

# Decomposition and Decoloration of Acid Orange 7 using Sub-critical Water Method

S. Daneshvar Hosseini, F. Salak Asghari, H. Yoshida

**Abstract**—Decomposition and decoloration of 4-(2-Hydroxynaphthylazo) benzenesulfonic acid sodium salt (acid orange 7) was studied as a model for textile wastes using a flow-type sub-critical water system. The experiments were performed in the temperature ranging from 180 to 374 °C at pressure range of 10-25 MPa. The main products from decomposition of acid orange 7 were found to be 1,1'-Binaphthalene-2,2'-diol, 2-naphthalenol, phenol, and N-(phenylmethylene)benzenamine. In order to identify the decomposition pathways, the products were also individually treated under a batch type sub-critical water condition. It was found that 2-naphthalenol underwent to further decomposition to 1,1'-Binaphthalene-2,2'-diol during the sub-critical water reaction. Other decomposition products were resulted from decomposition of directly acid orange 7.

**Key words**—Acid orange 7, Decoloration, Sub-critical water, Textile wastewater

## I. INTRODUCTION

Since the levels of wastes produced are increasing with the rise in human activity or industrial progress, natural processes do not have sufficient turnover to prevent these changes. Mainly, industrial plants generate a wide variety of water pollutants that are often difficult and costly to treat. For instance, the wastewater of synthetic color substances (dyes and pigments) is one of the most critical environmental problems we now face. This kind of wastewaters is generally high in both color and organic content.

At present over 100,000 different dyes are synthesized in industrial scale which the most applications are in the textile companies. One of the dyes used widely in the textile industries is acid dye. They are water soluble anionic dyes, containing one or more acidic groups along with one azo group.

By dyestuff manufacturing processes, a considerable

amount of high color intensity wastewater is generated which large quantities of these are released into the environment which have environmental impacts [1], [2]. The total dye consumption of the textile industry worldwide is in excess of  $10^7$  kg/year; consequently, approximately  $10^6$  kg/year of dyes are discharged into waste streams by textile industries [3].

For treatment of these kinds of wastewater, numerous conventional techniques so far have been reported [4]-[9]. Besides advantages of these methods in decolorization and toxicity reduction, these methods have some disadvantages. Since the mechanism involves flocculation, impurities are transferred from the wastewater to the sludge, which still needs ecologically questionable land-deposition [9].

Waste treatment processing by using water under its critical point may offer an alternative to the conventional methods. Sub-critical water (sub-CW) has been increasingly used for decomposition and degradation of variety of waste materials, as a green and environmentally friendly technique. Water at its critical status has properties that are different from water under normal conditions. Under conditions of high temperature and pressure, physicochemical properties of water are dramatically different from that of it at ambient temperature. Because of these properties, along with the low relative dielectric constant, which is comparable with that of methanol or acetone under ambient conditions, it seems to be a good alternative medium for variety of chemical reactions and processes.

So far there is no available report using water under its critical point for decomposition and decolorization of synthetic textile dyes and their wastewaters. Therefore in this research work, the aqueous solution of acid orange 7 (AO7) was selected for evaluation under sub-CW condition. The objective of this work is decomposition and decoloration of AO7 in flow-type sub-CW condition. Decomposition products were also identified in this research work.

## II. EXPERIMENTAL SECTION

### A. Materials

Chemicals (analytical grade) used in the experiments and calibration curves all were purchased from Wako Pure Chemical Industries, Ltd. (Japan). UPLC mobile phases were purchased from Waters Corporation (USA).

### B. Apparatus

We used home-built continuous sub-CW equipment depicted schematically in Fig. 1. The tube of this equipment made of stainless steel 316, od 1/16" and internal diameter of 0.5 mm (Swagelok AG, Switzerland). The feed solution (2000 ppm AO7), pre-heat solution (mili-Q water), and

**Submission date of camera ready: July 29, 2009**

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organic solvent (ethyl acetate) initially passed through multi channel degasser (Shimadzu degasser DGU-14A, Shimadzu Co. Japan). Two HPLC pumps (Shimadzu, LC-10AT, Shimadzu Co., Japan) were used to pump the feed and water to the reactor at required flow rates, respectively. The water after heating up to the same temperature as reaction temperature was mixed with the feed solution (AO7) and then passed through the reactor inside the salt bath. The salt bath was initially pre-heated to desire temperature. Flow rates of feed and water have been adjusted in order to stay in the laminar flow region and have a minimum deviation from an ideal isothermal plug flow reactor. Two single-path heat exchangers were used to cool the solutions to  $25 \pm 0.1$  and  $-5 \pm 0.1$  °C before and after reaction, respectively. In order to wash out the water insoluble products, an another HPLC pump (Shimadzu, LC-10AT, Shimadzu Co., Japan) was used to pump the organic solvent (ethyl acetate) into the line just before quenching the reaction (see Figure 1), the amount of ethyl acetate was always kept at 23% of total output solution. A back-pressure regulator (Tescom Corporation, USA) was used to maintain the pressure at the desired values.

