlorate-contaminated groundwater using highly selective, regenerable ion-exchange technologies. *Environ. Sci. Technol.* **2007**, *41*, 6277-6282.

13. Coates, J. D.; Achenbach, L. A. Microbial perchlorate reduction: Rocket-fuelled metabolism. *Nat. Rev. Microbiol.* **2004**, *2*, 569-580.

14. Lai, C.-Y.; Wu, M.; Lu, X.; Wang, Y.; Yuan, Z.; Guo, J. Microbial perchlorate reduction driven by ethane and propane. *Environ. Sci. Technol.* **2021**, *55*, 2006-2015.

15. Gu, B.; Dong, W.; Brown, G. M.; Cole, D. R. Complete degradation of perchlorate in ferric chloride and hydrochloric acid under controlled temperature and pressure. *Environ. Sci. Technol.* **2003**, *37*, 2291-2295.

16. Cao, J.; Elliott, D.; Zhang, W.-x. Perchlorate reduction by nanoscale iron particles. *J. Nanopart. Res.* **2005**, *7*, 499-506.

17. Xiong, Z.; Zhao, D.; Pan, G. Rapid and complete destruction of perchlorate in water and ion-exchange brine using stabilized zero-valent iron nanoparticles. *Water Res.* **2007**, *41*, 3497-3505.

18. Wang, C.; Huang, Z.; Lippincott, L.; Meng, X. Rapid Ti(III) reduction of perchlorate in the presence of β-alanine: Kinetics, pH effect, complex formation, and β-alanine effect. *J. Hazard. Mater.* **2010**, *175*, 159-164.

19. Hori, H.; Sakamoto, T.; Tanabe, T.; Kasuya, M.; Chino, A.; Wu, Q.; Kannan, K. Metal-induced decomposition of perchlorate in pressurized hot water. *Chemosphere* **2012**, *89*, 737-742.

20. Hurley, K. D.; Shapley, J. R. Efficient heterogeneous catalytic reduction of perchlorate in water. *Environ. Sci. Technol.* **2007**, *41*, 2044-2049.

21. Liu, J.; Choe, J. K.; Sasnow, Z.; Werth, C. J.; Strathmann, T. J. Application of a Re–Pd bimetallic catalyst for treatment of perchlorate in waste ion-exchange regenerant brine. *Water Res.* **2013**, *47*, 91-101.

22. Hurley, K. D.; Zhang, Y.; Shapley, J. R. Ligand-enhanced reduction of perchlorate in water with heterogeneous Re−Pd/C catalysts. *J. Am. Chem. Soc.* **2009**, *131*, 14172-14173.

23. Liu, J.; Choe, J. K.; Wang, Y.; Shapley, J. R.; Werth, C. J.; Strathmann, T. J. Bioinspired complex-nanoparticle hybrid catalyst system for aqueous perchlorate reduction: Rhenium speciation and its influence on catalyst activity. *ACS Catal.* **2015**, *5*, 511-522.

24. Liu, J.; Chen, X.; Wang, Y.; Strathmann, T. J.; Werth, C. J. Mechanism and mitigation of the decomposition of an oxorhenium complex-based heterogeneous catalyst for perchlorate reduction in water. *Environ. Sci. Technol.* **2015**, *49*, 12932-12940.

25. Ren, C.; Liu, J. Bioinspired catalytic reduction of aqueous perchlorate by one single-metal site with high stability against oxidative deactivation. *ACS Catal.* **2021**, *11*, 6715-6725.

26. Ren, C.; Yang, P.; Sun, J.; Bi, E. Y.; Gao, J.; Palmer, J.; Zhu, M.; Wu, Y.; Liu, J. A bioinspired molybdenum catalyst for aqueous perchlorate reduction. *J. Am. Chem. Soc.* **2021**, *143*, 7891-7896.

27. Gao, J.; Ren, C.; Huo, X.; Ji, R.; Wen, X.; Guo, J.; Liu, J. Supported palladium catalysts: A facile preparation method and implications to reductive catalysis technology for water treatment. *ACS ES&T Eng.* **2021**, *1*, 562–570.

28. Chaplin, B. P.; Shapley, J. R.; Werth, C. J. Regeneration of sulfur-fouled bimetallic Pd-based catalysts. *Environ. Sci. Technol.* **2007**, *41*, 5491-5497.

29. Batista, J. R.; McGarvey, F. X.; Vieira, A. R. The removal of perchlorate from waters using ion-exchange resins. In *Perchlorate in the Environment*; Springer, 2000; pp 135-145.

