



## THE PRETREATMENT OF ACRYLONITRILE AND STYRENE WITH THE OZONATION PROCESS

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### ABSTRACT

Acrylonitrile and styrene are used as the raw materials for manufacturing acrylic fiber, thus they are often found as pollutants in the petrochemical wastewater. This study utilizes ozone to decompose the organic nitrogen contained in acrylonitrile and styrene, and the oxidation process was monitored using on-line measurements of oxidation-reduction potential (ORP) and pH. The efficiency of organic nitrogen decomposition was also estimated based on the COD, organic nitrogen, TOC, ammonia-N, nitrite, and nitrate measurements. Both the initial pH and alkalinity are observed to affect the degradation rate of organic nitrogen. The acrylonitrile sample with the lowest initial pH value (i.e., 4.0) has a shorter  $t_{1/2}$  of 18.9 min and that for samples of the highest initial pH (i.e., 11) was 34 min. The alkalinity of one acrylonitrile sample was boosted by adding 500 mg/l  $\text{CaCO}_3$ , to simulate the field ABS (Acrylonitrile-Butadiene-Styrene) wastewater effluent. It was observed that within a short ozone contact time, the acrylonitrile sample spiked with 500 mg/l  $\text{CaCO}_3$  had the highest COD decomposition rate of  $0.411 \text{ min}^{-1}$ , or 1.3 times more than that for samples without addition of  $\text{CaCO}_3$ . Results of the ozonation process can be fitted with a modified Nernst equation for the various pH conditions. Additionally, the ozone treated synthetic ABS sample shows a faster COD removal rate in the subsequent biological process than those samples without ozone treatment. © 1997 IAWQ. Published by Elsevier Science Ltd

### KEYWORDS

ABS; acrylonitrile; acrylic fiber; Nernst equation; ORP; ozonation; petrochemical; styrene.

### INTRODUCTION

The ABS (Acrylonitrile-Butadiene-Styrene) industry is booming in South Eastern Asian countries and these countries are becoming the leading producers of ABS in the world. The major raw materials for manufacturing ABS resins include acrylonitrile and styrene; both are toxic and highly resistant to biological degradation. Field data show that the ABS wastewater contains high concentrations of COD, organic nitrogen, and high ratios of TKN/TOC and Org-N/COD as well as high alkalinity of 500 mg/l as  $\text{CaCO}_3$ .

The high organic nitrogen content combining with the aromatic structure of styrene makes the biological treatment process very inefficient in removing raw organic nitrogen from ABS wastewater, even if the biological system is operated at an excessive prolonged detention time. Discharge of wastewater containing untreated acrylonitrile and styrene into receiving water bodies will cause serious environmental problems.

Many advanced treatment processes using oxidizing agents have been proposed for treating ABS wastewater. Among the many oxidizing agents proposed, ozone is one of the most efficient oxidants for decomposing acrylonitrile and styrene contained in ABS waste effluents. The multiple bonds in the styrene molecule and the triple bonds between carbon and nitrogen in the acrylonitrile molecule require 614 and 819 kJ/mole of energy, respectively, to decompose (Graham, 1982). These energy requirements are much higher than that needed to destroy the single carbon bond structure (347 kJ/mole). Ozone is such a strong oxidant that it can theoretically provide sufficient energy in aqueous solution to degrade the strong chemical bonds in acrylonitrile and styrene. During the oxidizing process, ozone may react directly with chemical molecules in aqueous solution, it may also generate hydroxyl radicals to oxidize chemical molecules (Hoigne and Bader, 1976). The rate of hydroxyl radical generation by ozone is greatly affected by the pH of the aqueous solution and ions present in the solution.

