A Comprehensive Approach for the Characterization of Pulp and Paper Industry Post Oxygen Stage Effluent

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Abstract

The pulp and paper industry post oxygen stage effluents containing high percent of colour causing lignin and degraded lignin compounds have been analyzed using a combination of U.V-Visible, FTIR and ^{13}C NMR spectroscopy. The colour is mainly due to the presence of chromophoric groups in these compounds. The post oxygen effluent mainly contains lignin fragments and the possible compounds present may be vanillin, syringaldehyde , p-hydroxy benzaldehyde, vanillic acids, syringic acids, p-Hydroxy benzoic acid, fervilic acid and p-coumaric acids. The chromophoric groups can be oxidised by ozone treatment for the reduction of colour efficiently.

Keywords: Effluent, lignin, chromophore, spectral analysis.

Introduction

Wood and bamboo, the main raw materials used for pulping contain cellulose, hemicelluloses, lignin and extractives. The basis of pulping is to remove maximum content of lignin (an aromatic colored polymer which gives structural strength to wood) from cellulose fibres. Oxygen delignification is a commonly used process in paper industry to further remove lignin content and reduce the bleach chemicals and cost. The washing liquors from pulping and oxygen delignification stage are burned in recovery plant to get the input chemicals, and to produce energy and steam. The pulp from oxygen delignification stage still contains residual black liquor which is washed at post oxygen stage. The pulp from post oxygen stage is subjected to different bleaching sequences to produce bleached pulp. The washing liquors from post oxygen stage having large amount of dissolved organic materials from the degradation of lignin are mainly responsible for colour load in pulp and paper industry effluent.

The paper industry is highly water intensive. About 150-200 m^3 of fresh water is required for the production of one ton of paper and 75% of which is discharged as effluent[1]. The reutilization of the post oxygen stage effluent is highly essential in the process plant in order to reduce water consumption and for the decolourization of discharged effluent. During the past decade, a number of studies have been addressed to lignin oxidation with molecular oxygen under alkaline condition[2]. The early efforts centered on elucidating the reaction mechanism of oxygen delignification using lignin model compound under homogeneous reaction conditions[3-4]. Moieties bearing free phenolic hydroxyl groups exhibited a higher reactivity towards oxidation than their etherified counterparts[5-7]. A reaction mechanism was proposed earlier based on the accumulated data, which involves the phenolate anions formed under the alkaline conditions of the process, being converted into phenoxy radicals followed by the formation of hydroperoxides and the eventual degradation of aromatic rings to muconic acids[8]. Further developments in this area have been associated with structural studies of lignin isolated from oxygen delignified pulp using the effluent liquor. Condensed structures such as biphenyl methane and biphenyls are found to be resistant during oxygen delignification and are held responsible for the slow phase of oxygen delignification[9]. Phenyl coumaran structures are produced to be least stable among the resistant condensed moieties[10]. The α-hydroxyl phenyl and 5,5' biphenyl structure are found to be fairly stable towards oxidation and their structure remain in effluent. Despite of many research efforts, the question of which structures are responsible for activation and which are responsible for lignin deactivation during oxygen delignification still remain unanswered. In the present work, an attempt has been made to characterize the components in post oxygen stage effluents of pulp and paper industry using U.V-Visible, FTIR and ^{13}C- NMR spectroscopy.

Material and Methods

The waste water used in this study has been collected from the large scale Paper mill, having R.D.H pulping process and conducting oxygen bleaching sequence. The Post oxygen effluent water is taken for this study. The characterization task has been carried out by FTIR, ^{13}C-NMR and U.V spectrometer.

For I.R analysis the organic colour compounds from the effluent are separated from waste water through complete evaporation. The potassium bromide (KBr, Fisher scientific IR grade) is oven dried to complete dryness and stored in desiccator until use. The compound–KBr mixture has been prepared by accurately

weighing the KBr and organic compound. The mixture was quantitatively transferred to a mortar and ground with a pestle for 20-30 minutes to obtain a homogeneous mixture and a pellet has been prepared again. A pellet of same mass using pure KBr has been prepared similarly for blank reading. Analysis has been made for both the blank and organic compound –KBr pellets using a FTIR-Perkinelmer, Spectrophotometer-400.

