Enhanced catalytic reduction of aqueous bromate by metal-organic framework Ni(HBTC)(4,4'-bipy) with

NaBH₄

Nurbek Nurlan¹, Woojin Lee²

¹Nazarbayev University, Department of Chemistry, National Laboratory Astana, 53 Kabanbay Batyr Ave., Nur-Sultan 010000, Kazakhstan

²Nazarbayev University, Department of Civil and Environment Engineering, National Laboratory Astana, 53 Kabanbay Batyr Ave., Nur-Sultan 010000, Kazakhstan

Abstract

The occurrence of bromate during the ozonation process can cause serious health problems as it was suspected human carcinogen. The catalytic reduction of bromate with NaBH₄ is one of the promising techniques. Using solid H₂-generating compounds is relatively safe and cost-effective. MOFs in the presence of NaBH₄ have shown accelerated reduction kinetics and complete conversion of bromate to bromide in 1 hour with a rate constant of 0.140 min⁻¹. Moreover, the study found out that the increase in catalyst loading and NaBH₄ loading resulted in further enhancement of bromate reduction.

Introduction

- Ozonation of bromide leads to the formation of carcinogenic bromate. Maximal contaminant level in drinking water is 10 µg/L by WHO and EPA¹
- There are several technologies: elimination of bromate precursors, adsorption, filtration, however they are not effective and do not completely remove bromate from water.

Reduction after ozonation converts bromate back to bromide²³:

- Metal-organic frameworks (MOFs) have attracted considerable attention having a variety of interesting structures and various applications in wastewater⁴⁵
- This research study investigated the reactivity of Ni(HBTC)(4,4'-bipy) with NaBH₄ for the bromate reduction in an aqueous environment.

Results and Discussion

- Synthesis of the catalyst

SEM images showing the formation of crystals. The scale bar is 200 nm.

Ni(NO₃)₂·6H₂O, 1,3,5-benzenetricarboxylic acid and 4,4'-bipyridine in DMF and water with the ratio of 4:4:3 put in oil bath at 120°C for 24 hours. The obtained crystals were washed with DMF continuously and dried under vacuum at 100°C overnight

- Characterization

The disappearance of carbonyl bond from 1,3,5-benzenetricarboxylic acid at 1721 cm⁻¹ which corresponds to stretching vibration of free carboxylic acid. The result of reaction with Ni at 1610 cm⁻¹ and the decrease in value for the peak assigned C=N stretching in MOF-Ni. The carboxylic stretches at 1624 cm⁻¹, 1491 cm⁻¹, 1438 cm⁻¹ and 1367 cm⁻¹ can be confirmed⁶.

TEM images of Ni(4,4'-bipy)(1,3,5-btc) (fresh)

TEM was also performed to investigate the morphology of the catalyst in details. The image shows that the MOF aggregates formed by plates were similar to those particles observed using the SEM image.

- Reduction of bromate and control reactions
- BrO₃⁻ adsorption by the catalyst was negligible
 - NaBH₄ without catalyst was inefficient having a reduction ability about 3%
 - The catalyst with NaBH₄ showed a complete BrO₃⁻ reduction (100%) to bromide

- The different loadings of Ni(4,4'-bipy)(1,3,5-btc) in 60 min were examined by varying the amount from 250 to 1000 mg/L with fixed amount of NaBH₄. The bromate reduction was all increased as the loading of the catalyst increased.
- The lower amount of NaBH₄ has a different trend showing the fastest removal of bromate with the rate constant 0.18 min⁻¹. It occurred due to the competing effects such as pH changes during the reaction.

The higher pH values show the increased reactivity. It was gradually decreased after neutral pH.

At higher pH, the formation of hydroxyl anions inhibit the reduction of bromate on the surface of the catalyst

Modeling of kinetic parameters for reduction of bromate with 25 µg/L using Ni(4,4'-bipy)(1,3,5-btc) catalyst

Conditions (aerobic)			Pseudo-first-order	
Temp. (°C)	Ni(4,4'-bipy)(1,3,5-btc) (mg/L)	NaBH ₄ (mg/L)	k ₁ (min ⁻¹)	R ₁ ²
25	500	1000	0.072	0.859
25	500	150	0.177	0.967
25	500	250	0.161	0.991
25	500	500	0.140	0.995
25	1000	500	0.365	0.877

Aerobic and anaerobic conditions show roughly the similar reactivity of the catalyst. The highest rate constant equals to 0,177 min⁻¹ with 150 mg/L NaBH₄ loading.

It shows a highest kinetics compared to other studies¹²⁶ using much lower amount of NaBH₄.

Conclusions

- The Ni(HBTC)(4,4'-bipy) with NaBH₄ showed the reduction of bromate in 1 hour with higher rate constant
- The characterization of the catalyst was analyzed with FT-IR, SEM and TEM
- The effect of catalyst and NaBH₄ loadings were analyzed
- The pH conditions for the reduction was optimized

Reference

- Andrew Lin, K. Y.; Chen, S. Y. *RSC Adv.* **2015**
- Wang, X. K.; Liu, J.; Zhang, L.; Dong, L. Z.; Li, S. L.; Kan, Y. H.; Li, D. S.; Lan, Y. Q. *ACS Catal.* **2019**
- Hamid, S.; Abudanash, D.; Han, S.; Kim, J. R.; Lee, W. J. *Environ. Manage.* **2019**
- Qian, S.-L. et al. *ACS Appl. Energy Mater.* **2018**
- Liang, J. et al. *Inorg. Chem.* **2018**
- Marco, Y.; Garcia-bordejé, E.; Franch, C.; Palomares, A.E.; Yuranova, T. *Chem. Eng. J.* **2013**