

## Sonodegradation As An Effective Advanced Oxidation Process Tool For The Decontamination of Aniline Residues

<sup>1</sup>Mohammed Ashiq .S and \*Jayachandran.K<sup>2</sup>

Bioprocess Lab, School of Biosciences, Mahatma Gandhi University, P.D.Hills, Kottayam, Kerala, India

\*Corresponding author: jayachandrank@mgu.ac.in

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### Abstract

The destruction of toxic organic molecules using advanced oxidation process (AOPs) is a potent tool for pollution control and environmental protection. Ultrasound is a convenient and effective method of generating hydroxyl radicals which is the key oxidant in AOPs. In the present study an attempt was made to bring decontamination of aniline through sonodegradation, specifically at 350 HZ and 620 HZ in the pH range 4-10. The degradation profile was traced through estimation of aniline by diazocoupling reaction and also through HPLC. Sonodegradation at 620 HZ was found to be more effective than that at 350 HZ. Percentage degradation of aniline was found to be maximum at pH 4 and 7. Sonodegradation could bring down the concentration of aniline to a minimum value but could not effect complete removal. Combination of the process of sonodegradation with other techniques such as biodegradation is necessary to completely eliminate the aniline residues.

**Keywords:** Advanced oxidation process, sonodegradation,, aniline removal , pH , Diazo coupling method, HPLC

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### I. Introduction

Hazardous waste materials from industrial, commercial operations represents greatest challenge to the environment. Novel advanced oxidation processes (AOPs) show great promise for application in many wastewater treatment areas. AOPs utilize very strong oxidizing power of hydroxyl radicals to oxidize organic compounds to the preferred end products of carbon dioxide and water. During the past several years, ultrasound has been effectively applied as an emerging advanced oxidation process (AOP) for a wide variety of pollutants in wastewater treatment. It is proven to be an effective method for degrading organic effluents into less toxic compounds and able to mineralize the compounds completely in certain cases [1]. Various aromatic compounds, i.e., nitrobenzene, aniline, phenol, benzoic acid, salicylic acid, 2-chlorophenol, 4-chlorophenol, styrene, chlorobenzene, toluene, ethylbenzene and *n*-propylbenzene were decomposed under identical ultrasonic irradiation conditions [2]. The application of ultrasonic technology has been receiving wide attention in wastewater treatment and environmental remediation areas. The ultrasound process does not require addition of oxidants or catalyst, and does not generate additional waste streams as compared to adsorption or ozonation processes [3]. Ultrasound process is also not affected by the toxicity and low biodegradability of compounds [4].

When aqueous solutions are irradiated with ultrasound the H-O bond in water is homolytically cleaved to form hydroxyl radicals and hydrogen atoms. This process is the result of cavitation, whereby very high temperatures and pressures are generated within an imploding bubble. The fate of both these species depends on the conditions of the reaction and the presence of other (organic) compounds. The most common reaction is dimerisation of the hydroxyl radical producing hydrogen peroxide and the amount of H<sub>2</sub>O<sub>2</sub> generated is often used as a measure of the effectiveness of the ultrasonic equipment employed. The sono-degradation of simple polycyclic aromatic hydrocarbons follows first order kinetics [5] corresponded closely to the solubility of the substrates in water. The rate of degradation was substantially decreased in the presence of other organics due to radical scavenging. The studies were extended by investigating the cyclic hydrocarbons (C<sub>6</sub>H<sub>x</sub>): benzene, 1, 3-cyclohexadiene, 1, 4-cyclohexadiene and cyclohexene [6]. The sonolysis of 4-nitrophenol in argon-saturated water using 321 kHz and found that at pH 10, when the 4-nitrophenol was fully deprotonated, the degradation proceeded by hydroxyl radical action [7]. A study of the degradation of 4-nitrophenol using ultrasound operating at 25 and 40 kHz and, interestingly, a combination of these two frequencies showed that the joint mode of operation improved the rate of degradation probably due to an increase in acoustic pressure experienced with the dual frequency [8]. Aniline residues have been observed in many industrial effluents including that from textile and paint industries. Being a nitrogenous aromatic compound and also being produced in considerable amount in effluents it is difficult to bring complete removal of aniline residues in waste waters using a single process. In the present work sonodegradation at various frequencies have been evaluated for its efficiency to bring aniline

decontamination. Sonodegradation could be an effective choice at primary level as the treatment can be done at lesser time for a greater volume of wastewaters.

## II. Materials And Methods

### 2.1 Aniline containing Sample

Mineral salt aniline medium (MSAM) with the composition: 1g  $\text{KH}_2\text{PO}_4$ , 1g  $(\text{NH}_4)_2\text{SO}_4$ , 0.5g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.001  $\text{CaCl}_2$  anhydrous in one litre of aqueous medium with 5 mM aniline concentration was used for the sonodegradation studies.