For NMR analysis first chromophoric organic effluent materials are oven dried to complete dryness at 100°C and then dissolved in D_2O (deuterium oxide) solvent. The NMR spectra are obtained by using ^{13}C-NMR (Bruker avance II 400 NMR spectrometer). In order to obtain the U.V Spectra, first colour causing effluent compounds are dissolved in water and then the prepared solution is analyzed in Shimadzu, U.V-1700 spectrophotometer.

Results and Discussion

FTIR Spectral Analysis: FT-IR spectroscopy, which is a complementary and extensively used method, gives information about the molecular confirmation and hydrogen bonding patterns. As shown in the spectra of figure-1.

The wide absorption at 3448.62 cm^{-1} and 2851.34 cm^{-1} is attributed to O-H and –C-H stretching, corresponding to the aliphatic molecules in lignin. The band at 2851.34 cm^{-1} is due to C-H stretching of methyl, methylene and methine groups respectively. The absorption at 1638.96, 1627.40 cm^{-1} and 1578.4 cm^{-1} indicate the aromatic skeleton vibrations, while the band 1413.3 and 1337.48 are assigned to the C-H deformations and aromatic ring vibrations. The sharp band at 1182.58 and

1118.48 cm^{-1} and shoulder near 1033 (1034) cm^{-1} represents the aromatic C-H in-plane deformation in syringyl type and guaiacyl type, respectively. However, a slight difference can be clearly distinguished on closer examination. The shoulder near 1726 cm^{-1} in the spectrum is undoubtedly assigned to the ester linkage of carboxylic groups in ferulic and p-coumaric acids. The presence of the band near 1716 cm^{-1} in stretching, indicates the presence of unconjugated carbonyl groups. Conversely, the conjugated carboxyl absorption at 1638.96 cm^{-1}, manifested that the lignin fractions with conjugated carbonyl groups were liable to dissolve in hexane and diethyl ether, both of which have lower Hildebrand solubility parameters compared to other organic solvents. Moreover, the band at 1337.48cm^{-1} for the non-etherified phenolic –OH groups, mainly resulting from the cleavage of β-O-4 and α-O-4 linkages, under alkaline pulping conditions, severe condensation reactions accompanied the cleavage of ether linkages in phenolic phenyl propane units. The non-etherified phenolic –OH groups, therefore, mainly occurred in the low molecular weight fractions. may be due to the C-O stretching vibration of (–COOH) group shown in table-1.

^{13}C NMR Spectral Analysis: The ^{13}C NMR spectra of the compounds isolated from post oxygen effluent are shown in figure 2 and 3.

