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Actions of nitrogen plasma in the 4-chrolophenol degradation by pulsed high-voltage discharge with bubbling gas

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HIGHLIGHTS

- Nitrogen is dissociated to plasma to join in chemical process induced by discharge.
- This may decrease the efficiency of 4-chlorophenol degradation in discharge system.
- By bubbling O_2, air and N_2, the G_{50} is 0.91, 0.70 and 0.49 g (KW h)$^{-1}$ respectively.
- Nitrophenols and mineral nitrogenous such as HNO_2 and HNO_3 could be produced.
- The yield of HNO_3 increased linearly at a rate about twice to the degradation rate.

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ABSTRACT

Air is often used as bubbling gas with the purpose of improving the liquid discharge performance in some pulsed high-voltage discharge systems. Nitrogen in air could dissociate into active species that might participate in a series of liquid chemical reactions. In the discharge system with 4-chlorophenol as target contaminant, some more toxic intermediates were formed and the energy efficiency was decreased by bubbling air and nitrogen. The G_{50} (energy cost at 50% conversion) is about 0.91 g (KW h)$^{-1}$, 0.70 g (KW h)$^{-1}$ and 0.49 g (KW h)$^{-1}$ respectively by bubbling oxygen, air and nitrogen. Nitro- compounds such as 4-chloro-2-nitrophenol and 4-nitrocatechol were identified, providing evidence for the formation of nitro group. Chloride ion (Cl^-) dropped in the degradation process could be activated and react with non-degradable 4-chlorophenol to form 2,6-dichlorophenol. Phenol was also identified for higher yield of reductive radicals. Comparing 4-chlorophenol degradation by bubbling air or nitrogen with that by oxygen, the degradation rates of original contaminants and intermediate products were lower under same energy input. By discharging for 60 min with applied input energy density of 175 W L^{-1}, almost all of aromatic substances were removed with bubbling oxygen but they still remained at about 8.83% with bubbling air and 12.79% with nitrogen. Furthermore, nitrogen in the bubbling gas was transformed into inorganic nitrogen such as NO_2^- and NO_3^- that increased linearly with discharge time and achieved a formation rate twice as the degradation rate of original target contaminant.

1. Introduction

Pulsed high-voltage discharge as one of advanced oxidation technologies has received a great attention in the study of organic contaminants removal from contaminated water [1–4]. Because the average length of free path between liquid molecules is much shorter than that between gas molecules, the electrons inside the gas bubbles are more possible to be accelerated directly by discharge. It was found that low conductivity of the solution limited the development of corona and it was difficult to build up a strong electric field in the liquid of high salt concentration in the discharge reactor [5]. Therefore, many researchers have used bubbling gas to keep a stable discharge performance when applying the discharge technology to liquid [6–8]. In this case, air was used for the sake of convenience [9–11].

About 78% of the air is nitrogen. In many discharge processes, air is ubiquitously present in the discharge process, causing an unavoidable problem of the involvement of nitrogen plasma in contaminants degradation. Hydrogen peroxide, molecular oxygen and hydrogen and hydroxyl, hydroperoxyl, hydrogen, oxygen, and other radicals and, with the addition of air or oxygen at the high voltage electrode, ozone were produced by high-voltage discharge directly in water or in the gas phase above water [12,13].

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