#### The oxidation/reduction potential (ORP)

The oxidation process is known to be caused by transfer of electrons from the oxidant to the substances being oxidized. The Nernst equation can be used to relate the Oxidation/Reduction Potential (ORP) of the system to the concentration ratio of the oxidant and the substance being oxidized (Weber, 1972):

$$E = E_0 - (RT/nF) \ln([\text{Oxid}]/[\text{Red}]) \quad (1)$$

R = gas constant

T = absolute temperature

n = number of electrochemical gram equivalent per gram mole exchanged during the redox reaction

F = Faraday constant

E = oxidation/reduction potential (ORP) of the system, or electrode potential of chemical reactions

$E_0$  = standard electrode potential

[Oxid] = molar concentration of oxidant

[Red] = molar concentration of substance being oxidized

According to the Nernst equation, the system ORP is indicative of the ratio of the oxidant applied to the substance being oxidized at a given reaction time. Thus, the degree of the oxidation/reduction reaction can be monitored by on-line measurement of the system ORP value or the E value in the Nernst equation. The ORP measurement has been shown to be a useful indicator for monitoring both chemical and biological reactions. Charpentier *et al.* (1989) and Menardiere *et al.* (1991) examined the removal of carbonaceous, nitrogen, and phosphate substances using the ORP value as a control parameter. A good correlation between ORP and TKN was found, with the  $R^2$  value being 0.919 (Charpentier *et al.*, 1989). Chang *et al.* (1994, 1996) applied the ORP measurement to simulate the decolorizing mechanism of secondary textile effluent and dye stuff, and obtained satisfactory results. The ORP value has also been demonstrated to be related to chlorine consumption and the production of disinfection by-products during the chlorination process (Johnson and Jensen, 1986). Thus, it is a promising monitoring parameter for on-line control of the pre-ozonation process.

In this study, the ozonation process is used as a pretreatment to oxidize acrylonitrile and styrene contained in ABS wastewater so that the ozone treated wastewater becomes more amenable to the subsequent biological treatment. Ozone oxidation studies were carried out using synthetic ABS wastewater prepared with pure acrylonitrile and styrene. Among the many parameters only solution pH and alkalinity were selected to be varied for studying the oxidation process. The efficiency of the oxidation treatment is based on decomposition of both organic carbon and nitrogen. The Nernst equation is used to model the oxidation process. After the ozone oxidation, the oxidized ABS wastewater is subject to activated sludge treatment and

the biological treatment efficiency is compared to that obtained with the ABS wastewater samples without ozone pretreatment.

METHOD AND INSTRUMENTS

Pure acrylonitrile and styrene samples used in preparing the synthetic ABS wastewater were purchased from Merck (stock codes 800834 and 807679, respectively). In order to simulate the high alkalinity content in real ABS effluents, 500 mg/l CaCO<sub>3</sub> was added to one synthetic sample. For other samples without addition of CaCO<sub>3</sub>, the initial pHs were adjusted to 4, 6, 9, and 11 with either sodium hydroxide or sulfuric acid.

The ozonation study was carried out in a 2-litre batch reactor with its content maintained at 25°C. During the reaction period, ozone was continuously injected into the reactor at a rate of 33.4 mg/min ozone during the reaction period and the ORP and pH of the content were monitored with an on-line data acquisition system. Samples were periodically removed from the reactor for analyses of COD, TOC, organic nitrogen, nitrate, nitrite, and ammonia following the procedures published in Standard Methods (1992). Blank (or control) samples were included in the studies to eliminate the effect of volatilization. For both acrylonitrile and acrylonitrile samples with alkalinity varying from 0 to 800 mg/l CaCO<sub>3</sub>, the organic load measured as COD has a linear relationship to the concentrations of acrylonitrile implying the addition of CaCO<sub>3</sub> to ABS samples did not interfere with the organic matter measurement.

The samples are then subject to biological treatment studies using batch activated sludge systems with the sludge acclimated to synthetic ABS solution. Differences between the biodegradability of the pre-ozonated and un-ozonated ABS samples were evaluated using various F/M ratio loadings of 0.15, 0.23, and 0.35 d<sup>-1</sup>.

