The oxidation of toluene sorbed on activated carbon in the presence of H$_2$O$_2$ and manganese oxide
Si-Hyun Do and Sung-Ho Kong

ABSTRACT
We investigated the oxidation of toluene sorbed on activated carbon (AC) in the presence of hydrogen peroxide (H$_2$O$_2$) and pyrolusite (MnO$_2$). Sorbed toluene was prepared by reacting a toluene-saturated solution and AC. The amounts of sorbed toluene (mg of toluene/g of AC) decreased as the amounts of AC were increased. The reaction was conducted in a gas-purging (GP) reactor and the gas flow at the outlet of a GP reactor was carefully maintained. As a result, the percentage of toluene captured by ORBO tube was 28% in the control system with pure water. When H$_2$O$_2$ was catalyzed by AC (i.e. this forms a hydroxyl radical by electron transfer), approximately 17% of the desorbed toluene was oxidized and 68% of toluene remained on AC which was similar to the control system. However, when pyrolusite (650 mg/L) was added together with H$_2$O$_2$ (10,000 mg/L), only 5% of toluene was captured by the ORBO tube and 55% of toluene remained on AC, which indicated that both desorbed and sorbed toluene was oxidized. Moreover, toluene oxidation increased when concentrations of pyrolusite and H$_2$O$_2$ were increased. It was suggested that superoxide anion, which is generated by the reaction of H$_2$O$_2$ and pyrolusite, might stimulate toluene desorption and then toluene in the aqueous phase could be oxidized by hydroxyl radical.

Key words | activated carbon, hydrogen peroxide, hydroxyl radical, pyrolusite, superoxide anion, toluene oxidation

INTRODUCTION
Hydrogen peroxide-mediated chemical oxidation of organic contaminants in soil or sand has been investigated as a decontamination technique by several research groups (Miller & Valentine 1999; Watts et al. 1999; Watts & Teel 2005; Ciotti et al. 2009). These studies have highlighted the roles of reactive oxygen species other than hydroxyl radicals. Moreover, it has been reported that reactive oxygen species other than hydroxyl radicals might enhance the degradation of sorbed contaminants in the presence of hydrogen peroxide (Watts et al. 1999; Watts & Teel 2005).

We investigated the degradation of sorbed toluene on activated carbon (AC). Adsorption of organic molecules on activated carbon is attributed to two types of interactions: electrostatic and dispersive (Moreno-Castilla 2004; Lillo-Rodenas et al. 2005; Villacanas et al. 2006; Wibowo et al. 2007). Electrostatic interactions are likely to be significant at very high or very low pH values, while dispersive interactions are dominant over a broad range of pH values (Radovic et al. 1997). Three mechanisms, namely π–π interactions, hydrogen bond formation, and electron donor-acceptor complex formation, are thought to contribute to dispersive interactions (Moreno-Castilla 2004; Villacanas et al. 2006). In particular, π–π interactions are widely accepted to explain the adsorption of aromatic compounds to activated carbon in the aqueous phase (Radovic et al. 1997; Villacanas et al. 2006; Wibowo et al. 2007).

Georgi & Kopinke (2005) investigated the oxidation of organic contaminants in a H$_2$O$_2$/AC system and concluded that freely dissolved organic contaminants in the pores of activated carbon (AC) were oxidized by hydroxyl radicals that formed directly on the AC surface, while sorbed organic contaminants were not oxidized. The generally accepted mechanism for the catalysis of hydrogen peroxide by AC is shown below (Huang et al. 2003; Georgi & Kopinke 2005; Santos et al. 2009). Reactive oxygen species other than hydroxyl radicals or perhydroxyl radicals may contribute...
Decomposition of hydrogen peroxide results in the generation of various intermediates/products; the known reactive oxygen species other than hydroxyl radicals are hydroperoxide anions (HO$_2^-$), superoxide anions (O$_2$^-), and perhydroxyl radicals (HO$_2$). The superoxide anion (HO$_2$) is the conjugated base of hydrogen peroxide and a strong nucleophile (mostly based on its basicity) with a $pK_a$ of 11.6 (Edwards & Pearson 1962; Santos et al. 2009). The superoxide anion (O$_2^-$) is capable of functioning as a reductant in the presence of electron acceptors and an oxidant in the presence of electron donors at a pH of 7 (Poupko & Rosenthal 1973). Moreover, the superoxide anion is relatively long-lived at a pH above 7 (Behar et al. 1970). The perhydroxyl radical (HO$_2^-$) and superoxide anion are closely related to each other (i.e. HO$_2^-$ $\leftrightarrow$ H$^+$ + O$_2^-$, $pK_a$ = 4.8), and the perhydroxyl radical (HO$_2^-$) is a known oxidant (Rush & Bielski 1978; Smith et al. 2004).

