

Oxidative Remediation of Diphenylamine in Wastewater

I. S. Jamall, I. Brown

Risk-Based Decisions, Inc., 2033 Howe Avenue, Suite 240,
Sacramento, CA 95825, USA

Received: 15 October 2005/Accepted: 3 February 2006

Diphenylamine (DPA, CAS Number 122-39-4) is a plant growth regulator used post-harvest to control storage scald on apples and pears in order to extend their shelf life. After the fruits have been treated, the DPA-containing wastewater is considered a potentially hazardous waste in California and must be disposed of at an approved waste disposal facility. The regulatory review, approval and disposal processes are both costly and time consuming. Previously, the biodegradation of DPA was reported using ultraviolet photocatalytic oxidation in a TiO_2 slurry reactor (Bolduc and Anderson, 1997), an effective but costly technology to implement in the field. We report here on a simple, quick and cost-effective approach to treat the DPA-containing wastewater that can be scaled to accommodate a few hundred gallons to several tens of thousands of gallons of wastewater requiring treatment.

This paper describes the ability of the oxidants, potassium permanganate (KMnO_4) or Fenton's reagent (hydrogen peroxide, H_2O_2 , with iron as a catalyst at a pH of about 3.0-4.0), to oxidize DPA and potentially carcinogenic co-contaminants in a simple, inexpensive and easily implemented remediation method.

MATERIALS AND METHODS

Wastewater from an apple processing facility containing 400 mg/L DPA was obtained. In order to evaluate the effectiveness of potassium permanganate (KMnO_4) or acidified hydrogen peroxide and iron (Fenton's reagent) to treat the DPA, the following protocol was developed: Control Group: 200 ml wastewater and 200 ml distilled water; Treatment Group 1: 200 ml wastewater, 100 ml 0.07M KMnO_4 and 100 ml deionized water; Treatment Group 2: 200 ml wastewater and 200 ml 0.14M KMnO_4 ; Treatment Group 3: 200 ml wastewater, 5 ml (5% acetic acid to make the pH 3.5 - 4.0), 100 ml 35% H_2O_2 solution (effective H_2O_2 concentration 8.8%) and 95 ml deionized water.

The control and treatment groups were each prepared in triplicate, and the reaction was allowed to run for either one hour or overnight for 12 hours at room temperature (25 degrees Centigrade). The reaction was carried out in 500 ml

Correspondence to: I. S. Jamall

Erlenmeyer flasks with rubber stoppers. At the end of the treatment period, 100 ml of water (pH 8.5) was added to each of the control or treatment flasks to bring the volume in each flask up to 500 ml and to terminate the pH-sensitive Fenton's reaction. All samples were transferred into amber-color glass bottles to minimize photooxidation. The temperature was monitored before the reaction and at 5, 15, 30, 60 minutes and at 12 hours in each flask and was found not to change by more than 1.5 degrees Centigrade. At the end of the treatment period (1 hour or 12 hours), each sample was immediately prepared for analysis by USEPA Method 3510 and analyzed by USEPA Method 8270C.

The choice of 0.07M KMnO_4 (T-1) was derived from a pilot study in which a sample of water containing 1,200 mg/L of DPA was oxidized with KMnO_4 . This corresponds to an effective DPA concentration of about 0.007M but because of the presence of other organic material and the turbidity of the wastewater, we elected to use a 10-fold higher molar concentration of KMnO_4 , i.e. 0.07M as our starting point and also used a higher KMnO_4 concentration of 0.14M (T-2).

The H_2O_2 concentration in the Fenton's reaction was based on our earlier unpublished observations of concentrations that were able to oxidize the gasoline additive, methyl-tert-butyl ether (MTBE) at concentrations similar to the DPA concentration used here. Iron was measured in the wastewater sample and found to be present at concentrations of 20 to 53 mg/L. Therefore, no external iron was added to catalyze the Fenton's reaction.

RESULTS AND DISCUSSION

The data (Table 1) show that compared to the Control Group 96.7% of the DPA was oxidized using 0.07M KMnO_4 within one hour (T-1). Doubling the KMnO_4 concentration to 0.14M resulted in the virtually complete oxidation (99.9%) of DPA as shown for in the Table. Treatment for 12 hours did not significantly enhance the oxidation of DPA indicating that virtually all of the oxidation of DPA occurs within the first hour.

Similarly, of the other compounds present in the wastewater, the potential carcinogen, N-Nitrosodiphenylamine, was 89% degraded by 0.07M KMnO_4 (from a mean of 52 ppm in the Control Group to a mean of 5.5 ppm in the Group treated with 0.07M KMnO_4) and was 97% degraded by 0.14M KMnO_4 (52 ppm versus 1.4 ppm). Bis-2-ethylhexylphthalate, also a potential carcinogen, was detected at 0.15 to 0.17 ppm in the Control Group and was not significantly reduced (0.012 ± 0.06 ppm) with the 0.07M KMnO_4 although it was reduced to non-detectable levels ($\text{ND} < 0.01$ ppm) with 0.14M KMnO_4 at 1-hour or 12 hours of treatment. Nitrobenzene was not detected (< 0.05 ppm) in the Control Group but was detected at low concentrations (0.15 and 0.19 ppm) with 0.07M KMnO_4 and increased to about 0.70 to 0.72 ppm when treated at the higher KMnO_4 concentration but with no significant effect of duration of treatment.