Table 1. The initial COD removal rate, organic nitrogen decomposition rate and t<sub>1/2</sub> of various initial pH acrylonitrile samples during ozonation

Initial conditions		Initial COD Removal Rate		Organic Nitrogen Decomposition Rate		
		K <sub>COD,i</sub> (min <sup>-1</sup> )	R <sup>2</sup>	K <sub>D,Org-N</sub> (min <sup>-1</sup> )	t <sub>1/2</sub> (min)	R <sup>2</sup>
pH <sub>i</sub>	4	0.297	0.999	0.027	18.9	0.974
	6	0.300	1.000	0.024	21.0	0.989
	9	0.297	0.982	0.019	29.6	0.993
	11	0.297	0.993	0.015	34.0	0.943
spiked with 500 mg/L CaCO <sub>3</sub>		0.411	0.916	0.014	34.7	0.992

RESULTS AND DISCUSSION

Decomposition of COD and organic nitrogen

The results shown in Figure 1 indicate that degradation of organic-N follows zero order reactions for all samples. The reaction rate constants for degradation of organic nitrogen are listed in Table 1. Samples with lower initial pHs have higher degradation rates as seen by their higher reaction rate constants. The sample with its initial pH adjusted to 11 has almost the same reaction rate constant as the sample spiked with 500 mg/l CaCO<sub>3</sub> (0.015 vs. 0.014 min<sup>-1</sup>). Theoretically, ozone may transfer the organic nitrogen of acrylonitrile into ammonia-nitrogen (NH<sub>3</sub>-N). The decomposition of Org-N can be expressed by:

$$[\text{Org-N}]_t / [\text{Org-N}]_0 = K_{D,\text{Org-N}} \times Nt \tag{2}$$

- [Org-N]<sub>t</sub> = initial Org-N, mg/l,
- [Org-N]<sub>0</sub> = Org-N at time t, mg/l,
- K<sub>D,Org-N</sub> = the decomposition rate of Org-N, min<sup>-1</sup>
- t = reaction time, min.

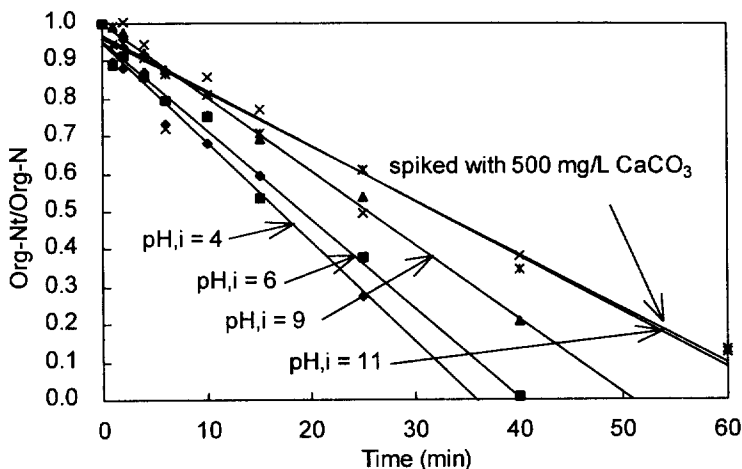


Figure 1. The organic nitrogen decomposition of acrylonitrile samples of various initial pHs and spiked with 500 mg/l  $\text{CaCO}_3$  during ozonation.

Based upon the observed zero-order degradation of the organic nitrogen, the time needed to complete 50% of the degradation reaction ( $t_{1/2}$ ) for each sample can be estimated and is listed in Table 1. The calculated  $t_{1/2}$  values are 18.87 min for the sample with the lowest initial pH of 4 and decreases with increasing initial pH levels. The ozone oxidation of organic nitrogen is accomplished through direct reaction by ozone and low pH condition is favorable to the reservation of molecular ozone. Anionic carbonate ions formed by alkalinity or carbon dioxide dissolved in the aqueous solution and some types of intermediate organic compounds can shorten the half-life time of ozone molecule, thus decreasing the organic nitrogen decomposition rate during higher initial pH ( $>pK_a = 6.3$  of  $\text{HCO}_3^-$ ) as well as under alkaline conditions (Hoigne and Bader, 1976; Guittouneau *et al.*, 1990).