### 2.2 Sonodegradation of aniline sample

#### 2.3 The equipment

The device used for sonodegradation was Transducer L 3 ELAC (Nautik) powered by an Allied Signal with RF amplifier T and C power communication (Model AG 1006). Ultra sound is considered to be the region between 18 KHz up to 10MHz and is responsible for a huge number of chemical and physical effects.

#### 2.3 Sonodegradation

The sonodegradation studies were performed with 100ml MSAM with 5 mM aniline concentration and was subjected to degradation under 350KHz, 60W, 1 hr at 25°C and 620 KHz, 60W, 1 hr at 25°C. After one hr, 5 ml of sample was taken from flask and was extracted with equal volume of ether. Same condition without sonodegradation was used as the control. The extracted sample was analysed with spectrophotometer (555nm, diazocoupling method) and HPLC. The degradation test was performed at different pH of 4, 6, 7, 8, and 10 and the respective concentration of aniline in each case was noted both spectrophotometrically and also through HPLC.

#### 2.4.Hplc

All the extracted samples were subjected to HPLC analysis. The instrument was High Performance Liquid Chromatography (Shimadzu LC 10 AS) coupled with UV-Vis detector (Shimadzu SPD 10A). An isocratic elution of acetonitrile and water (78:22) at a flow rate of 1 ml min<sup>-1</sup> (250 mm × 4.6 mm × 5 μm Supelcosil C18 column) was used for the analysis of all samples.

## III. Results And Discussion

Aniline and its derivatives are highly toxic compounds, with many number of reports on carcinogenic effects[9]. Hence removal of aniline from respective industrial effluents is highly essential. Eventhough many physical, chemical and biological methods have been designed for the removal of aniline from industrial effluents, none of these methods is individually efficient. Hence it is always the combination of various strategies which is found to be practically efficient, particularly in the large scale treatment of the effluent. Generally ultrasonic degradation is a non-random process, with cleavage taking place roughly at the centre of the molecule and the rate of degradation is reported to be faster with larger molecules [10]. Sonodegradation also facilitates large scale treatment of the effluent in minimum time. Decontamination of aniline residues generally necessitates application of combined effect of various strategies for the complete mineralisation. In the present study sonodegradation has been considered as a physical method of waste water treatment at the primary level for the decontamination of aniline. The effectiveness of Sonodegradation in the decontamination of specific pollutants is very much determined by the frequency and the pH at which the treatment is done. The ultrasound enhanced degradation of aniline was studied in the presence of ozone [11]. It was found that little decomposition was observed with ultrasound alone although ozone on its own did give complete removal after 25 min. The combination technique was not only effective in rapidly oxidising aniline but gave a much better TOC decrease.

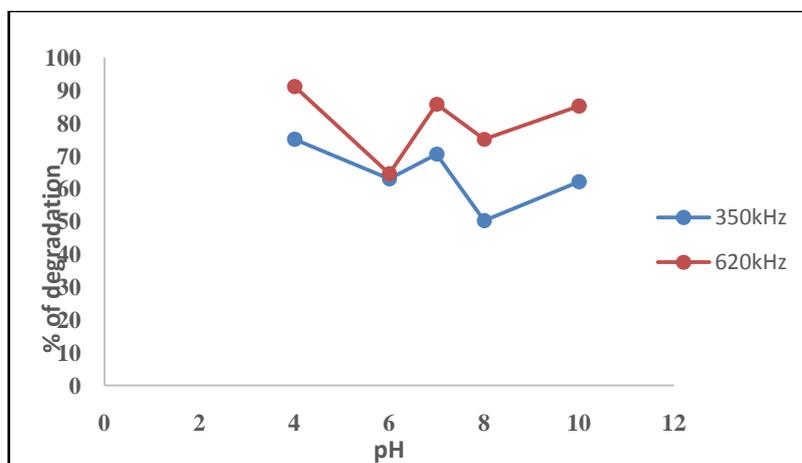
The sonolytical degradation of *p*-nitrophenol in aqueous solution and interpreted the results using an elaborate model involving both hydroxyl attack and pyrolysis reactions [12]. The sonication of phenol yields acetylene as well. The formation could be inhibited almost completely by increasing the pH, thus ionizing the phenol molecule. Increasing the pH also decreased the degradation of phenol significantly, which shows that phenol degrades at least partially by pyrolysis in the bubble phase [13].