At the end of the line of equipment, an UV-Vis detector (Shimadzu SPD-10AVP, Shimadzu Co., Japan) with A/O converter coupled with a PC was set to monitor the total absorbance of outlet reaction solution. The obtained absorbance of outlet solution indicated that the time was needed to reach to the steady-state conditions after experimental conditions changing.

### C. Procedure

The feed concentration of AO7 was kept at 2000 ppm. After mixing the pre-heat water (milli-Q water) and feed solution, because of the equal flow rates of them, the concentration of AO7 was diluted twice. The actual residence time ( $\tau$ ) was calculated as follows:

$$\tau = V\rho Fr^{-1} \quad (1)$$

where  $V$  is the reactor volume,  $Fr$  is the mass flow rate, and  $\rho$  is the density of reaction mixture.

The reaction temperature was fixed at from 180 to 374 °C using pressures up to 25 MPa and residence time 60s. Samples were taken in 25 cm<sup>3</sup> flasks and analyzed for remaining substrate and decomposition products.

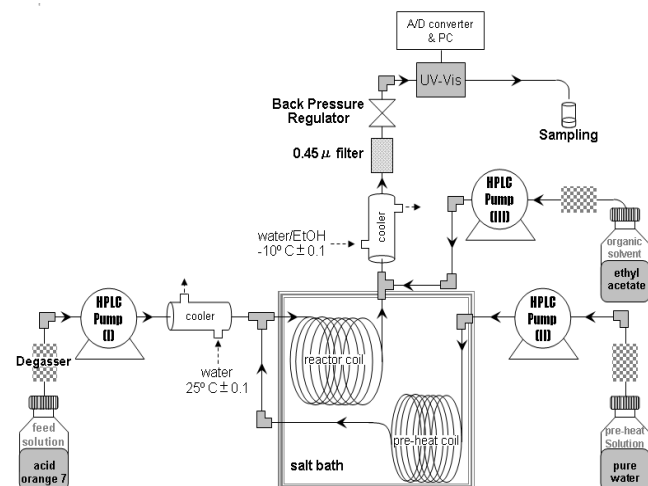


Fig. 1. Experimental set-up for flow-type sub-CW.

### D. Analysis

30 μL of internal standard solution (biphenyl, 12.480 g/L) was added to the 25 cm<sup>3</sup> sample solution (contained 77% of aqueous phase and 23% of ethyl acetate); after mixing well, it was transferred to a 50-cm<sup>3</sup> test tube containing 0.5 g NaCl as salting out agent. Then, the 25 cm<sup>3</sup> flask was rinsed 3 times with 2 cm<sup>3</sup> of water/ethyl acetate mixture (1:1), the rinsed solution (total volume of 6 cm<sup>3</sup>) were added to the above test tube. The test tube was shaken at 90 rpm on a rotary shaker at 20 °C for 1 h or longer to extract compounds from aqueous phase into ethyl acetate phase. Ethyl acetate and aqueous phases were analyzed for products and remained AO7 separately, respectively.

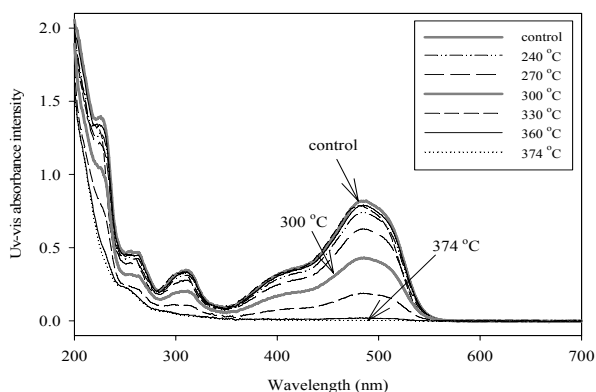
A GC-MS (Gas Chromatograph Mass Spectrometer GC-17A and GCMS-QP5050, Shimadzu) with an Ultra Alloy capillary column (15 m, id. 0.25, and film thickness of 0.25 μm) was used to identify the decomposition products of AO7. For quantification of products, the ethyl acetate phase was evaporated and resolved composition in 3 cm<sup>3</sup> of acetonitril. Then it was analyzed by an Acquity UPLC BEH C18, 1.7 μm, 2.1 × 50 mm column in an Ultra-Performance Liquid Chromatography (UPLC, Waters, USA) apparatus, using a Waters (Binary Solvent Manager) solvent delivery module coupled with TUV detector which was set at 270 nm (Waters, USA). Column temperature was kept at 30 °C. For quantification of remained dye in aqueous phase, a simple photometric method using a Shimadzu UV-2450 double beam UV-Visible spectrophotometer (Shimadzu Co. Japan) was utilized.