Table 1 also lists the COD removal rate for the initial 2 minutes of reaction time. Samples with initial pHs adjusted to 4-11 have high but similar initial COD removal rates of around  $0.3 \text{ min}^{-1}$ . This observation indicates that the COD removal rate is not affected by the initial solution pH. In contrast, the acrylonitrile sample spiked with 500 mg/l  $\text{CaCO}_3$  shows the highest initial COD removal rate of  $0.411 \text{ min}^{-1}$ , which is 1.38 times higher than those of the samples without addition of  $\text{CaCO}_3$ . This implies that the C=C double bond of acrylonitrile can be oxidized by direct reaction with molecular ozone within a reasonable ozonation time (Hoigne and Bader, 1983).

#### ORP model

Variations of the solution pH and ORP during the ozonation of styrene- and acrylonitrile-containing ABS samples are shown in Figures 2 and 3. The strong oxidation reaction of ozone may react with the acrylonitrile solution especially for samples with low initial pH, and jump to the ultimate level within a very short period of time. The oxidation reaction may also decrease the solution pH simultaneously. Acrylonitrile and styrene samples with high initial pHs or spiked with 500 mg/l  $\text{CaCO}_3$  theoretically has more buffering capacity to resist change of pH with addition of acids, or it takes a longer time to reduce or increase its ORP level.

Utilizing a modified Nernst equation as proposed by Chang *et al.* (1994, 1996), variations of the ORP levels during the ozonation of acrylonitrile under various initial pH conditions can be simulated. The general form of the modified Nernst equation is shown in Equation (3):

$$\text{ORP} = A + B \times \text{pH} + C \times \ln[\text{Org-N}] + D \times \ln[\text{NH}_3\text{-N} + \text{NO}_3^-\text{-N}] \quad (3)$$

ORP = the red/oxid potential,  
 Org-N = organic nitrogen, mg/l,  
 $\text{NH}_3\text{-N}$  = ammonia nitrogen, mg/l,  
 $\text{NO}_3\text{-N}$  = nitrate nitrogen, mg/l.

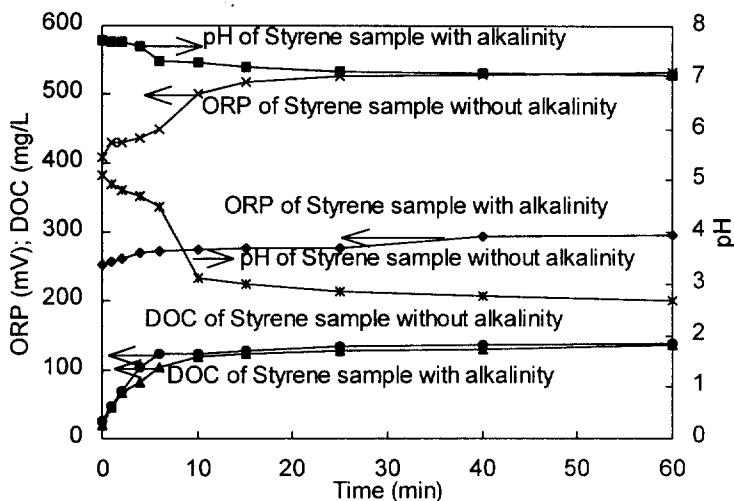


Figure 2. The pH and ORP profiles of styrene and styrene spiked with alkalinity during ozonation.

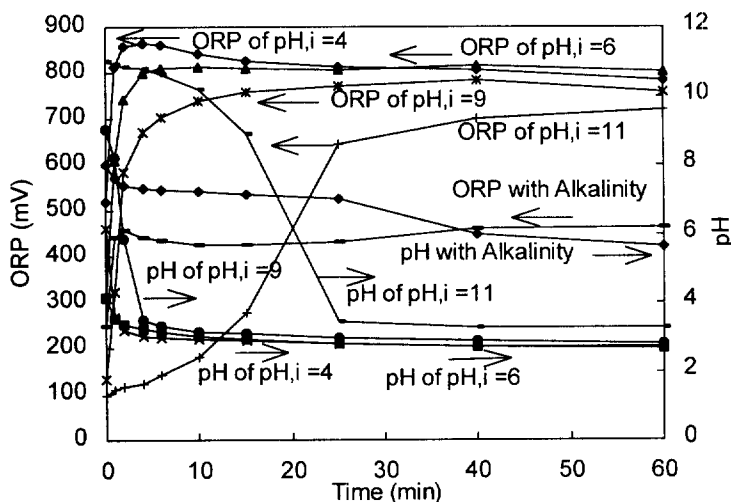


Figure 3. The pH and ORP profiles of acrylonitrile samples with various initial pH and alkalinity during ozonation.