In the present study sonodegradation of aniline was performed at a frequency of 350 HZ and 620 HZ at pH of 4,6,7,8 and 10. Spectrophotometric estimation by diazocoupling method showed effective removal of aniline both at 350 HZ and 620 HZ [Fig.1]. In the Fig. 2 representing the control at pH 4 the aniline specific peak was observed at 3.4 minutes and the peak area corresponding to the concentration of aniline was 121.4 which on sonodegradation at 350 HZ got reduced to 28.560 on treating at 350 HZ and to 8.68 on treating at 620 HZ [Fig.3 A and B]. At pH 6 the control peak area was 96.5 and after the sonodegradation at 350 HZ and 620 HZ the area respectively got reduced to 34.99 and 33.121. At pH 7 the degradation efficiency was better; i.e. a peak area reduction from 231.25 to 66.25 at 350 HZ (71.34% reduction) and to 33.95 at 620 HZ (85.33% reduction).

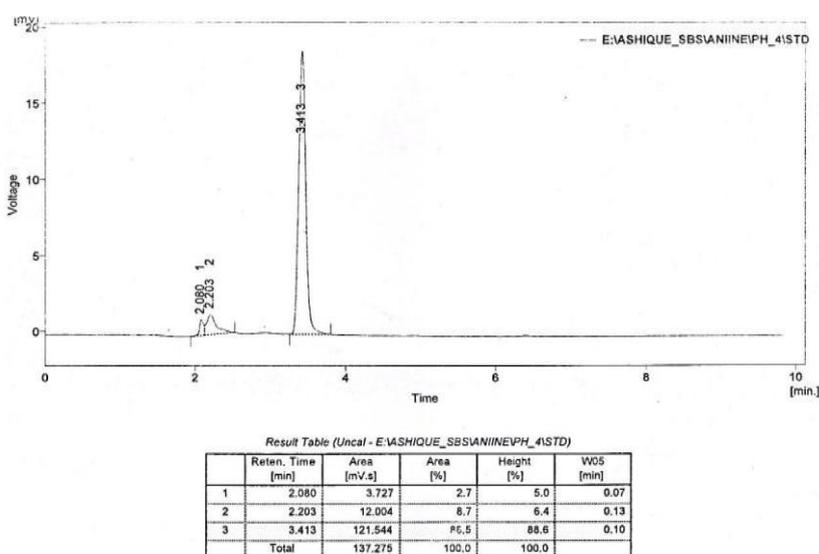
The degradation rate was higher on treatment at 620 HZ all pH tested. At both the frequencies better removal was observed at pH 4 and 7. Eventhough complete removal of aniline could not be achieved in both the cases; considerable reduction could be initiated at pH 4 and 7. The same trend was observed with HPLC analysis [Fig.2 to Fig.11].

The percentage degradation analysis based on HPLC peak area proved highest reduction in aniline concentration in the sample treated by sonodegradation at pH 4 with frequency of 620 HZ. [Table]. Another observation which could be made based on the present study was reduction in the rate at both pH 6 and 8 in both the cases of 350HZ and 620 HZ. However both at pH 4 and 7 the percentage reduction in aniline concentration was higher. Aniline is an aromatic primary amine compound and hence it is weakly basic. In water aniline is mostly existing as anilinium ion ( conjugate acid) and hence is less stable and easy to get degraded. The less stable nature of anilinium ion is based on the various resonating structures and hence influenced by the pH at which it is present .This might be the reason for getting different percentage reduction at various pH on sonodegradation.

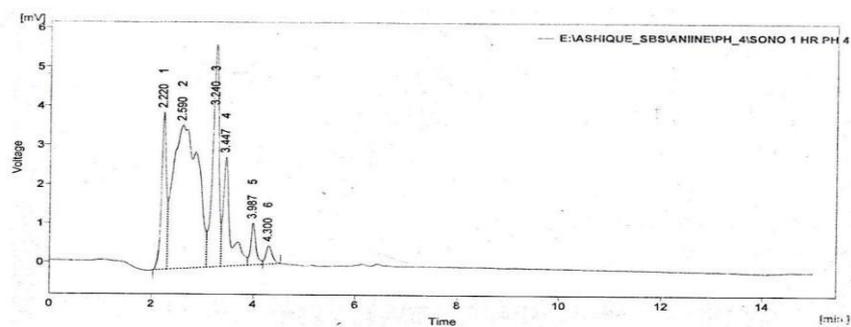
Eventhough complete degradation is not achieved by sonodegradation, the present strategy can be considered as a primary treatment method for the large scale treatment of the aniline containing effluent. When much reduction of the initial higher concentration of the specific pollutant is achieved ,the secondary treatment involving that of biological action can be more effectively implemented for the large scale management of the aniline containing effluent from various industries.