## III. RESULTS AND DISCUSSION

In order to evaluate the possibility of decomposition of AO7 under sub-CW conditions, a series of experimental studies were conducted under temperatures ranging from 180 to 374 °C at 25 MPa for reaction time 60 s. By increasing the temperature, the color of solution turned from orange to colorless, and finally at above 360 °C completely colorless solution was obtained.

Uv-vis scanning spectra of above solutions are shown in Fig. 2. Mainly, AO7 showed three absorbance peaks around 485, 310, and 230 nm. By increasing sub-CW temperature, the peaks were declined and reached zero at temperatures higher than 360 °C. It clearly proved decoloration and consequently decomposition of AO7 to other compounds under sub-CW condition.

Several reaction products have been identified from decomposition of AO7. Some of them are listed in Table I. In a previous report [10], to obtain more insight into reaction paths, products were also treated (as substrate) under the same conditions as initial feed; however, in this research work because of insolubility of decomposition products, for evaluation of decomposition pathways, all identified products were treated as substrate in batch type sub-CW reactor. AO7 was only treated under flow-type sub-CW condition.



**Fig. 2.** UV-Vis spectrum of AO7 before and after sub-CW treatment at residence time of 60 s and pressure of 25MPa.

Results proved that except 1,1'-Binaphthalene-2,2'-diol, all products derived directly from decomposition of AO7; however, sub-CW treatment of 2-naphthalenol produced 1,1'-Binaphthalene-2,2'-diol as main product. 1-naphthalenol was resulted from decomposition of AO7, we did not identify it from sub-CW treatment of 2-naphthalenol.

Meanwhile, the concentrations of main products along with remained AO7 were quantified. Fig. 3 shows the temperature course of remained AO7, phenol, N,1-di(phenyl)methanimine, 2-naphthalenol, and 1,1'-Binaphthalene-2,2'-diol.

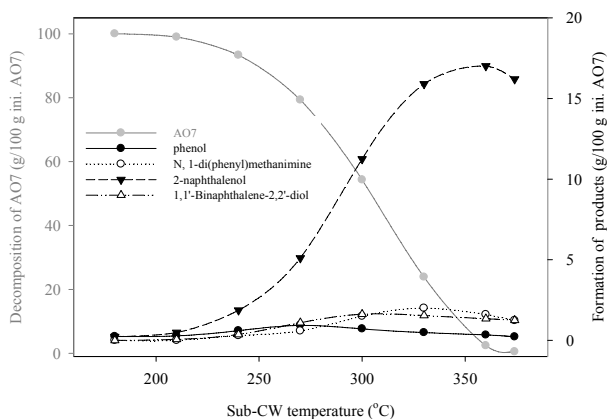
AO7 concentration declined by increasing temperature; decomposition products generally increased by temperature up to from 330 to 360 °C, afterward declined by increasing temperature due to decomposition reactions. Compare to other products, 2-naphthalenol was the main decomposition product.

**Table I.** Identified products from typical decomposition of AO7 and 2-naphthalenol in typical sub-CW condition.

substrate			
Acid Orange 7		2-naphthalenol	
a	phenol	a'	1,1'-Binaphthalene-2,2'-diol <sup>2</sup>
b	1-naphthalenol <sup>1</sup>	b'	
c	2-naphthalenol	c'	
d	1,1'-Binaphthalene-2,2'-diol	d'	
e	N,1-di(phenyl)methanimine	e'	

1. minor products

2. the only identified product from 2-naphthalenol



**Fig. 3.** Concentration profiles of AO7 and formation products as function of sub-CW temperature at 25 MPa for 60s.

#### IV. CONCLUSION

Decomposition of AO7 as a model for textile wastewater was investigated in flow-type sub-CW at temperature range of 180 to 374 °C and pressure of 10-25 MPa. The decomposition of AO7 was a function of treatment temperature and residence time. The main identified product was 2-naphthalenol. Other small decomposition products were phenol and N,1-di(phenyl)methanimine. Also, it was found that 1,1'-Binaphthalene-2,2'-diol was produced by decomposition of 2-naphthalenol.

Results proved that sub-CW was capable to efficiently decolorize and decompose AO7 using water as clean, the most abundant, and no toxic solvent. This proposed green method can be scaled up to industrial levels for treatment of dye containing textile wastewaters without the problem of plugging.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of a part of this work provided by the ministry of Education, Culture, Sports, Science and Technology of Japan in the form of 21st Century COE program (E19, Science and Engineering for Water Assisted Evolution of Valuable Resources and Energy from Organic Wastes).

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