Aqueous bromate (BrO_3^-) reduction in drinking water by nanoscale zero-valent iron (NZVI)-based bimetallic catalyst

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Abstract

Multiple experiments were performed to find out the efficiency of the bimetallic catalysts for the aqueous BrO_3^- reduction, a disinfection byproduct. Control experiments with various monometallic catalysts (Sn/NZVI, Cu/NZVI, Ni/NZVI, Zn/NZVI, In/NZVI) were conducted to select the most efficient combination of metals in the catalyst, and the Cu/NZVI and Sn/NZVI demonstrated the best removal efficiencies of 100% and about 99% in 10 min. Scanning electron microscope (SEM) results revealed that the average size of NZVI particles is ~100 nm. In general, Pd was uniformly distributed over the NZVI surface. Currently, these experiments are repeated with a larger amount of time sampling points (with 2 and 5 min) to calculate rate constants of the reaction.

Introduction

- ✓ BrO_3^- is a 2B carcinogen (IARC, 2019), produced as ozonation and chlorination byproduct (WHO limit in drinking water: 0.01 mg/L) (Soares et al., 2016).
- ✓ Treatment technologies for BrO_3^- include ion exchange, adsorption by activated carbon, biological remediation, photocatalysis, and electrochemical reduction. However, undesirable acidic pH conditions, high operating costs, concentrated secondary streams, and long retention time are major drawbacks of these technologies (Hamid et al., 2019; Soares et al., 2016).
- ✓ NZVI based bimetallic catalysts are widely used for the reduction of various contaminants, including nitrates and may be efficient for the BrO_3^- reduction (Bae et al., 2016).
- ✓ The objective of this study is to investigate the feasibility of applying bimetallic catalyst technology for the BrO_3^- reduction and select the most effective promoter metal.

Results

Results of synthesis

- ✓ About 100 nm-size Fe^0 particles of irregular shape (Figure 1a)
- ✓ Pd is distributed evenly on the surface of NZVI (Figure 1b)

Figure 1. SEM results for Pd/NZVI catalyst (A) NZVI nanoparticles, (B) Pd distribution

Figure 2. Reaction kinetics for monometallic metals

Figure 3. Mass balance for the Sn/NZVI catalyst

Results of kinetics tests

- ✓ No significant photolysis, adsorption by PTFE and rubber septum were observed in control tests (Figure 2).
- ✓ Br^- is the main byproduct of BrO_3^- reduction (Figure 3).
- ✓ Sn/NZVI and Zn/NZVI showed removal efficiency of about 100% respectively in 10 min. It is the best removal efficiency compared to other catalysts (Figure 2).
- Ni/NZVI → 100% (30 min)
 - In/NZVI → 14% (1 h)
 - Zn/NZVI → 51% (1 h)
- ✓ Based on kinetic rate constant Sn/NZVI is faster (0.47 min^{-1} , $R^2=0.99$) than Zn/NZVI (0.40 min^{-1} , $R^2=0.98$) and Cu/NZVI (0.13 min^{-1} , $R^2=0.95$).

Table 1. Comparison of the bromate removal

Catalyst	Removal efficiency	Kinetic rate constant	Reference
Pd/NaY	100% (60 min)	Not reported	(Soares et al., 2016)
Pd/AC	100% (15 min)	Not reported	(Restivo et al., 2015)
Pd/CNT-BM-U (carbon nanotube after ball milling)	100% (20 min)	0.167 min^{-1} (catalyst/ BrO_3^- =12.5)	(Soares et al., 2019)
ZIF-derived Cobalt/Carbon cage- NaBH_4	100% (60 min)	0.071 min^{-1} (catalyst/ BrO_3^- =5)	(Lin and Chen, 2015)
Sn/NZVI	100% (<10 min)	0.47 min^{-1} (catalyst/BrO_3^-=2)	Current study

Experimental conditions

1 Synthesis

1.49 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.11 M) in 150 mL of H_2O
 1.7 g of NaBH_4 (0.9 M) in 50 mL of H_2O
 3.1 g of NZVI

Sonicate & wash

2 Synthesis → Experiment @Anaerobic chamber

Firstly, dropwise addition of the promoter metal and washing (Pd, Sn, Cu, Ni, In, Zn)
 Next, 20 mL batch reactor is prepared:
 ✓ 1 mL contaminant
 ✓ 0.315 mL catalyst
 ✓ 18.685 mL water
 Reactor is sealed with PTFE cap and aluminum seal

3 Experiment @Anaerobic chamber

- ✓ The solution is spiked first with BrO_3^-
- ✓ The reactor is shaken at 20 rpm
- ✓ 2 mL sample is taken in duplicate with a 3 mL syringe

Conditions:

BrO_3^- loading: 25 ppm (0.19 mM)
 Catalyst loading: 50 ppm (3.2 g/L)
 Metal loading in monometallic NZVI: 4 wt%
 Promoter metals tested: Sn/NZVI, Cu/NZVI, Zn/NZVI, Ni/NZVI, In/NZVI

4 Analysis

Ion chromatography (Metrosep A Supp 5 - 150/4 mm)

- ✓ Sample diluted 10 times
- ✓ 6 standard solutions (0, 4, 8, 16, 40, 80 µM)

Conclusion

1. Synthesized catalyst demonstrated an efficient reduction of BrO_3^- and Sn/NZVI showed the fastest removal efficiency (99% removal in 10 min).
2. SEM results indicate even distribution of Pd.
3. With Sn as a selected promoter metal, a further research on an effect of catalyst loading, metal loading, and noble metal selection has to be carried out to identify the most optimum conditions for the BrO_3^- removal.
4. Sn/NZVI is a cost-effective and sustainable solution to treat BrO_3^- contaminated water.

References

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