**Fig.1.**Percentage degradation of aniline at various pH by sonodegradation at a frequency of 350 HZ and 620 HZ-aniline estimated by diazocoupling method



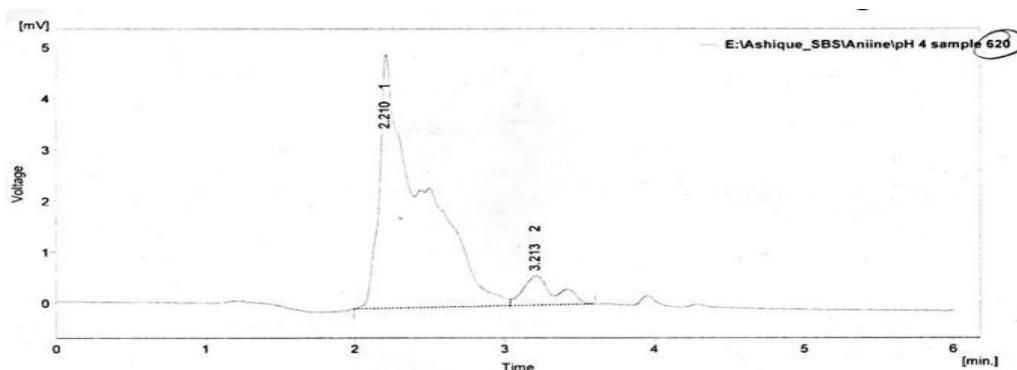
**Fig- 2.** HPLC of control ( pH 4) showing aniline (3.4min.RT) specific peak area 121.54  
 B. Sonodegradation at 620 kHz frequency, specific peak area 8.680.



Result Table (Uncal - E:\ASHIQUE\_SBS\ANIINEPH\_4\SONO 1 HR PH 4)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]
1	26.143	10.9	22.7	0.11
2	124.511	52.0	20.7	0.64
3	48.208	20.1	32.1	0.13
4	28.560	11.9	15.8	0.12
5	7.545	3.2	6.1	0.10
6	4.201	1.8	2.6	0.14
Total	239.269	100.0	100.0	

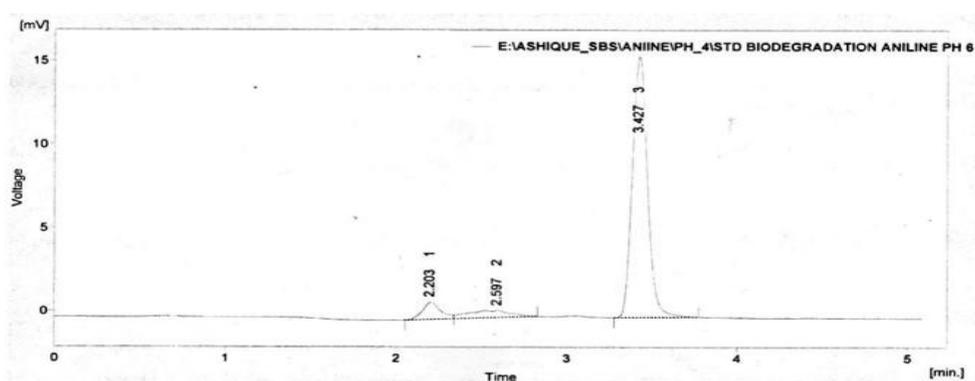
A. Sonodegradation at 350 kHz frequency, specific peak area 28.560



Result Table (Uncal - E:\Ashique\_SBS\AniinepH 4 sample 620)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]
1	97.628	91.8	89.6	0.19
2	8.680	8.2	10.4	0.18
Total	106.308	100.0	100.0	

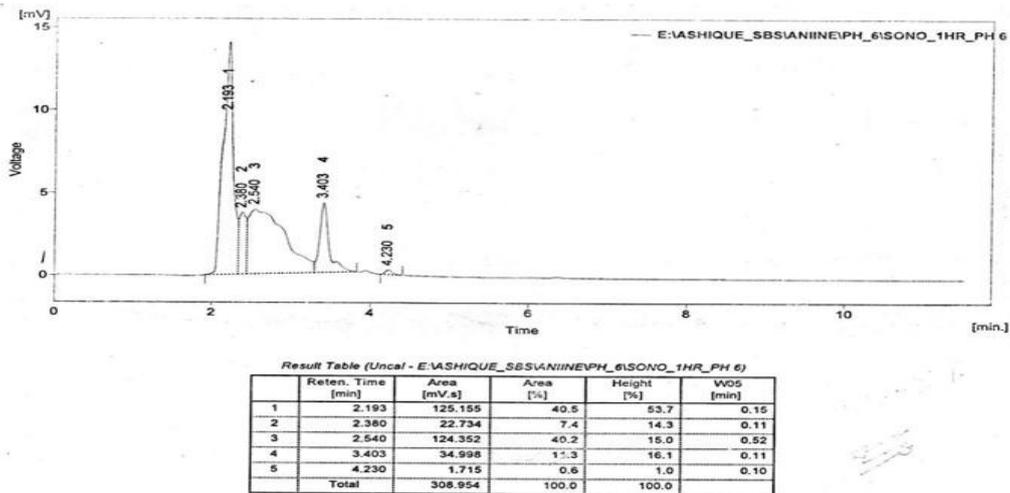
Fig-3. HPLC of sonodegraded sample(pH 4) showing aniline (3.4 RT) A and B