The production of reactive oxygen species including superoxide and hydroperoxide anions during hydrogen peroxide-based decomposition of manganese oxide has been reported (Hasan et al. 1999; Do et al. 2009). Manganese oxide-based catalytic H$_2$O$_2$ oxidation was effective at a pH of around or above 7.0 (Watts et al. 2005; Do et al. 2009; Tizaoui et al. 2010). Do et al. (2009) showed that the decomposition rates of H$_2$O$_2$ and the production of reactive species (i.e. superoxide and hydroperoxide anions) depended on the concentrations of H$_2$O$_2$ and pyrolusite. Moreover, the production of reactive species increased as the pyrolusite concentration increased.

A number of studies have concluded that the superoxide anion can destroy chlorinated hydrocarbons (Smith et al. 2004; Watts et al. 2005; Furman et al. 2009). Smith et al. (2004) found that carbon tetrachloride was degraded by the superoxide anion, and the reactivity of the superoxide anion was strongly correlated with the addition of solvents, including H$_2$O$_2$. Recently, Furman et al. (2009) degraded hexachloroethane (HCA) by using birnessite ($\gamma$-MnO$_2$)-catalyzed H$_2$O$_2$ and showed that the presence of surfaces, similar to the addition of solvents, enhanced the reactivity of the superoxide anion.

Our objective in this study was to investigate the oxidation of toluene sorbed on activated carbon when hydrogen peroxide was reacted with pyrolusite at a neutral pH. A gas-purging (GP) reactor was used to evaluate the distribution of toluene among the desorbed (ORBO tube), dissolved (aqueous solution), and sorbed (activated carbon) phases. Moreover, we also determined the effects of H$_2$O$_2$ and pyrolusite concentrations on toluene oxidation.

**MATERIALS AND METHODS**

**Materials**

All chemicals used in this research were reagent grade. Double deionized water (DDW) with a resistivity of above 18.2 cm·MΩ was used (Milli-Q Model Gradient A10). Toluene and hydrogen peroxide (35%) were obtained from Junsei Chemical Company. Manganese oxide (particle size less than 0.088 mm) from near Pullman WA, previously identified as pyrolusite, was used (Do et al. 2009). Granular activated charcoal (AC) manufactured by Shinyou Pure Chemicals Co., Ltd was purchased and AC between 18 to 25 mesh in size was used for toluene adsorption. A standard carbon tube (ORBO 32) manufactured by Supelco Co. was used as an adsorbent for capturing toluene in the gaseous phase. Carbon disulfide produced by J.T Baker was used for toluene extraction. The initial solution pH was adjusted using either 5 mol/L HCl or 5 mol/L NaOH.

**Preparation of the sorbed toluene**

Activated carbon (AC) was pretreated by washing it several times with double-deionized water, drying it at 110 °C overnight, and then storing it in desiccators to reduce possible side effects due to dust and microorganisms. To eliminate the possible effects of organic solvent, DDW saturated with toluene as a pure chemical reagent was prepared in an Erlenmeyer flask and stirred for a period of 2 days. Before each experiment was conducted, a fresh toluene-saturated solution was prepared and residual toluene as a non-aqueous phase liquid (NAPL) was separated by a separatory funnel after 24 h of gravity separation. Toluene was used at a final concentration of 420 ± 14 mg/L for the experiments. Toluene adsorption to various amounts of AC (i.e. 2, 4, and 6 g) was investigated in 1 L volumetric flasks.

**The gas-purge (GP) reactor**

A scheme of the system, including the GP batch reactor, is shown in Figure 1. The total volume of the GP reactor was
120 mL and the volume of solution was 40 mL. Nitrogen gas was used as a purging gas and the temperature in the water bath was kept at 25°C. Because of oxygen evolution from the reaction of H₂O₂ and pyrolusite, the flow profile produced by oxygen evolution, the inflow of purging gas was controlled to maintain a gas flow at the outlet of the GP reactor. A bubble flow meter was used to check the flow at the gas outlet every 10 min. The flow of gas at the outlet was maintained at 140 ± 10 ml/min, which was higher than the flow produced by oxygen evolution. Most oxygen evolved within 20 min of starting the reaction, so the inflow of purging gas during that period was lowered and it was increased. When the experiment was started, toluene sorbed to AC in the GP reactor was partially distributed into the sorbed (remained on AC), the dissolved (released into aqueous solution) and the desorbed (captured by ORBO tube) phases.

