Studies on Degradation of Syntan used in Leather Tanning Process using Ozone

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Abstract—Degradation of syntan used in leather tanning process has been studied using ozone. Studies were carried out by varying operational parameters like initial syntan concentration, pH and ozone dose. The removal of COD, tannin and UV absorbing constituents has been determined. Degradation of syntan in terms of COD, Tannin and UV absorbing constituents was maximum at pH 7.

Index Terms—Ozone, COD, Tannin, UV254nm

I. INTRODUCTION

Leather industry is one of the oldest industries in India and one of the leading foreign exchange earners for the country and has been characterised under the Red category-The most polluting industries. The tanneries are associated with the generation of huge amount of liquid effluent. The effluents generating from tanneries are complex waste induced by a series of chemical and biological activity to convert the collagen matrix of the skin/hide in to the leather having high concentration of pollutants and a great variety of composition, which results from changeability of technological processes conducted in tanneries.

Presence of refractory organic compounds like tannin in tannery wastewater imparts recalcitrance and toxicity. Synthetic tanning materials or syntan are high molecular organic compounds capable of rendering hides and skins into an imputrescible substance called leather. Most widely known syntans such as melamine based syntan, acrylic syntans are manufactured by treating aromatic substances, e.g., cresols, phenols, naphthalene, etc., with formaldehyde and sulphuric acid. Choice of the raw materials used in the manufacture of syntan depends mainly on nature of its applications. Syntans are not completely absorbed by the skin and remain in effluent. Constituent of syntan such as Phenol and formaldehyde are difficult to be degraded by biological treatment and found to be toxic to aquatic life¹. Considering the refractory nature of tannin observed in the biological treatment, alternate methods involving advanced oxidation processes (AOPs) have been identified as a feasible option. Ozone treatment of several types of wastewater containing refractory compounds such as phenol, dyes, and pesticides has resulted in reduction in chemical oxygen demand (COD) 2,3,4,5. Ozonation of some biorefractory organic compounds like naphthalene sulfonic acids can improve biodegradability and thereby allowing an appropriate sequencing of ozonation followed by an aerobic biological treatment step⁶. Study on the degradation of

tannic acid by ozonation has reported total mineralization of tannic acid⁷.

Ozone decomposition in the aqueous solution gives rise to the formation of peroxide HO₂ radicals, then hydroxyl OH radicals⁸:

The aim of the present study was to optimize the process condition for ozonation of syntan to be suitable for further treatment for safe disposal.

Degradation of syntan (aromatic sulfonic acid condensation product) used in the leather tanning process has been studied using ozone. Studies were carried out by varying operational parameters such as initial concentration of syntan, pH and Ozone dose. The removal of COD, Tannin and UV absorbing organic constituents has been determined.

II. EXPERIMENTAL

A. Leather tannin

Commercially available syntan (Aromatic sulfonic acid condensation product) containing 55-60% tannin of 95% purity used in the leather manufacturing process was chosen for the study.

B. Apparatus

Ozonation experiment was carried out in a bench scale glass reactor of 40mm diameter and 1600mm height fitted with a ceramic diffuser for dispersion of ozone. A lab scale ozone generator (Faraday Model No .L6G, India) was used to supply ozone in the range of 1-6g/hr and ozone was produced from dry and pure oxygen generated from oxygen generator (Airsep, USA). The oxygen flow rate to the generator was maintained at 5l/min. The ozone concentration at the inlet and outlet of the reactor was determined by iodometric titration.

Ozone gas was passed through series of gas washing bottles containing 2%KI solution. Ozone reacted with KI according to the following equations

The concentration of the ozone in the inlet and outlet gas was measured by taking samples from the KI trap during each experimental run and titrating the iodine in the samples with Na₂S₂O₃ according to standard methods.

In order to study the effect of pH on degradation of syntan a series of experiments were conducted at pH of 5, 7 and 9 by adjusting pH using 0.1N NaOH and by adding

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appropriate phosphate and borate buffer to maintain it throughout ozonation. In order to study the effect of sytan concentration on degradation, sytan solutions of concentration 100,300,500,700mg/L were used.

C. Analytical methods

Samples were withdrawn at predefined time intervals for a period of 60 min for COD, Tannin, and UV absorbance at 254nm analysis according to procedures recommended in APHA manual⁹. pH was measured using pH meter. COD was determined by colorimetric technique after digesting the sample by closed reflux method. Tannin content was determined by tannin-Lignin methods according to standard methods. UV absorbance at 254 nm was determined using UV spectrophotometer (Hitachi, ModelU2000).

III. RESULT AND DISCUSSIONS

A. Effect of Initial sytan concentration

Fig 1 Degradation of sytan at pH 7, ozone dose 1g/hr

The study was carried out at pH 7 by varying initial concentration from 100 to 700ppm with ozone dose of 1g/hr. Fig1 and 2 shows variation of tannin and COD with time during the ozonation of sytan at different initial sytan concentration. It was observed that sytan degradation was rapid at lower initial concentration as compared to other initial sytan concentrations. Fig.3 shows the reduction of UV absorbing constituents at UV 254nm during ozonation. Absorption in the ultraviolet range is dependent upon electronic structure of the molecule and at a wavelength of 254nm, is largely limited to conjugated carbon-carbon double bonds. COD, tannin and UV absorbing compounds removal decreases with increase in initial concentration.