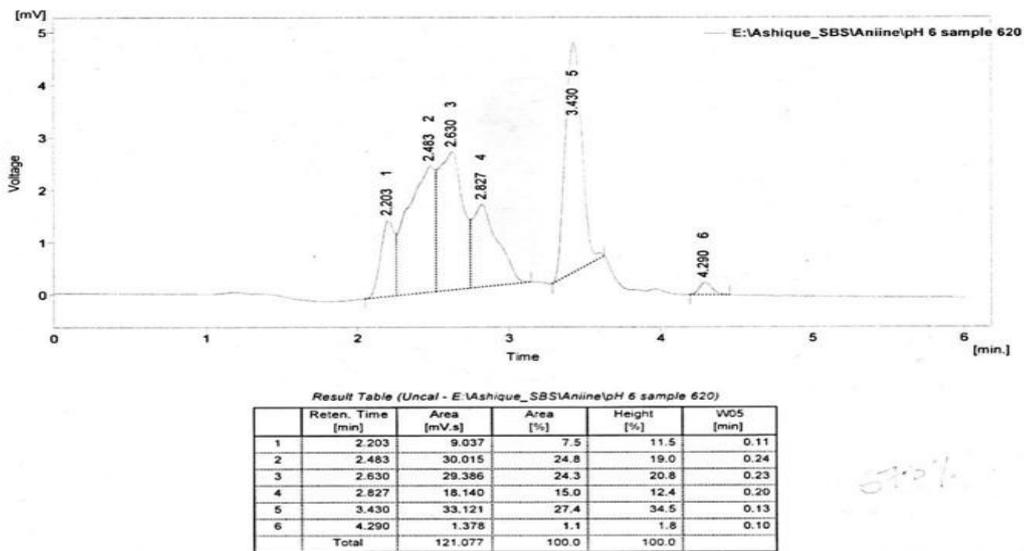
Result Table (Uncal - E:\ASHIQUE\_SBS\ANIINEPH\_4\STD BIODEGRADATION ANILINE PH 6)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]
1	7.476	6.7	6.0	0.11
2	7.526	6.7	2.4	0.33
3	96.608	86.6	91.6	0.10
Total	111.610	100.0	100.0	

Fig- 4. HPLC of control ( pH 6) showing aniline (3.4min.RT) specific peak area 96.5



A. Sonodegradation at 350 kHz frequency, specific peak area 34.99



B. Sonodegradation at 620 kHz frequency, specific peak area 33.121

Fig-5. HPLC of sonodegraded sample(pH 6) showing aniline (3.4 RT)- A and B

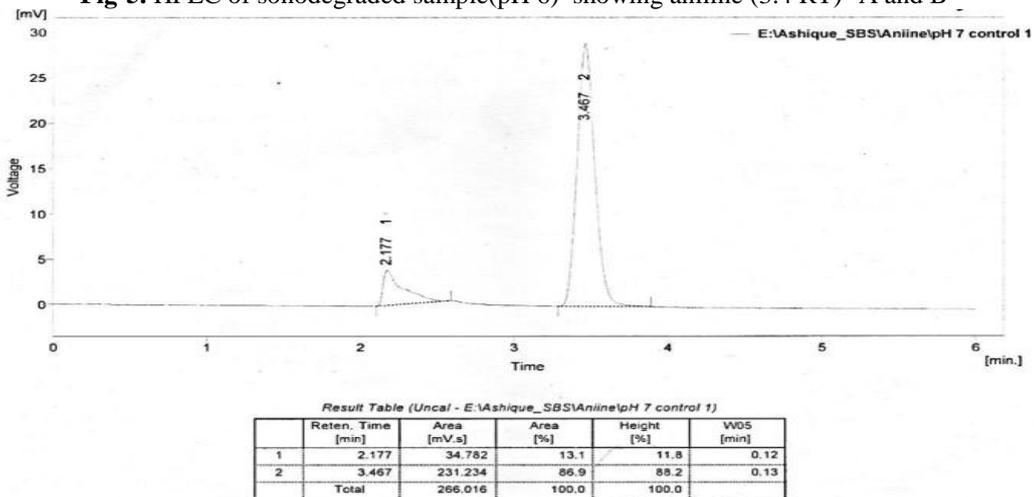
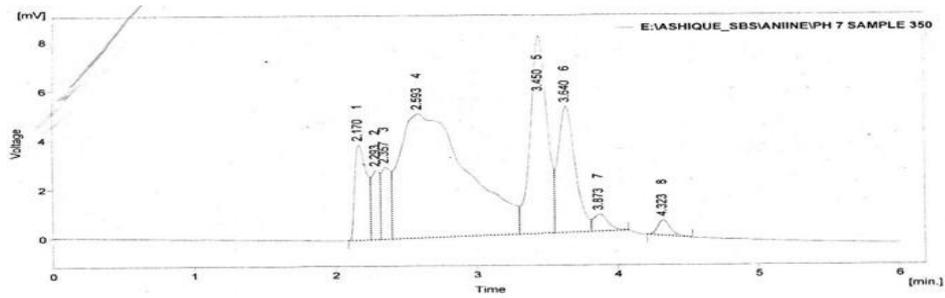