This section gives the structural information of the chromophoric groups present in the post oxygen effluent water. The peak assignment is given in table-2.
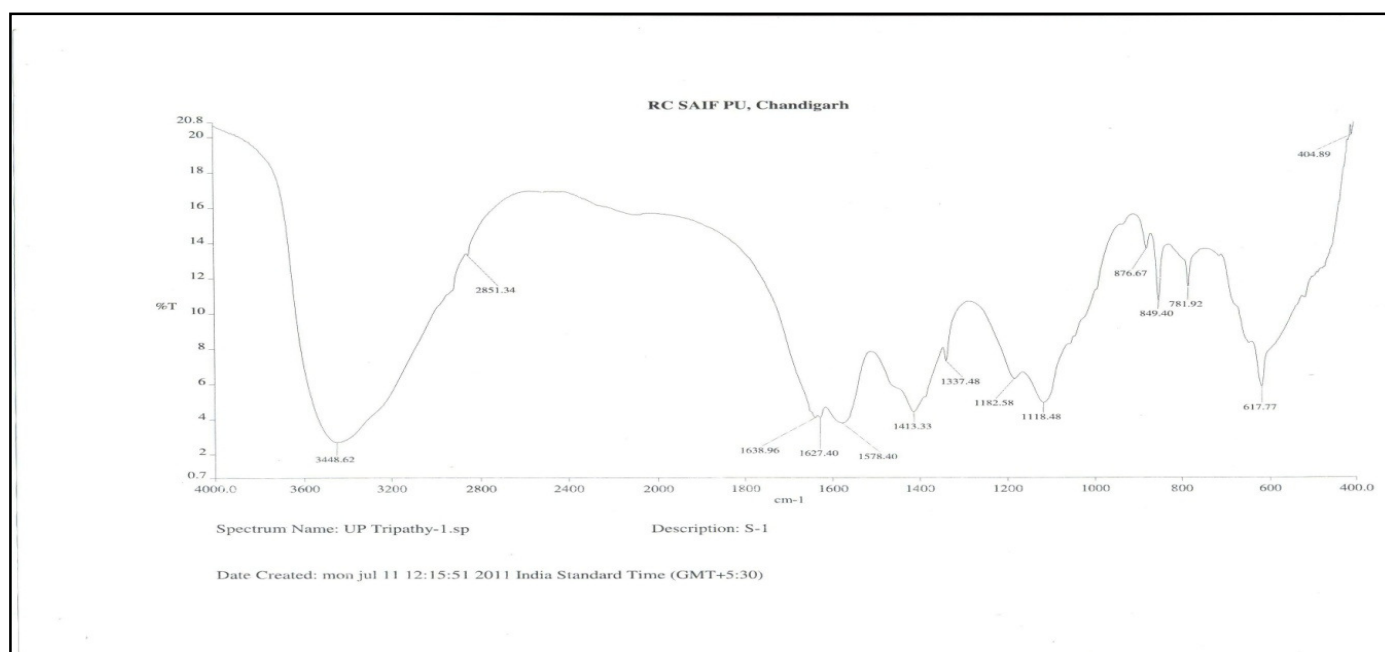

Figure – 1
Typical FTIR Spectra of the total solids in post oxygen stage effluent

The data reported by .the aromatic part of oxidized lignin appears in the reason between 100 and 160 ppm, while the degraded fragment units show in lower range between regions 61.55 to 4.4505 in the C^{13}-NMR spectra. Since the NMR technique is sensitive to the presence of water or more specifically the hydrogen atom in water, the dried coloured material redissolved in deuterium oxide is taken for NMR analysis. After the reaction of lignin with superoxide anion (O_2^-) [i.e. their decomposition] singlet peaks at δ180.11,178.96, 170.23 & 163.90 in ^{13}C- NMR spectrum are observed which corresponds to aromatic carboxylic or methoxy groups along with aldehydic or hydroxyl groups which are probably formed from the oxidation of the side chain of lignin by superoxide anion radical. The peak at δ 61.55 in the ^{13} C NMR may be due to Phenylcoumaran or aliphatic C-O units. The group of peaks at δ 39.06-37.79 indicates the alkyl units while the δ-values at 31.04 and 24.12 may be due to saturated hydrocarbon structures in aliphatic side chain from degradation of phenolic β-aryl ethers. The other lower peak values having δ-values from 10.80 to 4.4505 may be due to fragment units of alkyl groups. These data also supported by the previous report[6] of lignin oxidation with O_2^- shows peak at δ174.5 and 167 in the ^{13}C NMR spectra in which they reported the presence of aromatic carboxyl group probably formed from the oxidation of side chain of lignin by the superoxide anion radical. In the present study we also observe peak at δ 170.23 and 163.90 which is nearly resemblance. The signals in 80-60ppm region are attributed to oxygenated and non oxygenated inter unit linkages in lignin[11-12].

U.V Spectral Analysis: The U.V spectra of compounds present in post oxygen stage effluent in figure-4 shows a strong peak at wavelength 210 nm but the lignin molecule shows a characteristic peak at 280nm. Such a hypsochromic shift may be attributed to the breakage of chromophoric[13] groups of lignin compounds during kraft cooking and oxygen delignification. Again after ozone treatment the post oxygen effluent shows a characteristic peak at 220nm (bathochromic shift) as in figure-5. This clearly indicates the degradation of chromophoric compounds of lignin on oxidation.

