

Effect of ozonation on activated sludge from pulp and paper industry

S. Gupta, S. K. Chakrabarti and S. Singh

ABSTRACT

Aerobic biological treatment with activated sludge is the predominant process all over the world for treatment of pulp and paper industry wastewater. 50–70% of the biodegradable organic material is oxidized to CO₂ and the rest is converted to bacterial biomass, typically termed as excess sludge or waste activated sludge (WAS). Handling and disposal of WAS in general and in particular from the pulp and paper industry face different processing difficulties, regulatory stringency due to organochlorine contamination and reluctance of people for reuse. With an objective of reducing the net disposable biomass, ozonation of WAS from a pulp and paper mill and from a laboratory scale batch activated sludge process operated with the wastewater and bacterial seed of the same pulp and paper mill have been carried out. With the mill sludge having predominant filamentous organisms 18% MLSS was reduced at an ozone dosage of 55 mg O₃/g dry MLSS solid (DS) resulting in 2.5 times COD increase. With the laboratory sludge which is well structured and flocculating, only 6% MLSS was reduced at an ozone dosage of 55 mg O₃/g DS. Ozonation mineralizes 26% and 20% AOX compounds embedded in the secondary sludge in the mill and laboratory sludge respectively at an ozone dosage of 55 mg O₃/g DS. During ozonation, absorbed/adsorbed lignin on biomass was released which resulted in increased colour concentration. Ozonation can be a potential oxidative pretreatment process for reducing the WAS and paving the way for cost effective overall treatment of WAS.

Key words | activated sludge process, AOX, ozonation, pulp and paper industry wastewater, sludge reduction, waste activated sludge

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INTRODUCTION

Aerobic biological treatment by activated sludge process (ASP) is the most widely used and proven process for treatment of pulp and paper mill effluent. In ASP micro-organisms oxidize dissolved and particulate organic matter into simple end products with generation of additional biomass. An equivalent amount of produced biomass is separated and disposed of in a concentrated form called excess sludge or waste activated sludge (WAS). Being biological in nature, handling, dewatering and disposal of secondary sludge is very difficult. As a consequence of several factors that include increasing production demand, regulatory constraints as well as rising public awareness and

sensitivity to sludge disposal, sludge management and disposal costs have been rising. About 40–60% of the cost of wastewater treatment is associated with the handling, treatment and disposal of the excess sludge (Elliott *et al.* 1999; Low & Chase 1999; Chakrabarti 2005).

Although several methods exist for achieving sludge minimization, sludge ozonation processes have been extensively studied and characterized, and show immense promise as a viable method for attaining consistent and reliable reduction of excess sludge. Yasui & Shibata (1994) first reported the minimization of excess sludge by ozonation, afterwards many researchers have reported ozone for

minimization of excess sludge by varying ozone dosage and disintegration number (Sakai *et al.* 1997; Kamiya & Hirotsuji 1998; Ahn *et al.* 2002; Lee *et al.* 2005; Paul & Debellefontaine 2007).

Ozonation of biomass causes lysis of microbial cells which results in breakdown of cell walls. Thus, cell walls are defragmented and release intracellular compounds into the medium; the lysis products are then recycled back to the aeration basin thus providing an autochthonous substrate that contributes to the organic loading. The effective reduction in excess sludge is achieved when the disintegrated VSS (bacterial cells) is biodegraded in the aeration basin.

WAS originating from pulp and paper industry (P&P) contains various organic, inorganic and microbiological contaminants. Organochlorines viz, chlorophenols, chlorocatechol, chloroguaiacol, dioxins and dibenzofurans are some of the toxicants. Chlorinated organic compounds, formed during the bleaching of kraft pulp with chlorine, chlorine dioxide and hypochlorite bleaching agents, are collectively measured in pulp mill effluent as adsorbable organic halides (AOX) and extractable organic halides (EOX). During biological treatment of effluent containing AOX compounds, ~25–60% AOX compounds are removed (Reeve 1991; Taghipour & Evans 1996) and 1.7–3.0% of AOX compounds are wasted in adsorbed form with excess sludge (Chakrabarti *et al.* 2004). Many researchers have worked on ozone treatment of excess sludge for its reduction from municipal/synthetic wastewater but the WAS from P & P industry is different from the latter with respect to its chemical contaminants. The sludge containing AOX compounds bearing sludge has been classified as hazardous waste under Schedule-I of the Hazardous Waste (Management and Handling) Amendment Rules, 2003, Govt. of India.

Although many organochlorine compounds are readily biodegradable, many other synthetic and naturally occurring molecules are recalcitrant. Furthermore, microorganisms can easily be inhibited by the presence of these toxic compounds. Ozone oxidation processes have been studied by number of researchers for mineralization of the organochlorine compounds (Poznyak & Vivero 2005; Manojlovic *et al.* 2007). However the cost associated with a chemical process alone can be expensive for wastewater treatment. As an economic way to treat recalcitrant organic chemicals

in wastewaters, studies pointed out the possibilities of the integration of ozonation and biological treatment process. Ozonation of organic compounds usually produces oxygenated products and low molecular weight acids that are less toxic and more biodegradable (Adams *et al.* 1997; Sandra *et al.* 2005). Combination of ozone with biological treatment for pulp and paper mill effluent has resulted in better elimination of COD, Colour and AOX (Helble *et al.* 1999). The ASP treating pulp and paper mill effluent suffers with major problem of foaming during aeration. Significant reduction of foaming by ozonation process has been observed as a result of the greater vulnerability of filamentous, foam causing bacterial species to sludge ozonation (Fabiya *et al.* 2007).