Table 2 lists the modified Nernst equation for samples with pH values of 4, 6, 9, and 11. When all the laboratory data are taken into account, a correlation among the parameters used in Equation (3), i.e. A, B, C, and D are plotted vs. the solution pH in Figure 4. Thus, Equation (3) can be used to predict the ORP profile of the overall reaction. As shown by the plot in Figure 5, a good prediction of the calculated ORP values is obtained for the entire reaction period especially for the initial short period of reaction. Since the ozone oxidation rate of acrylonitrile is the highest during the initial short period of reaction time, the modified Nernst equation is of importance for the objective of optimizing the reaction time of the ozonation process.

Table 2. The modified Nernst equation of ORP during the ozonation of acrylonitrile under various initial pH cases

Initial conditions		Modified Nernst Model	R <sup>2</sup>
pH <sub>i</sub>	4	ORP = 1697.9 - 189.9 pH + 2.26 ln[Org-N] - 75.7 ln[NH <sub>3</sub> -N+NO <sub>3</sub> <sup>-</sup> -N]	0.738
	6	ORP = 1538.8 - 135.2 pH - 2.63 ln[Org-N] - 72.3 ln[NH <sub>3</sub> -N+NO <sub>3</sub> <sup>-</sup> -N]	0.945
	9	ORP = 642.9 - 43.9 pH + 29.53 ln[Org-N] - 41.2 ln[NH <sub>3</sub> -N+NO <sub>3</sub> <sup>-</sup> -N]	0.955
	11	ORP = 958.7 - 66.2 pH - 31.02 ln[Org-N] + 14.2 ln[NH <sub>3</sub> -N+NO <sub>3</sub> <sup>-</sup> -N]	0.998

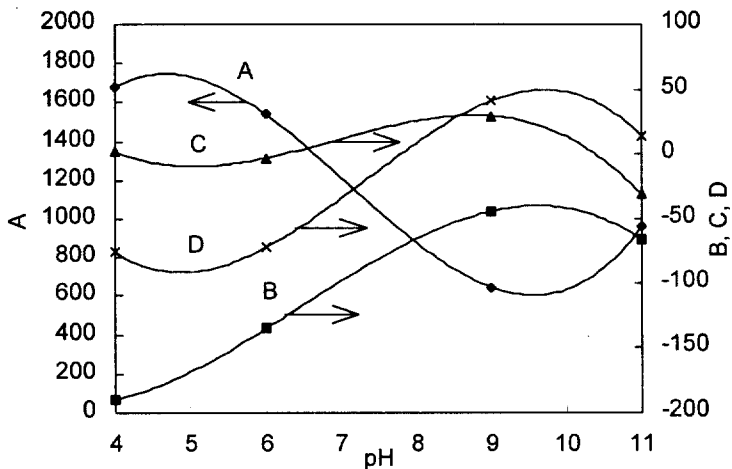


Figure 4. The A, B, C, D of modified Nernst equation (Eqn. 3) under various initial pH cases during ozonation of acrylonitrile.