30. Gingras, T. M.; Batista, J. R. Biological reduction of perchlorate in ion exchange regenerant solutions containing high salinity and ammonium levels. *J. Environ. Monit.* **2002**, *4*, 96-101.

31. Lehman, S. G.; Badruzzaman, M.; Adham, S.; Roberts, D. J.; Clifford, D. A. Perchlorate and nitrate treatment by ion exchange integrated with biological brine treatment. *Water Res.* **2008**, *42*, 969-976.

32. Abu-Omar, M. M.; Espenson, J. H. Facile abstraction of successive oxygen atoms from perchlorate ions by methylrhenium dioxide. *Inorg. Chem.* **1995**, *34*, 6239-6240.

33. Rechnitz, G. A.; Laitinen, H. A study of the molybdenum catalyzed reduction of perchlorate. *Anal. Chem.* **1961**, *33*, 1473-1477.

34. Ren, C.; Yang, P.; Gao, J.; Huo, X.; Min, X.; Bi, E. Y.; Liu, Y.; Wang, Y.; Zhu, M.; Liu, J. Catalytic reduction of aqueous chlorate with MoO_x immobilized on Pd/C. *ACS Catal.* **2020**, *10*, 8201-8211.

35. Liu, B. Y.; Wagner, P. A.; Earley, J. E. Reduction of perchlorate ion by (N-(hydroxyethyl) ethylenediaminetriacetato) aquatitanium(III). *Inorg. Chem.* **1984**, *23*, 3418-3420.

36. Chen, X.; Huo, X.; Liu, J.; Wang, Y.; Werth, C. J.; Strathmann, T. J. Exploring beyond palladium: Catalytic reduction of aqueous oxyanion pollutants with alternative platinum group metals and new mechanistic implications. *Chem. Eng. J.* **2017**, *313*, 745-752.

37. Chaplin, B. P.; Reinhard, M.; Schneider, W. F.; Schüth, C.; Shapley, J. R.; Strathmann, T. J.; Werth, C. J. Critical review of Pd-based catalytic treatment of priority contaminants in water. *Environ. Sci. Technol.* **2012**, *46*, 3655-3670.

38. Majumdar, A.; Pal, K.; Sarkar, S., Selectivity of thiolate ligand and preference of substrate in model reactions of dissimilatory nitrate reductase. *Inorg. Chem.* **2008,** *47*, 3393-3401.

39. Ehweiner, M. A.; Wiedemaier, F.; Belaj, F.; Mösch-Zanetti, N. C., Oxygen Atom Transfer Reactivity of Molybdenum (VI) Complexes Employing Pyrimidine-and Pyridine-2-thiolate Ligands. *Inorg. Chem.* **2020,** *59*, 14577-14593.

40. Prüsse, U.; Vorlop, K.-D. Supported bimetallic palladium catalysts for water-phase nitrate reduction. *J. Mol. Catal. A Chem.* **2001**, *173*, 313-328.

41. Cui, Y.; Kwok, S.; Bucholtz, A.; Davis, B.; Whitney, R. A.; Jessop, P. G. The effect of substitution on the utility of piperidines and octahydroindoles for reversible hydrogen storage. *New J. Chem.* **2008**, *32*, 1027-1037.

42. Irfan, M.; Petricci, E.; Glasnov, T. N.; Taddei, M.; Kappe, C. O. Continuous flow hydrogenation of functionalized pyridines. *Eur. J. Org. Chem.* **2009**, *2009*, 1327-1334.

43. Namasivayam, C.; Sangeetha, D. Removal of molybdate from water by adsorption onto $ZnCl_2$ activated coir pith carbon. *Bioresour. Technol.* **2006**, *97*, 1194-1200.

44. Fotouhi-Far, F.; Bashiri, H.; Hamadanian, M.; Keshavarz, M. H. A new approach for the leaching of palladium from spent Pd/C catalyst in HCl–H_2O_2 system. *Prot. Met. Phys. Chem. Surf.* **2021**, *57*, 297-305.

45. Fontana, D.; Pietrantonio, M.; Pucciarmati, S.; Torelli, G. N.; Bonomi, C.; Masi, F. Palladium recovery from monolithic ceramic capacitors by leaching, solvent extraction and reduction. *J. Mater. Cycles Waste Manag.* **2018**, *20*, 1199-1206.

46. Nogueira, C. A.; Paiva, A. P.; Costa, M. C.; da Costa, A. M. R. Leaching efficiency and kinetics of the recovery of palladium and rhodium from a spent auto-catalyst in HCl/$CuCl_2$ media. *Environ. Technol.* **2019**, *41*, 2293-2304.

