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# Degradation of aqueous phenol by simultaneous use of ozone with silica-gel and zeolite

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## Abstract

Phenol in water was degraded by simultaneous use of ozone and silica-gel or zeolite. When $Al_2O_3$-supported silica-gel or $TiO_2$-supported silica-gel was conjugated with ozonation, the phenol degradation was significantly enhanced, although raw silica-gel did not show such effect. When zeolite was conjugated with ozonation, phenol degradation was significantly enhanced as well. The ion-exchange of $Na^+$ in zeolite by $Ni^{2+}$ or $Co^{2+}$ and supporting metallic Ni or Co thereon did not show significant influence on this effect.

*Keywords:* Advanced oxidation treatment; Ozone; Silica-gel; Zeolite; Phenol

## 1. Introduction

Recently, water purification using ozone reaction to degrade organic compounds has been widely developed [1–3] due to some reasons as follows: (1) reactivity of ozone is quite strong so that organic compounds can be degraded effectively; (2) ozone can be generated easily by use of ultraviolet light or electric discharge; (3) ozone itself can be converted to $O_2$ easily; (4) ozone reaction can be combined with other method to achieve enhanced water purification. Also, the studies about water purification using porous media, such as silica-gel [4–6], zeolite [7–9], activated carbon [10–12], have a long history due to their simple applications when they are used as adsorbents and catalyst supports.

So far, there are numerous reports about the simultaneous use of ozone reaction and additional effects such as solid catalysts, photolysis and photo-catalysis, and ultrasound [13–20]. Among such advanced oxidation processes, the use of ozone and solid media has been receiving special attention because of its simplicity and synergetic effect which shows additional reactivity to the independent use of ozone and the solid media [14,16,17]. In their cases, activated carbon, silica-gel, and alumina were used as solid media, and the effects of loading metals or metal oxides were investigated. However, there are many aspects unknown in such enhancement effects by the simultaneous use of ozone and metal-loaded porous media. In the present work, we investigated the effects of loading of metals and ionic metals on silica-gel and zeolite for water purification to degrade phenol.

## 2. Experimental

Fig. 1 shows the experimental set-up (set-up #1) when silica-gel was used as the porous media. Silica-gel beads (diameter = 0.85–1.7 mm, Fuji Silysia Chemical) were packed in a glass tube (inner diameter = 40 mm) to packing bed height of 100 mm. The target water was supplied from the bottom of this packing bed, and the water flew upward. To stabilize the silica-gel beads bed, this packing bed was pressed softly by stainless steel net at its top. We stabilized the silica-gel beads bed because the surfaces of the silica-gel beads were damaged and the water became clouded in white with silica-gel fine powders when the beads were fluidized. Oxygen containing ozone was also supplied from the bottom of the silica-gel beads bed and it passed through the packed bed with the target water. The target water was prepared by dissolving phenol in distilled water at 20 mg/L. Target water

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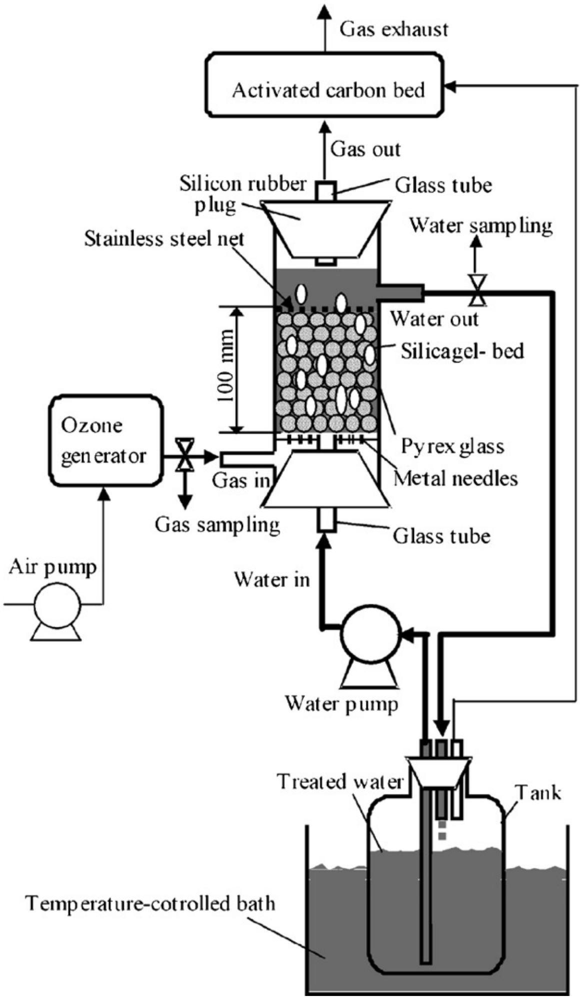

