Elimination of Micropollutants in Catalytic Ozonation using Aniline-Derived Metal-Carbon Composite (Me-N-C): Process Efficiency and Mechanistic Understanding

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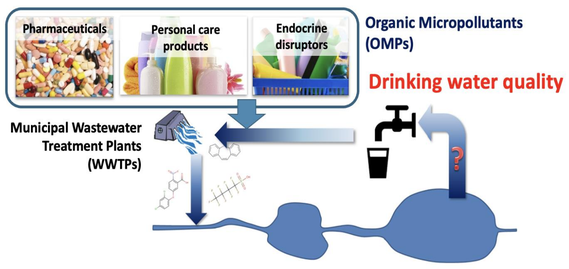
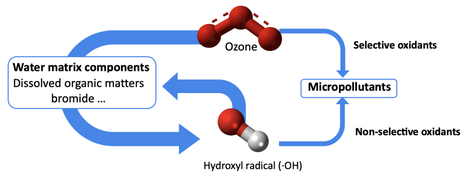
Introduction

Micropollutant issue in urban water cycle



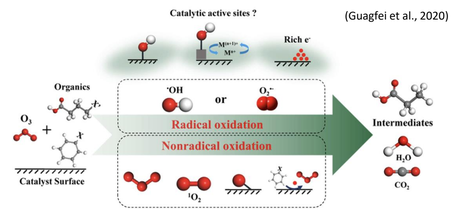
❖ Micropollutants such as pharmaceuticals, personal care products, and industrial chemicals are found in various water environments including drinking water source. Some of them can exert negative impact on aquatic organisms and drinking water quality[1]

Ozonation and Reactivity of Ozone and OH radicals



❖ Ozonation is widely used for drinking water treatment for the purpose of disinfection and oxidation
❖ Ozone is selective oxidant reacting with electron-rich moieties, whereas OH radicals are non-selective oxidants and can oxidize a wide range of compounds
❖ Conversion of ozone into OH radical, which is the basis of ozone-based advanced oxidation process (AOP), is required to oxidize ozone-resistant micropollutants

Catalytic Ozonation as Advanced Oxidation Processes



(Guagfei et al., 2020)

❖ Catalytic ozonation is an AOP, that enhances the degradation of contaminants by facilitating the decomposition of ozone into OH radical using catalysts
❖ Aniline-Derived Metal-Carbon Composites (Me-N-C) have been used for persulfate activation, and can potentially used for catalytic ozonation
❖ Different types of metals can be used in Me-N-C preparation, and the catalytic ozonation performance of different Me-N-C catalysts has not been investigated

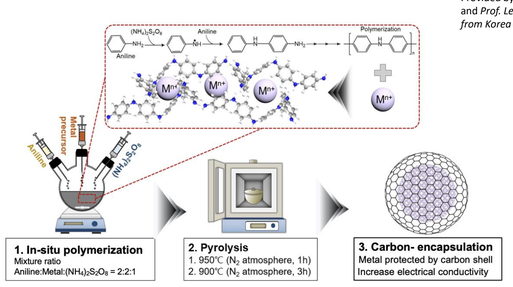
Research Objectives

❖ To investigate the efficacy of various catalysts (Me-N-Cs) in enhancing ozone decay and OH radical formation in catalytic ozonation process
❖ To determine the efficiency of micropollutant elimination during catalytic ozonation (Ni-N-C) and to elucidate the main mechanisms responsible for such elimination