47. Choe, J. K.; Mehnert, M. H.; Guest, J. S.; Strathmann, T. J.; Werth, C. J. Comparative assessment of the environmental sustainability of existing and emerging perchlorate treatment technologies for drinking water. *Environ. Sci. Technol.* **2013**, *47*, 4644-4652.

48. Sharbatmaleki, M.; Batista, J. R. Multi-cycle bioregeneration of spent perchlorate-containing macroporous selective anion-exchange resin. *Water Res.* **2012**, *46*, 21-32.

49. Faccini, J.; Ebrahimi, S.; Roberts, D. J. Regeneration of a perchlorate-exhausted highly selective ion exchange resin: Kinetics study of adsorption and desorption processes. *Sep. Purif. Technol.* **2016**, *158*, 266-274.

50. U.S. Environmental Protection Agency. Revisions to the unregulated contaminant monitoring regulation (UCMR 3) for public water systems. *Fed. Regist.* **2012**, *77*, 26072-26101.

51. Zhou, D.; Luo, Y.-H.; Zheng, C.-W.; Long, M.; Long, X.; Bi, Y.; Zheng, X.; Zhou, C.; Rittmann, B. E. H_2-Based membrane catalyst-film reactor (H_2-MCfR) loaded with palladium for removing oxidized contaminants in water. *Environ. Sci. Technol.* **2021**, *55*, 7082-7093.

52. Luo, Y.-H.; Long, X.; Wang, B.; Zhou, C.; Tang, Y.; Krajmalnik-Brown, R.; Rittmann, B. E. A synergistic platform for continuous co-removal of 1,1,1-trichloroethane, trichloroethene, and 1,4-dioxane via catalytic dechlorination followed by biodegradation. *Environ. Sci. Technol.* **2021**, *55*, 6363-6372.

53. Zhao, H.-P.; Ontiveros-Valencia, A.; Tang, Y.; Kim, B. O.; Ilhan, Z. E.; Krajmalnik-Brown, R.; Rittmann, B. Using a two-stage hydrogen-based membrane biofilm reactor (MBfR) to achieve complete perchlorate reduction in the presence of nitrate and sulfate. *Environ. Sci. Technol.* **2013**, *47*, 1565-1572.

54. McNab, W. W.; Ruiz, R.; Reinhard, M. In-situ destruction of chlorinated hydrocarbons in groundwater using catalytic reductive dehalogenation in a reactive well: Testing and operational experiences. *Environ. Sci. Technol.* **2000**, *34*, 149-153.

55. Schüth, C.; Kummer, N.-A.; Weidenthaler, C.; Schad, H. Field application of a tailored catalyst for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater. *Appl. Catal. B: Environ.* **2004**, *52*, 197-203.

56. Davie, M. G.; Cheng, H.; Hopkins, G. D.; Lebron, C. A.; Reinhard, M. Implementing heterogeneous catalytic dechlorination technology for remediating TCE-contaminated groundwater. *Environ. Sci. Technol.* **2008**, *42*, 8908-8915.

57. Tomar, M.; Abdullah, T. H. Evaluation of chemicals to control the generation of malodorous hydrogen sulfide in waste water. *Water Res.* **1994**, *28*, 2545-2552.

58. Liu, J.; Wu, D.; Su, X.; Han, M.; Kimura, S. Y.; Gray, D. L.; Shapley, J. R.; Abu-Omar, M. M.; Werth, C. J.; Strathmann, T. J. Configuration control in the synthesis of homo- and heteroleptic bis (oxazolinylphenolato/thiazolinylphenolato) chelate ligand complexes of oxorhenium(V): Isomer effect on ancillary ligand exchange dynamics and implications for perchlorate reduction catalysis. *Inorg. Chem.* **2016**, *55*, 2597-2611.

59. Liu, J.; Han, M.; Wu, D.; Chen, X.; Choe, J. K.; Werth, C. J.; Strathmann, T. J., A new bioinspired perchlorate reduction catalyst with significantly enhanced stability via rational tuning of rhenium coordination chemistry and heterogeneous reaction pathway. *Environ. Sci. Technol.* **2016,** *50*, 5874-5881.

60. Liu, J.; Su, X.; Han, M.; Wu, D.; Gray, D. L.; Shapley, J. R.; Werth, C. J.; Strathmann, T. J. Ligand design for isomer-selective oxorhenium(V) complex synthesis. *Inorg. Chem.* **2017**, *56*, 1757-1769.