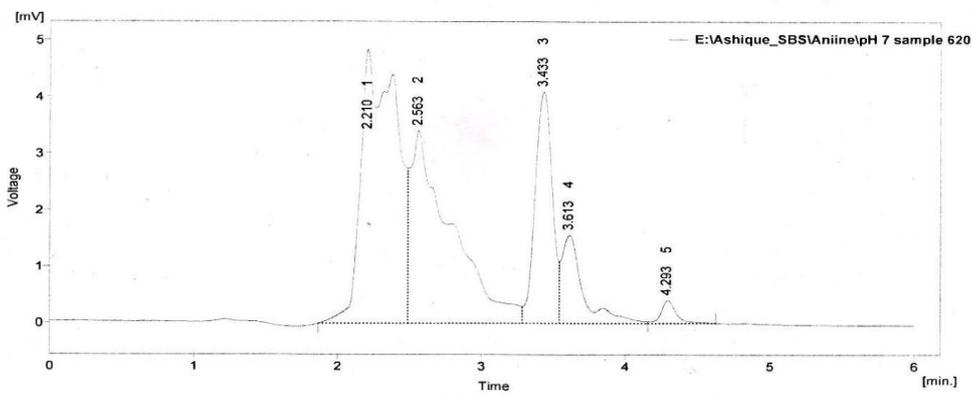
Fig- 6. HPLC of control ( pH 7) showing aniline (3.4min.RT) specific peak area 231.23



Result Table (Uncal - E:\ASHIQUE\_SBS\ANIINE\PH 7 SAMPLE 350)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]
1	22.891	6.8	13.3	0.12
2	11.354	3.4	9.7	0.07
3	13.581	4.0	10.0	0.08
4	170.418	50.8	17.3	0.57
5	66.255	19.7	27.6	0.13
6	43.619	12.9	17.6	0.16
7	4.948	1.5	2.4	0.12
8	3.828	1.1	2.1	0.10
Total	336.895	100.0	100.0	

A. Sonodegradation at 350 kHz frequency, specific peak area 66.25

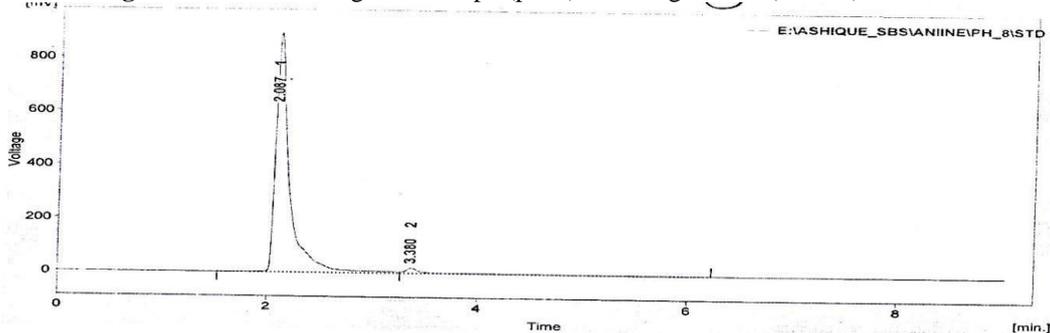


Result Table (Uncal - E:\Ashique\_SBS\Aniine\pH 7 sample 620)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]
1	83.414	40.9	33.9	0.34
2	67.331	33.0	23.8	0.34
3	33.925	16.6	28.6	0.13
4	16.273	8.0	10.9	0.14
5	2.939	1.4	2.8	0.10
Total	203.882	100.0	100.0	