Conclusion

Finally, In the present work, it is identified that the lignin compound present in the wood chips are oxidized in kraft cooking and oxygen delignification processes and form the degraded oxidized lignin fragments which are removed in post oxygen back water. The 5, 5' biphenyl structures and p-hydroxy phenyl structures are relatively inert towards oxidation and accumulated with in residual lignin. Due to presence of these chromophoric fragments of lignin molecule, the post oxygen effluent is looking dark brown in colour. From the U.V, FTIR and C^{13}-NMR analysis it may be concluded that the post oxygen effluent mainly contains lignin fragments. The possible compounds present may be vanillin, syringaldehyde , p-Hydroxy benzaldehyde, vanillic acids, syringic acids, p-Hydroxy benzoic acid, fervilic acid and p-coumaric acids. For the reutilization of the post oxygen effluent, it is essential to oxidize the lignin fragments to decolourize the effluent. For that oxidative treatment with ozone is the best method.

Acknowledgment

Table-1
Typical FTIR Spectral data of the total solids in post oxygen stage effluent

Sl. No.	Peak value	Type of peak	Possibility of functional group
1	3448.62	Broad	Ar-OH (S broad)
2	2851.34	Sharp	C-H stretching (-CH2)m,s
3	1638.96	Sharp	C=O stretching(s)
4	1627.4	Sharp	Ar-CH=CH-R(s) group
5	1578.4	Broad	C-O stretching
6	1413.33	Sharp	Ar-C-C stretching
7	1337.48	Sharp	Ar-N stretching
8	1182.58	Sharp	C-O streching(due to –COOH group)
9	1118.48	Broad	R-COOH,RCOOR'
10	876.67	Sharp	C-H out of plane(m)aromatic
11	849.40	Sharp	C-H out of plane(m)
12	781.92	Sharp	C-H out of plane(m)
13	617.77	Sharp	C-H bending

Table-2
Typical ^{13}C-NMR Spectral data of the total solids in post oxygen stage effluent