Oxidation of the sorbed toluene in the GP reactor

A toluene-saturated solution and AC (0.2 g of AC and 40 mL of toluene-saturated solution) were combined in a vial with a sealed closure and mixed for 7 h in an incubator shaker (New Brunswick Scientific Co., Inc). After 6 h of mixing, the AC and solution were separated using a 0.45 μm membrane filter. The toluene-sorbed AC (0.2 g of AC) was rapidly transferred into the GP reactor and 30 mL of DDW was added. Pyrolusite and 10 mL of hydrogen peroxide (H₂O₂) were then introduced to give a total reaction volume of 40 mL. The reactor was then immediately closed using a rubber closure equipped with an ORBO tube. All experiments were conducted at pH 7.0 ± 0.1 and 25°C. The concentrations of pyrolusite and H₂O₂ were 650 mg/L (26 mg in 40 mL solution) and 10,000 mg/L, respectively. The reaction time for oxidation of the sorbed toluene using the H₂O₂ system only or the H₂O₂/pyrolusite system was 4 h. In addition, the effect of the concentration of pyrolusite (425 to 2,200 mg/L) was investigated at a fixed H₂O₂ concentration of 10,000 mg/L, and the effect of the H₂O₂ concentration (2,500 to 10,000 mg/L) was investigated at a fixed pyrolusite concentration of 1,300 mg/L. The ORBO tube was exchanged every 1 h for a new one.

Analytical methods

The toluene sorbed on the AC and ORBO tube was extracted with carbon disulfide (ASTM D 3686 and D 3687). For the ORBO tube, the glass wool inside the tube was removed to transfer charcoal into a vial filled with 10 mL of carbon disulfide to extract the toluene. After sampling 15 mL of solution to analyze toluene in the aqueous phase, the remaining solution was dumped to separate the AC from solution. Then AC was also transferred into a vial filled with 10 mL of carbon disulfide to extract the sorbed toluene. Toluene on the AC and charcoal (from the ORBO tube) was extracted by a 20-min sonication (8510R-DTH, Banson) and the amount of toluene present was analyzed by gas chromatography (HP 6890 with a FID detector; HB-5 column, 80°C initial temperature, 180°C final temperature, 10°C/min temperature increase). To analyze toluene in the aqueous phase, UV detection was used (Scinco Co., Ltd S-2150, wavelength: 273 nm). The specific surface area was measured by BET (ASAP 2010, micrometrics) using nitrogen as a carrier gas. The BET surface area of pyrolusite and AC were 6.06 and 353 m² g⁻¹, respectively.

RESULTS AND DISCUSSION

Toluene adsorption on AC

We investigated the adsorption of toluene to various amounts of AC (Supplementary Material Figure S1, available online at http://www.iwaponline.com/wst/066/467.pdf). Adsorption rates decreased dramatically after 2 h of reaction time and toluene uptake (mg) per g of AC increased as the amount of AC decreased. Toluene uptake on 2, 4 and 6 g AC for a 4 h reaction time was 77, 69, and 59 mg/g, respectively. The total mass of sorbed toluene in each system was 154, 276, and 354 mg, respectively. Because the mass of toluene in the toluene-saturated solution was 420 ± 14 mg, the percentage toluene adsorption for 2, 4,
and 6 g of AC was 37, 66, and 84%, respectively. This indicates that toluene adsorption increased gradually as the amount of AC increased in the present experimental conditions.

Oxidation of the sorbed toluene in the GP reactor

Toluene oxidation in the gas-purge (GP) reactor was evaluated in the presence of pyrolusite and H₂O₂. The measured value of toluene sorbed on AC was 14 (± 0.5) mg when 40 mL of toluene-saturated solution (i.e. 17 mg of toluene in solution) was reacted with 0.2 g of AC for 6 h. The control system comprised sorbed toluene and DDW. The sorbed toluene (T on AC) and the desorbed toluene (T in the ORBO tube) experimental results obtained after a 4 h reaction time are shown in Figure 2. Note that the amount of dissolved toluene (i.e. toluene in the aqueous phase) was negligible in the GP reaction system.