At the end of 60min tannin removal efficiency was 98%,92%,90%,72%, COD removal was 91%,86%,79%,48% and UV absorbing constituents removal was 91%,92%,76%, 61% at a concentration of 100,300,500 and 700ppm respectively.

Fig 2 Degradation of sytan at pH 7, ozone dose 1g/hr

Fig 3 Degradation of sytan at pH 7, ozone dose 1g/hr

B. Effect of pH

Fig 3 and 4 depict the effect of initial pH on degradation of sytan in terms of removal of tannin, COD and UV absorbing compounds. Maximum removal was observed at pH 7. This shows that both molecular ozone and OH radical oxidation pathway, which becomes more pronounced at pH 7 due to the accelerated ozone decomposition, play significant role in the degradation of sytan. The lower degradation of sytan at pH 9 may be due to the formation of oxygen ion during the rapid decomposition of ozone, whose reactivity is lower than that of hydroxyl radical¹⁰. Fig 5 indicate that reduction in UV 254nm may be via oxidation of both O₃ and OH pathways. This may be due to the hydroxyl radical preceded mainly on the aromatic moieties of the molecule. Similar observation has been reported in the study of ozonation of tertiary treated pharmaceutical wastewater¹¹. At the end of 60 min the removal of aromatics was 72%, 91%, 91% and the most effective removal of aromatics were attained at pH7.

Fig 4 Degradation of sytan in terms of tannin at concentration of 100ppm, ozone dose 1g/hr

Fig 5 Degradation of sytan in terms of tannin at concentration of 100ppm, ozone dose 1g/hr

Fig 6 Degradation of aromatics in sytan during ozonation at concentration 100ppm, ozone dose 1g/hr

Fig.7 Ozone consumption rate for the degradation of sytan during ozonation at concentration 100ppm, ozone dose 1g/hr

C. Ozone consumption on decomposition of sytan

Initially ozone consumption has rapidly increased due to the destruction of readily degradable complex bonds present in the sytan (Fig 7). It is also observed from the trends shown in the graph that ozone consumption is related to pH up to 5min and relatively independent after 50min. The ozone consumption between 5 and 50 minutes of reaction time vary due to variation in the concentration of various degraded products generated during ozonation process as the rate of reaction of ozone with such degraded products is pH dependent.

IV. CONCLUSION

Experimental results of the study confirmed that ozonation is an effective process for treatment of synthetic tannin in the tannery wastewater. Maximum removal of COD, tannin and aromatic compounds was achieved at pH 7.

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REFERENCE

- [1] T. Tisler and J. Zagorc-Koncan, *Comparative assessment of toxicity of phenol, formaldehyde and industrial wastewater to aquatic organisms*. Water, Air, Soil Poll., vol 97, 1997, pp 315–322.
- [2] V.M. Correia, T. Stephenson, and S.J. Judd, *Characterization of textile wastewater-a review*. Environ. Tech., vol15, 1994, pp 917–929.
- [3] P. Ormad, S. Cortes, A. Puig and J.L. Ovelleiro, *Degradation organochlorine compounds by O₃ and O₃/H₂O₂* Wat. Res., vol 31, 1997, pp 2387–2391.
- [4] S.Baig, P.A and Lichits, *Ozone treatment for biorefractory COD removal* Water.Sci.Tech, Vol 43, issue 2, 2001, pp 197–204.
- [5] K I Abe, K.Tanaka, *Degradation of phenol, asulam and lignin in aqueous solution by ozonation* Toxicol.enviro.nchem.Vol 54, 1996, pp 54–59.
- [6] Y.Y., Win, M.U. Kumke, C.H.Specht, A.J.Schindelin, G.Kolliopoulos, G.Ohienbusch, G. Kleiser, S. Hesse, F.H.Frimmel, *Influence of oxidation of dissolved organic matter (DOM) on subsequent water treatment processes*, Water Res, Vol 34, issue7, 2000 pp2098–2104.

- [7] J. Perkowski, U. Dawidow, W.K. Jozwiak. *Advanced oxidation of tannic acid in aqueous solutions*, Ozone Sci. Eng., Vol 25 Issue 3, 2002, pp 199–209.
- [8] J. Perkowski, Lech Kos, *Decoloration of Model dye house wastewater with advanced oxidation process*. Fibres Text. East. Eur. July/September., 11:3, Vol 42, 2003, pp 67-71.
- [9] Standard methods, American public Health Association 20th edition.
- [10] S. Imamura, H. Umeta, N. Kawabata and M. Teramoto. *Ozonation of Organic Compounds in Alkaline Aqueous Media* The Canadian Journal of chemical engineering, Vol 60, 1982, pp 853-858.
- [11] E.C. Wert, F.L. Rosario-Ortiz, S. A. Synder, *Using ultraviolet absorbance and color to assess Pharmaceutical Oxidation during Ozonation of Wastewater* Environ. Sci. Technol., vol 43, 2009, pp 4858-4863.