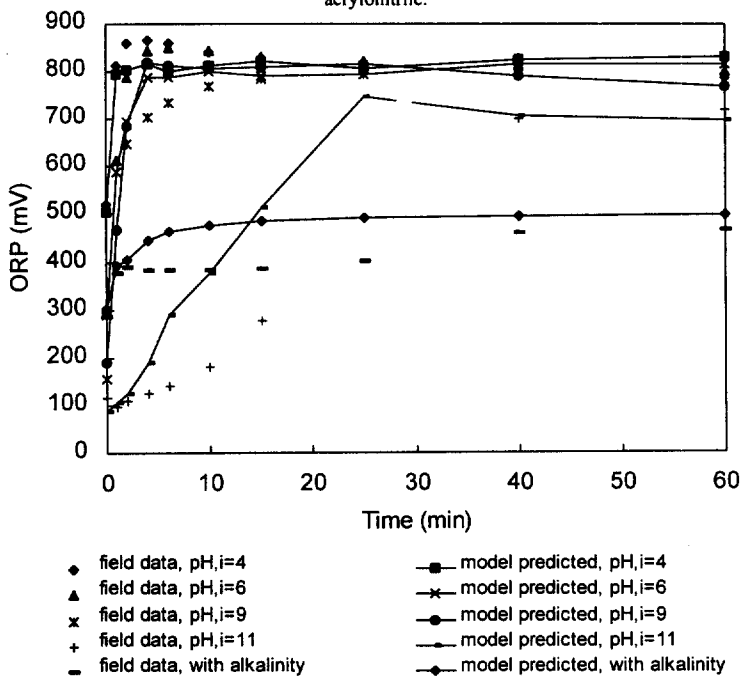


Figure 5. The simulated and observed data of acrylonitrile samples with various initial pH and alkalinity during ozonation.

Comparison of the COD removal of synthetic samples with pre-ozonation treatment for 5~10 min and of samples without ozone pre-treatment in the subsequent batch activated sludge treatment is shown in Figure 6. All samples shows a linear decrease of COD versus aeration time. For the three F/M values of 0.15, 0.23 and 0.35 day<sup>-1</sup>, samples with previous ozonation treatment have higher COD reduction rates than those without pre-ozonation treatment. This indicates that pre-ozonation will convert acrylonitrile and styrene molecules into more biodegradable substances such as soluble organic intermediates thus improving the COD removal efficiency of the subsequent biological process.

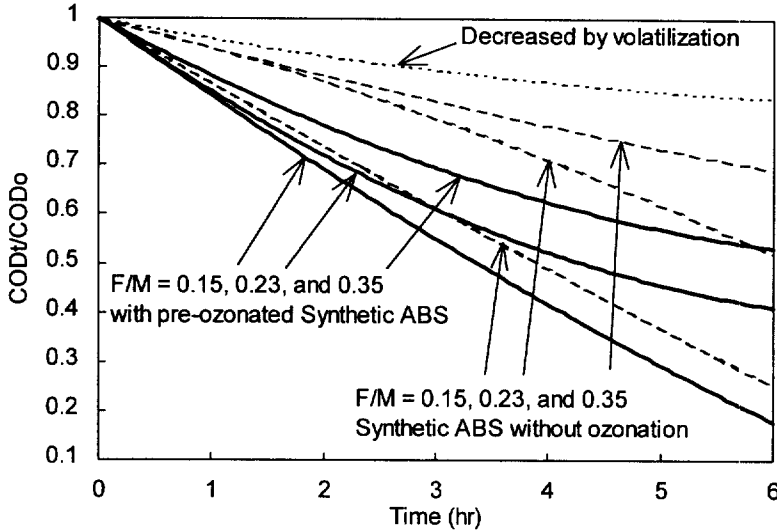


Figure 6. The removal rate of pre-ozonated and raw AN after batch biological treatment.

CONCLUSIONS

The ozonation process has been studied as a pre-treatment to oxidize the acrylonitrile and styrene molecules contained in a synthetic ABS wastewater. The high-alkalinity acrylonitrile sample has a high initial COD decomposition ( $K_{COD,i}$ ) rate, and the lower initial pH sample had a high organic nitrogen decomposition ( $K_{D,Org-N}$ ) rate. The modified Nernst model may be applied to simulate the variation of ORP values and thus can be used for controlling a proper ozone contact time during the decomposition of acrylonitrile. After the ozonation pre-treatment, styrene is converted to soluble organic intermediates which are more amenable to biological degradation. The ozone pre-treated synthetic ABS samples show better COD removal efficiencies in the subsequent batch activated sludge process than those without the pre-ozonation treatment.

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