Fig. 1. Apparatus to degrade aqueous phenol by use of silica-gel and ozone (set #1).

was circulated through a liquid tank (glass tank) with a constant temperature at 20 °C. The volume of the target water and its flow rate were, respectively 1000 $cm^3$ and 1000 $cm^3$/min. Hydraulic retention time through the silica-gel bed in sets #1 was 0.8 s. The initial pH of the treated water was approximately 6.7, and it turned to be approximately 4.7 after reactions. Ozone was generated by discharge-based ozone generator from oxygen. The flow rate of the ozone-contained gas was 1000 $cm^3$/min. Ozone concentration in gas and water were measured by polarographic on-line ozone analyzer (TOA-DKK, OZ20 and OZ30). The ozone concentration in gas was approximately 22 mg/L, and that in water reached approximately 4 mg/L. Ozone contained in the exhaust gas from the reactor was removed by adsorption using activated carbon bed.

Fig. 2 shows the experimental set-up (set-up #2) when zeolite beads (beads diameter = 1.40–2.36 mm, TOSO) were used. We did not use the set-up #1 for zeolite beads because the amount of the metal-loaded zeolite beads that we obtained was not in sufficient quantity for the set-up #1. Thus, the set-up #2 is smaller than set-up #1. In set-up #2, the water purification process was carried out batch-wise. The temperature of the reactor was kept constant at 20 °C. The ozone generation and gas exhaustion were done in the same manner in the set-up #1. The gas flow rate in set #2 was 1500 $cm^3$/min. In the set-up #2, the volume of the target water and initial concentration of phenol were, respectively 20 $cm^3$ and 400 mg/L. The change of pH occurred as well as that in the set #1.

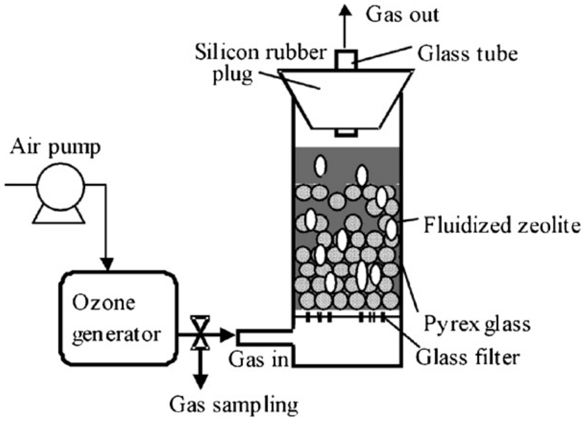

Fig. 2. Apparatus to degrade aqueous phenol by use of zeolite and ozone (set #2).

Table 1
Physical properties of the catalysts

| Catalyst | Porosity ($cm^3$/g) | Specific surface area ($m^2$/g) | Particle size (mm) |
|---|---|---|---|
| NaX | 0.30 | 476 | 1.40–2.36 |
| Co-NaX | 0.24 | 228 | 1.40–2.36 |
| Ni-NaX | 0.25 | 254 | 1.40–2.36 |
| 4A | 0.05 | 12 | 1.40–2.36 |
| Co-4A | 0.07 | 38 | 1.40–2.36 |
| Ni-4A | 0.19 | 263 | 1.40–2.36 |
| $SiO_2$ | 1.01 | 332 | 0.85–1.70 |
| $TiO_2/SiO_2$ | 0.87 | 300 | 0.85–1.70 |
| $Al_2O_3/SiO_2$ | 0.89 | 317 | 0.85–1.70 |

The concentration of phenol was analyzed in passing times by high performance liquid chromatography (HPLC, SPD-10Avp, Shimadzu) with adsorption column (ODS-UG-5, Nomura Chemical) and carrier liquid of aqueous solution of acetonitrile (2%)/phosphoric acid (0.1%). Total organic carbon (TOC) was analyzed by a TOC meter based on catalytic-oxidation (TOC-5000, Shimadzu).

The detailed specifications of the catalysts used in this study are described in Tables 1 and 2. The loading ratios of $TiO_2$ and $Al_2O_3$ on $SiO_2$ are, respectively 9.6 and 7.7 wt.%. The packing density was 0.46 g/$cm^3$ (310 particles/$cm^3$) and

Table 2
Results of elemental analysis of NaX and 4A

| Catalyst | Si (%) | Al (%) | Na (%) | Co (%) | Ni (%) |
|---|---|---|---|---|---|
| NaX | 16.3 | 14.5 | 9.1 | | |
| Co-NaX | 16.3 | 14.5 | 3.6 | 6.5 | |
| Ni-NaX | 16.3 | 14.5 | 4.0 | | 6.3 |
| 4A | 14.3 | 14.4 | 9.5 | | |
| Co-4A | 14.3 | 14.4 | 5.8 | 4.6 | |
| Ni-4A | 14.3 | 14.4 | 7.9 | | 2.6 |