| Sl. No.	Peak value (ppm)	Type of peak	Possibility of functional group
1	180.11	Singlet	C=O in φ-CH=CH-CHO
2	178.96	Singlet	C=O in φ-COOH
3	170.23	Singlet	C=O in acids and esters
4	163.90	Singlet	C in φ-OCH$_3$, C-alkene or aromatic carbon.
5	61.55	Singlet	R-CH$_2$-OH, C-γ in β-5 unit C-5 in xyl internal unit C-γ in β-O-4 units ,-OCH3 units in Vanillin or Syringyl units
6	39.06,38.85,38.63,38.42,38.21,38.00,37.79	Multiplet	-CH$_3$ and other alkyl units having no oxygen.
7	31.04	Singlet	Phenyl-CH$_2$ -
7	24.12	Singlet	-CH$_3$, -CH$_2$, -CH
8	10.80	Singlet	R-CH$_3$, -CH$_2$, -CH
9	8.2690	Singlet	C- alkyl carbon
10	4.6068,4.5682,4.5563, 4.5057,4.4733, 4.4505	Multiplet	C-alkyl carbon
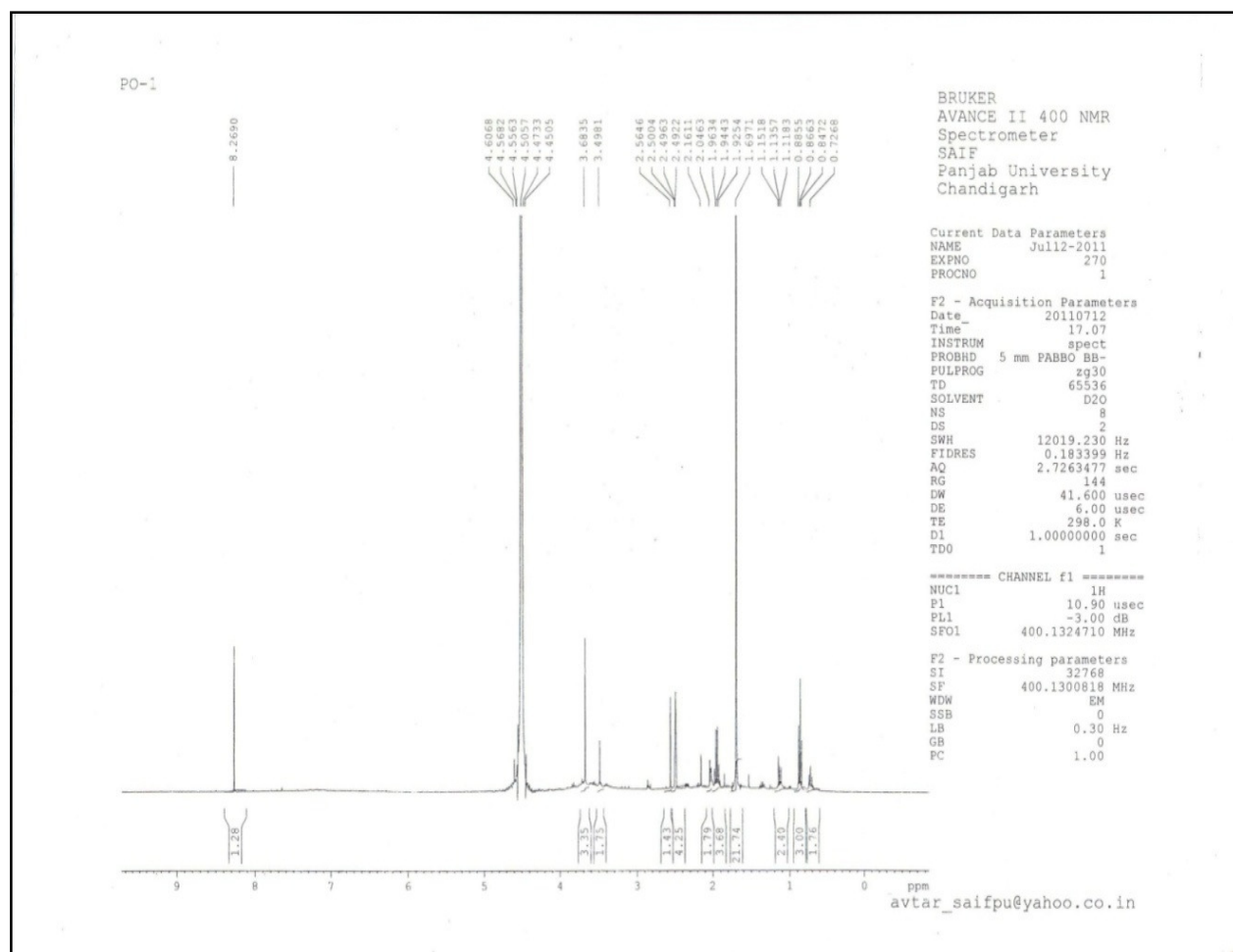
Figure-2
Typical ^{13}C-NMR Spectra of the total solids in post oxygen stage effluent (range 0-10 ppm)
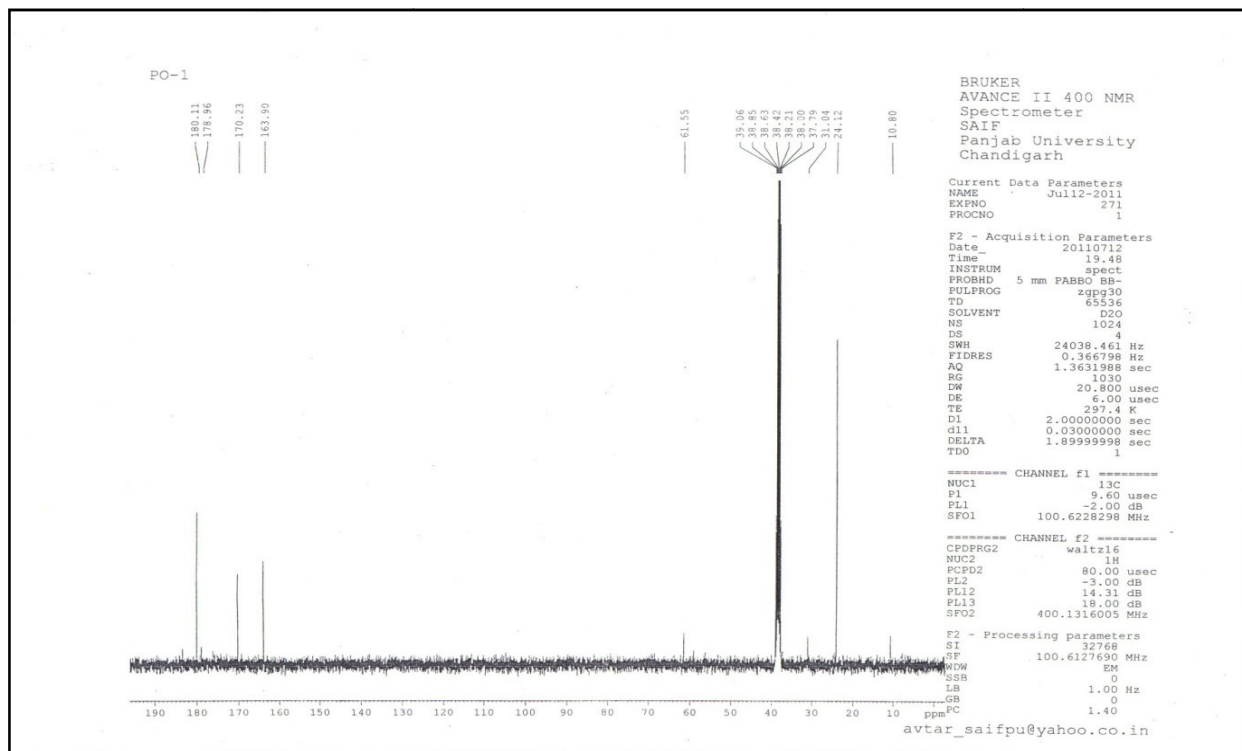
Figure-3
Typical ^{13}C-NMR Spectra of the total solids in post oxygen stage effluent (range 10-200 ppm)
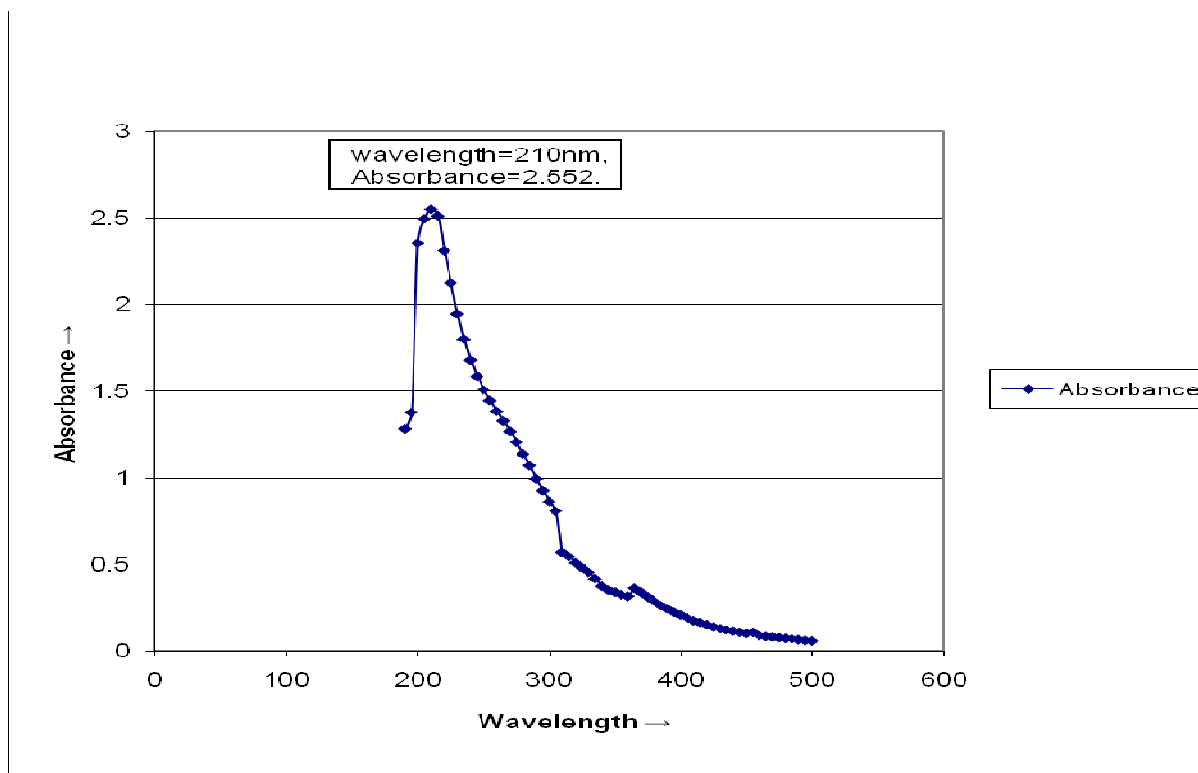