B. Sonodegradation at 620 kHz frequency, specific peak area 33.95

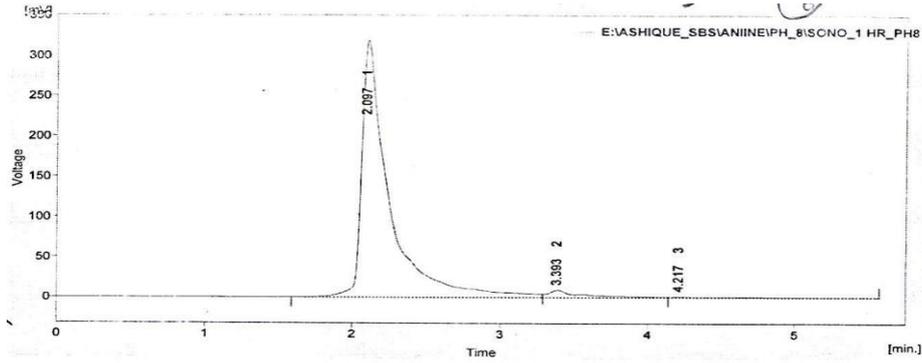
Fig-7. HPLC of sonodegraded sample(pH 7) showing aniline (3.4 RT)-A and B



Result Table (Uncal - E:\ASHIQUE\_SBS\ANIINE\PH\_8\STD)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]
1	8233.350	96.1	97.8	0.12
2	335.597	3.9	2.2	0.12
Total	8568.947	100.0	100.0	

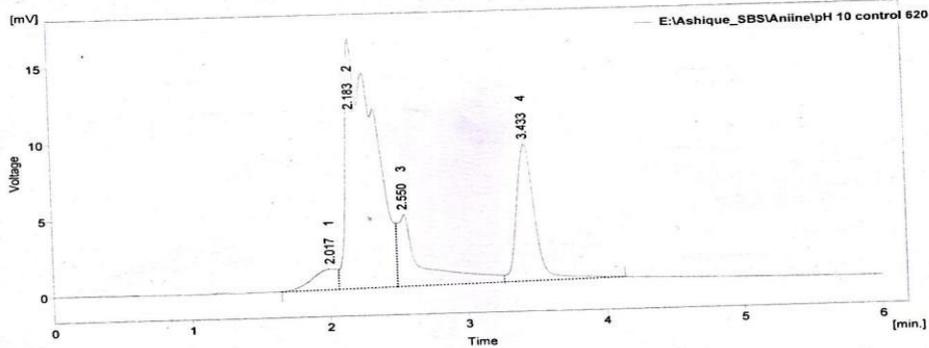
Fig- 8. HPLC of control ( pH 8) showing aniline (3.38min.RT) specific peak area 335.567



Result Table (Uncal - E:\ASHIQUE\_SBS\ANIINE\PH\_8\SONO\_1 HR\_PH8)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]	
1	2.097	4120.492	95.1	96.7	0.16
2	3.393	165.752	3.8	2.8	0.16
3	4.217	46.811	1.1	0.5	0.44
Total		4333.054	100.0	100.0	

A. Sonodegradation at 350 kHz frequency, specific peak area 165.72

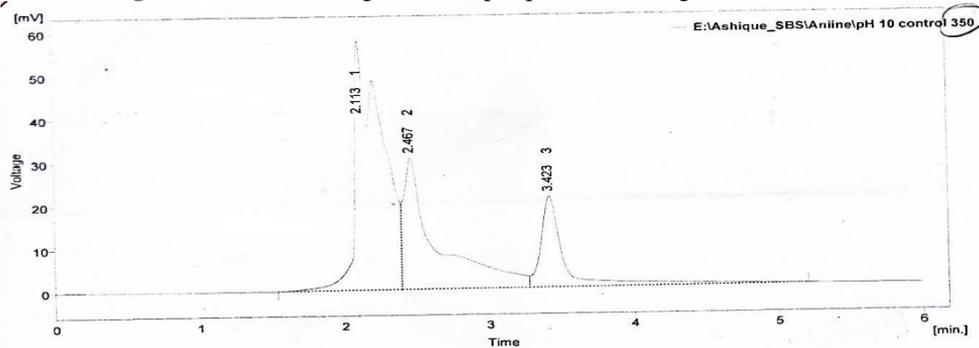


Result Table (Uncal - E:\Ashique\_SBS\ANIINE\pH 10 control 620)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]	
1	2.017	17.291	4.3	4.3	0.20
2	2.183	238.687	60.0	52.0	0.27
3	2.550	59.782	15.0	15.0	0.11
4	3.433	81.836	20.6	28.6	0.14
Total		397.595	100.0	100.0	