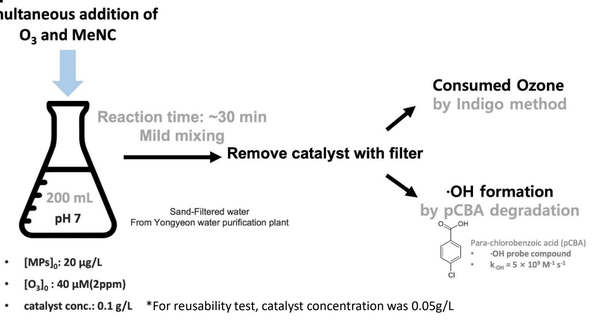
Methods

Catalyst preparation

Provided by Oh, Hoon and *Prof. Lee, Jaesang from Korea University*

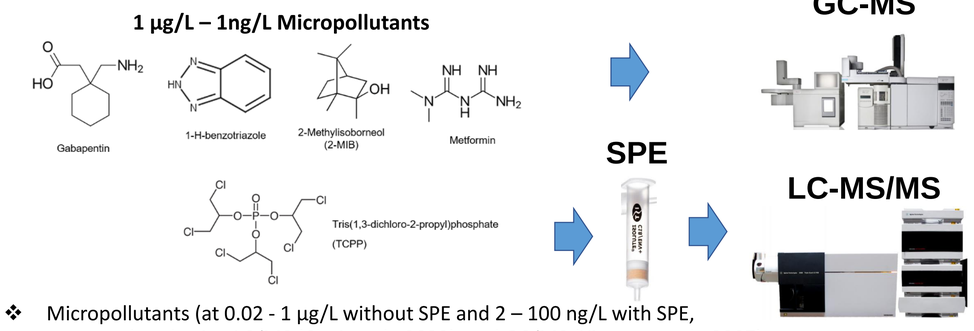


Experimental Scheme



- $[MPs]_0$: 20 μg/L
- $[O_3]_0$: 40 μM(2ppm)
- catalyst conc.: 0.1 g/L *For reusability test, catalyst concentration was 0.05g/L

Analysis

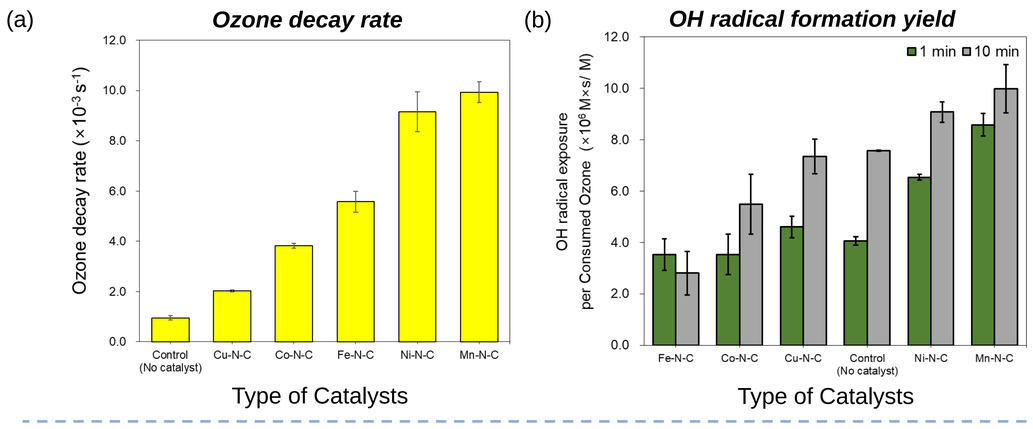


❖ Aniline-derived metal-carbon catalysts (Fe-N-C, Cu-N-C, Co-N-C, Mn-N-C, Ni-N-C) were prepared and used as catalysts in ozonation.

❖ Micropollutants (at 0.02 - 1 μg/L without SPE and 2 – 100 ng/L with SPE, were analyzed using LC/MS (Choi et al., 2022) and GC/MS (Xiaoyan et al., 2007).

Results & Discussion

Aniline-derived Metal-Carbon Catalysts (Me-N-C): Comparing Ozone Decay Rates and OH Radical Formation Efficiency



❖ All tested Me-N-C catalysts enhanced the ozone decay. Mn catalyst showed the highest performance for the ozone decay. The performance of different metal catalysts on the ozone decay was in the following order:
Mn (9.9×10^{-3} s^{-1}) > Ni (9.2×10^{-3} s^{-1}) > Fe (5.6×10^{-3} s^{-1}) > Co (3.8×10^{-3} s^{-1}) > Cu (2.0×10^{-3} s^{-1}) > Control (9.5×10^{-4} s^{-1}).

❖ The OH radical formation efficiency (evaluated by OH radical exposure per consumed ozone, 10 min reaction time) was in the following order: Mn (10.0×10^{-6} s) > Ni (7.3×10^{-6} s) > Control (7.6×10^{-6} s) > Cu (6.1×10^{-6} s) > Co (5.5×10^{-6} s) > Fe (2.8×10^{-6} s). All metal catalysts showed normally comparable performance in OH radical formation efficiency compare to control (i.e., conventional ozonation without catalyst).

❖ The performance of Mn-N-C and Ni-N-C exhibited the highest efficacy among the tested metal catalysts for both ozone decay and OH radical formation, promising candidates for applications for catalytic ozonation.