Figure-4
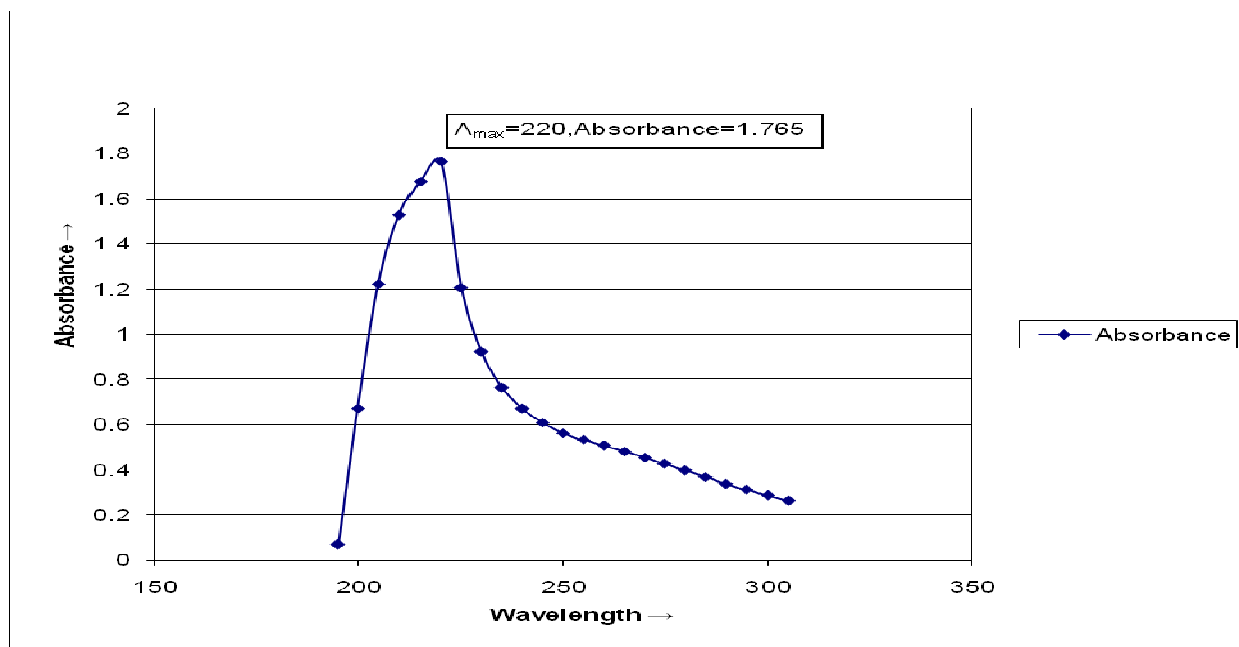**Typical U.V Spectra of the total solids in post oxygen stage effluent**

Figure-5
Typical U.V spectra of the total solids in post oxygen stage effluent after ozone treatment

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