B. Sonodegradation at 620 kHz frequency, specific peak 81.83

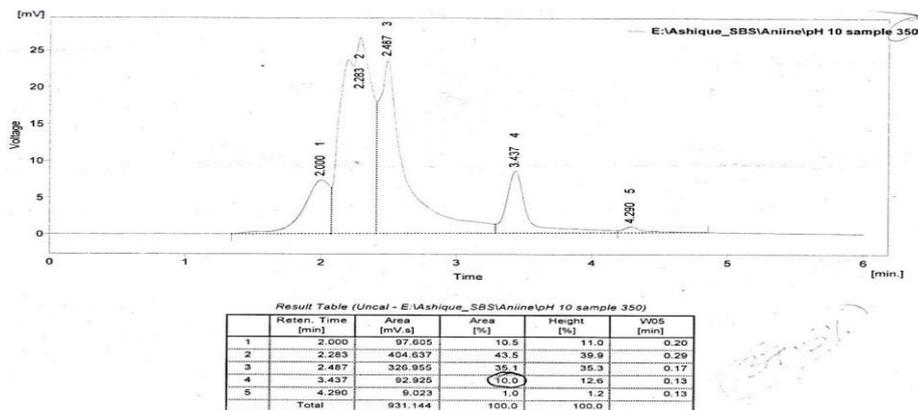
Fig-9. HPLC of sonodegraded sample (pH 8) showing aniline (3.4 RT)



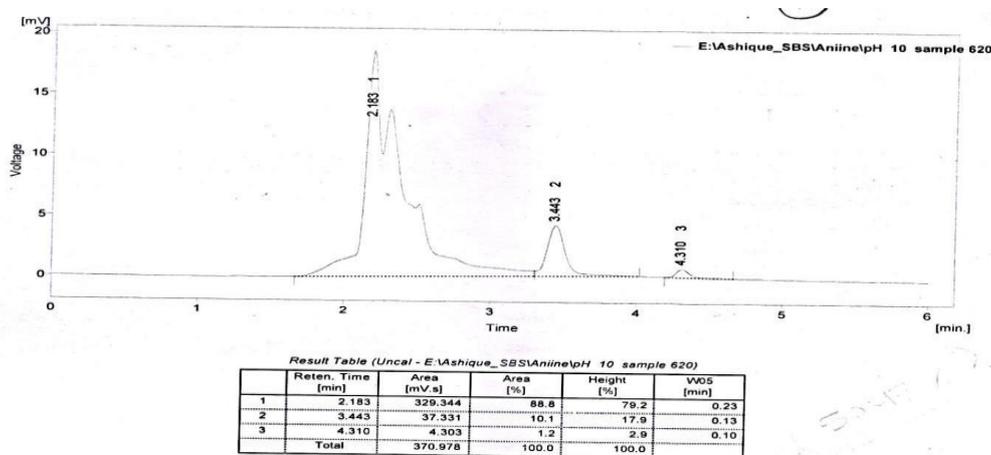
Result Table (Uncal - E:\Ashique\_SBS\ANIINE\pH 10 control 350)

Reten. Time [min]	Area [mV.s]	Area [%]	Height [%]	W05 [min]	
1	2.113	774.514	51.8	52.8	0.25
2	2.467	482.325	32.2	27.9	0.14
3	3.423	238.829	15.0	19.3	0.13
Total		1495.768	100.0	100.0	

Fig- 10. HPLC of control ( pH 10) showing aniline (3.38min.RT) specific peak area 238.92



A. Sonodegradation at 350 kHz frequency, specific peak area 92.925



B. Sonodegradation at 620 kHz frequency, specific peak 37.33

Fig-11. HPLC of sonodegraded sample(pH10) showing aniline (3.4 RT)

Table Percentage degradation of aniline at various pH by sonodegradation at a frequency of 350 HZ and 620 HZ-aniline estimated by HPLC

pH	Aniline peak area (3.4 RT)	Sonodegradation			
		350kHz	% of degradation	620kHz	% of degradation
4	121.54	28.56	<b>76.05</b>	8.68	<b>92.85</b>
6	96.60	34.99	<b>63.77</b>	33.12	<b>65.71</b>
7	231.23	66.25	<b>71.34</b>	33.92	<b>85.33</b>
8	335.56	165	<b>50.82</b>	83.54	<b>75.10</b>
10	238.92	92.92	<b>61.10</b>	37.33	<b>84.37</b>

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