Table. Destruction of DPA and co-contaminants by KMnO₄ or Fenton's reagent

	Control Group (1 Hour)	Control Group (12 Hour)	Treatment Group 1A (1 Hour) (0.07M KMnO ₄)	Treatment Group 1B (12 Hour) (0.07M KMnO ₄)	Treatment Group 2A (1 Hour) (0.14M KMnO ₄)	Treatment Group 2B (12 Hour) (0.14M KMnO ₄)	Treatment Group 3A (1 Hour) (8.8% H ₂ O ₂)	Treatment Group 3B (12 Hour) (8.8% H ₂ O ₂)
DPA Conc. (mg/L)	190±11.4	189±12.4	6.2±0.67	5.9±0.31	0.13±0.04	0.11±0.07	190±13.7	180±10.7
Average % DPA Destruction	0	0	96.7	96.9	99.9	99.9	0	5.3
N-Nitroso-diphenylamine (mg/L)	52±4.3	54±4.3	5.5±0.66	6.1±0.41	1.4±0.23	1.3 ± 0.13	66± 8.9	68±9.5
bis-2-ethyl hexylphthalate (mg/L)	0.17±0.07	0.15±0.06	0.012±0.06	ND<0.01	^a ND<0.01	^a ND<0.01	0.21±0.07	0.21±0.05
Nitrobenzene (mg/L)	^a ND<0.05	^a ND<0.05	0.15±0.09	0.19±0.06	0.72±0.22	0.70±0.25	^a ND<0.05	^a ND<0.05

Concentrations reported are the mean ± standard deviation of the triplicates for each Group.
^aND = Not detected above 0.01 or 0.05 mg/L, as indicated.

Fenton's Reagent, using 8.8% H₂O₂ concentration had virtually no effect on the destruction of DPA compared to the Control Group. However, this treatment increased the concentration of the carcinogenic co-contaminant, N-Nitrosodiphenylamine, by about 26%. Treatment with Fenton's reagent also increased bis-2-ethylhexylphthalate by about 30% to 0.21 ppm. As in the Control Group, nitrobenzene was not detected (<0.05 ppm) in the Fenton's reagent treatment group.

Fenton's reagent has previously been shown to degrade a wide range of pollutants in waste water (Rivas et al., 2001; Gozmen et al., 2003). The reaction involves the generation of the potent oxidant, the hydroxyl free radical, through an iron-catalyzed breakdown of H₂O₂ to generate the potent hydroxyl free radical. The optimal reaction occurs in a range of pH 3 to pH 5.5 (www.h2o2.com/applications/industrialwastewater/fentonsreagent.html) and typically requires the presence of 3 to 15 mg/L iron. Although the iron concentrations in our test (20 to 53 mg/L) were much higher, the Fenton's reaction was ineffective in destroying DPA under the conditions described above and appeared to have resulted in higher concentrations of the potential carcinogen, N-Nitrosodiphenylamine and bis-2-ethylhexylphthalate compared to the Controls.

KMnO₄ has shown to be a powerful in situ oxidant against a several recalcitrant pollutants, including TCE and PCE (Nelson, et al., 2001; Lee et al., 2003; Hrapovic et al., 2005) although its use in treating contaminated groundwater has been limited by concerns that residual permanganate and manganese dioxide precipitates might alter the permeability of the aquifer and increase the dissolution of potentially toxic metals (Crimi and Siegrist, 2003).

Under the treatment conditions described here, the oxidation of DPA-containing wastewater can be carried out in an aboveground polypropylene Baker tank. Based on the almost complete destruction obtained with 0.14M KMnO₄, this approach provides a simple, cost-effective and rapid approach to an otherwise costly environmental problem. The supernatant from the reaction vessel can be discharged to the storm drain or sewer directly or by passing it through activated carbon in most instances, without need for permitting.

DPA is moderately soluble in water (39.4 ppm), has a relatively high octanol/water partition coefficient (K_{ow} = 3,860), and a high vapor pressure (6.39 x 10⁻⁴ torr). It is moderately toxic to fish and aquatic invertebrates. Although DPA has been classified by the United States Environmental Protection Agency (USEPA) as having low toxicity and not likely to be carcinogenic, an impurity or co-contaminant in commercial grade DPA, diphenylnitrosamine, is classified as a "probable human carcinogen (USEPA, 1998). DPA is on the third European Union (EU) list of priority pollutants and has been comprehensively reviewed with regard to its uses, chemistry, toxicology, and environmental fate (Dryzga, 2003).

Using a concentration of 0.14M KMnO_4 we were able to achieve greater than 99% degradation of DPA and of the potentially carcinogenic co-contaminants, N-Nitrosodiphenylamine and bis-2-ethylhexylphthalate in one hour. Fenton's Reagent, under the experimental conditions used, was ineffective.

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