Figure 1. (a) *Ozone decay rate constant (s^{-1}) and (b) OH radical exposure per consumed ozone, during ozonation of drinking water with different Me-N-C catalysts, The drinking water sample was taken from effluents of sand filtration in a full-scale drinking water treatment plant)*

Reusability test for Ni and Mn catalysts

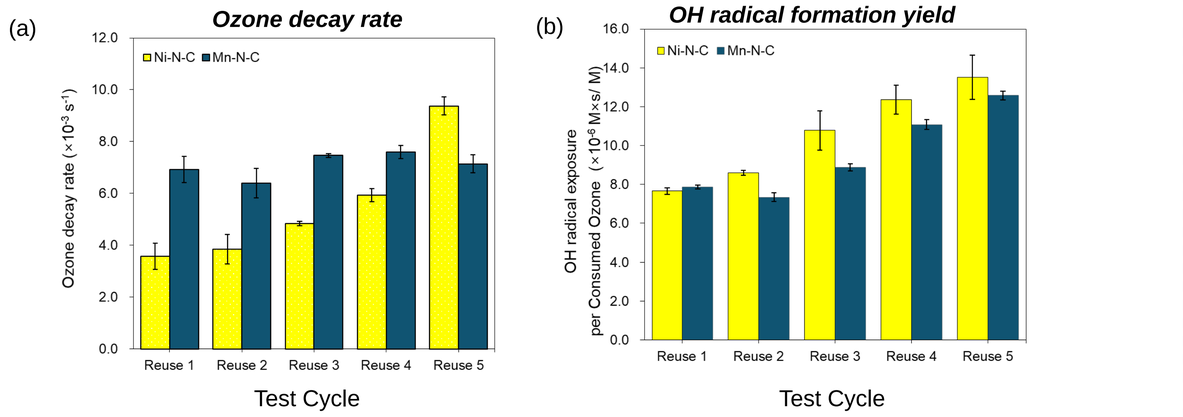


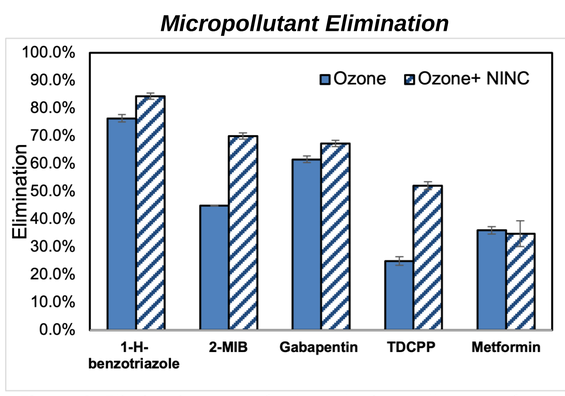
Figure 2. *Reusability tests of the Ni and Mn catalysts for* ***(a)*** *ozone decay and* ***(b)*** *OH radical formation*

❖ The reusability of the Ni and Mn catalysts was evaluated across five consecutive applications.

❖ Ni-N-C consistently facilitated ozone decay over multiple cycles, while Mn-N-C maintained a similar level of performance through repeated use.

❖ Regarding OH radical formation efficiency, Ni and Mn catalysts demonstrated consistent catalytic effects through five testing cycles.

Micropollutant Elimination Efficiency of Ni catalyst



Second-order rate constants of micropollutants with ozone and •OH

Compound	k_{O3}($M^{-1}s^{-1}$)	$k_{\cdot OH}$($M^{-1}s^{-1}$)
1-H-Benzotriazole	79.6	7.1×10^{9}
2-Methylisoborneol (2-MIB)	1	8.2×10^{9}
Gabapentin	15	9.1×10^{9}
Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)	<1	1.6×10^{9}
Metformin	1.2(±0.2)	1.4×10^{9}

Figure 3. *Elimination rate of selected micropollutants after ozonation without and with Ni catalyst. The micropollutants were spiked into a drinking water matrix (effluent of sand filtration) and treated by ozonation*

❖ The efficiency of micropollutant elimination has been enhanced for the catalytic ozonation (Ni-N-C)
The efficacy of micropollutant elimination was in the following order:
1-H-Benzotriazole (84.4%) > 2-MIB (70.1%) > Gabapentin (67.4%) > TDCPP (52.2%) > Metformin (34.9%).

❖ The mechanisms involved in the catalytic ozonation process encompass elimination via ozone, OH radicals, and adsorption

❖ Main mechanisms of micropollutant elimination in catalytic ozonation (Ni-N-C) :
- Due to ozone and OH radicals: 1-H-benzotriazole, 2-MIB, Gabapentin, Metformin
- Due to adsorption: TDCPP.

Conclusions

❖The Mn and Ni catalysts exhibited promising performance in catalytic ozonation system among tested Me-N-C catalysts, maintaining stable catalytic activity across five test cycles.
❖Catalytic ozonation using Ni catalysts was shown to be highly effective, with micropollutants being more susceptible to elimination via ozone and OH radical reactions, and also removal by adsorption.
❖These findings highlight the promise of Mn and Ni catalysts in advancing ozonation techniques for water treatment and micropollutant removal.

Acknowledgement

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