In the control (i.e. DDW with AC), 28% of toluene was desorbed from AC and collected in the ORBO tube (Figure 2). Moreover, the sorbed toluene was as high as 67%. For the H₂O₂/AC system, only 15% of toluene was collected in the ORBO tube and 68% of toluene remained on the AC when 10,000 mg/L H₂O₂ was used. This indicates that the H₂O₂/AC system could only oxidize desorbed toluene (i.e. approximately 15%), which exists freely in the aqueous phase. Several researchers have investigated the catalytic characteristics of AC in the presence of H₂O₂ (Huang et al. 2003; Georgi & Kopinke 2005; Santos et al. 2009). Georgi & Kopinke (2005) showed that hydroxyl radical produced from AC-catalyzed H₂O₂ could oxidize dissolved organic contaminants, but not sorbed contaminants. Our results are consistent with these previous results; sorbed toluene was not oxidized by hydroxyl radical. Interestingly, we detected only 5% toluene in the ORBO tube when 650 mg/L of pyrolusite was introduced together with 10,000 mg/L H₂O₂. Moreover, the amount of sorbed toluene decreased to 55%, lower than that in the system without pyrolusite. This clearly shows that the H₂O₂/pyrolusite/AC system can oxidize toluene effectively, even sorbed toluene.

It has been known that superoxide anion was generated by the reaction between H₂O₂ and pyrolusite (Hasan et al. 1999; Do et al. 2009). Therefore, the most important reactive species in the H₂O₂/pyrolusite/AC system are likely the superoxide anion and hydroxyl radical. The hydroxyl radical appears to have less activity with regard to the oxidation of sorbed toluene than the superoxide anion. Therefore, superoxide anion might: (1) oxidize toluene in the sorbed phase; or (2) weaken an interaction between toluene and AC to stimulate toluene desorption.

Because of the role of the superoxide anion as a reductant and the preference of toluene for reaction with oxidants, the oxidation of the sorbed toluene by the superoxide anion might be implausible (Buxton et al. 1988; Watts et al. 2005; Furman et al. 2009). Superoxide anion is a nucleophile (Furman et al. 2009). Therefore, superoxide anion might react with toluene through nucleophilic substitution, and it might change the electron density to weaken π–π interaction, which is the most accepted mechanism of toluene adsorption on AC (Radovic et al. 1997; Villacanas et al. 2006; Wibowo et al. 2007; Headen et al. 2010). Therefore, toluene might be likely desorbed and then in the aqueous phase could be oxidized by hydroxyl radical.

Effects of H₂O₂ and pyrolusite concentration

The effects of increasing pyrolusite and H₂O₂ concentrations on toluene oxidation are shown in Figure 3(a) and 3(b).

In Figure 3(a), the experiment with only H₂O₂ present is labeled ‘none’. The ability of H₂O₂ to oxidize toluene (desorbed and the sorbed) gradually increased as the pyrolusite concentration increased (from 425 to 2,200 mg/L). In Figure 3(b), the pyrolusite-only experiment is labeled ‘none’; it is clear from these results that toluene oxidation increased as the H₂O₂ concentration increased (from 2,500 to 10,000 mg/L) when pyrolusite was fixed at
1,300 mg/L. The amount of toluene oxidized under each experimental condition is tabulated in Table 1.

CONCLUSIONS

The oxidation of toluene, especially sorbed toluene (i.e. toluene sorbed on activated carbon), was investigated in a \( \text{H}_2\text{O}_2/\text{MnO}_2/\text{AC} \) system. When \( \text{H}_2\text{O}_2 \) was catalyzed by AC at neutral pH, approximately 17% of toluene in solution was degraded to a limited extent by oxidants. However, when pyrolusite was added to the system, as much as 49% of the toluene was oxidized. This observation indicated that both hydroxyl radicals and superoxide anions generated from the \( \text{H}_2\text{O}_2/\text{pyrolusite}/\text{AC} \) system enhanced the oxidation of toluene. Superoxide anions, which are generated by the reaction of \( \text{H}_2\text{O}_2 \) and pyrolusite at neutral pH, may be able to weaken the interaction between toluene and AC to stimulate toluene desorption. After that, hydroxyl radical could oxidize toluene in the aqueous phase.

REFERENCES


Hasan, M. A., Zaki, M. I., Pasupulety, L. & Kumari, K. 1999 Promotion of the hydrogen peroxide decomposition activity...


First received 14 May 2012; accepted in revised form 26 June 2012