Cost analysis has been carried out by many researchers and reveals that ozonation processes can be more economic than other processes for sludge treatment and disposal for wastewater treatment plants (Yasui *et al.* 1996; Park *et al.* 2003). The present study deals with the laboratory scale findings on ozonation of secondary sludge generated during treatment of pulp paper mill effluent at different ozone dosage and its effect on solubilisation of biomass, supernatant characteristics and fate of AOX compounds.

MATERIALS AND METHODS

For ozonation experiments secondary sludge was collected from two sources and four sets of experiments were performed using sludge from each source. Both the samples were concentrated by settling before ozonation experiments.

- A) Sludge from effluent treatment plant (ETP) of medium scale integrated kraft pulp and paper mill in North India: The mill uses a $C_D E_{OP} D_1 D_2$ bleaching sequence and production capacity is 200–220 t paper/d.
- B) Sludge from lab scale batch reactor: Initially sludge was acclimated by taking 1:1 part of cow dung and secondary sludge from the same mill. Effluent from C_D stage (40% ClO_2 substitution), E_{OP} stage and weak black liquor were collected from the same mill and mixed and diluted to give COD, BOD, AOX in the range of 450–550, 130–170 and 8–12 mg/l respectively. The reactor was allowed to stabilize for more than two months before withdrawing sludge for ozone experiments.

Ozonation of sludge was performed in 2 litre air tight glass reactor by taking 1 litre of sludge (5–11 g/l MLSS) each time and gas was distributed through G2 grade sintered diffuser under mechanical agitation at 500 RPM. Ozone was fed on the basis of dry mixed liquor suspended solid (MLSS) at nearly neutral pH. Ozone concentration in the feed gas was estimated by passing 1 litre gas into buffer KI solution (Masschelein *et al.* 1998) and accordingly dosage were calculated for ozonation of sludge. Unreacted ozone was estimated by connecting the outlet of reactor with sampling train containing buffer KI solution.

For MLSS and MLVSS 100 ml of mixed sludge sample was centrifuged and washed with distilled water before transferring to pre-weighed silica crucible. The sample was oven dried at 105°C over night. Dried material was taken as MLSS and the same crucible ignited at 550°C and loss in weight was taken as MLVSS. The sludge sample was allowed to settle and supernatant was filtered through rough filter paper to remove coarse particles. The sludge was concentrated by filtration up to ~20% solid level. pH, TSS, TDS, Color, COD, BOD of supernatant and viable count were performed as per Standard Methods 1998.

AOX of solid and liquid samples were estimated as per DIN 38414 (P18) and ISO 9562: 1989 respectively using Euroglass make AOX analyser and p-chlorophenol (Merck, Germany) as standard.

RESULTS AND DISCUSSION

The sludge collected from the mill (sludge A) contained excessive filamentous organisms, pinpoint flocs and the ASP suffered from foaming problems. Sludge from the lab scale batch reactor (sludge B) had good settling and contained fewer filamentous organisms, a few diffuse and pin point flocs, and higher organisms like protozoa, rotifers etc. Initially due to reaction of ozone with soluble, easily oxidisable organic compounds, there was a higher absorption of ozone, which gradually decreased with time. In case of sample A, there was foam formation near 60–70 mg O₃/g DS.

Pin point flocs and filamentous organisms are more susceptible to ozonation due to higher exposed surface area and start to get ruptured as ozone dosage increases. The compact flocs are resistant towards ozone. In case of sludge

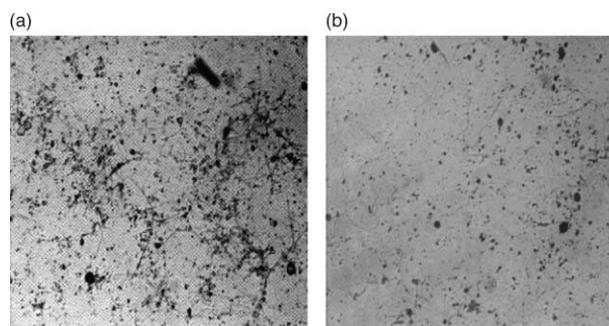


Figure 1 | a) Before ozonation. b) After ozonation.

A, most of the diffused flocs and filament organisms were ruptured after ozonation at 50 mg O₃/g DS (Figure 1(a, b)). In case of sludge B, diffused and pinpoint flocs were ruptured but there was no appreciable change in structure of dense flocs at 50 mg O₃/g DS (Figure 2(a, b)). Dispersion of flocculated sludge might be possible by applying high shear force to make it more suitable for ozonation (the study is in progress).

Mobility and survival of higher organisms were found to be linked with dosage of ozone. At low dosage of the oxidant, the organism had low mobility and at an ozone dosage near to 30 mg/g DS, organisms were totally inactive. Number of microbial survivors decreased sharply with increase of ozone dosage. This clearly indicates that ozone treatment inactivates most of the organisms. There was 70% reduction in colony forming units (CFU) at an ozone dosage near to 40 mg O₃/g DS in both the sludge samples (Figure 3).

During ozonation higher molecular weight compounds were oxidized to lower molecular weight ones and pH decreased due to formation of fatty acids. The same observation has been reported elsewhere (Fontanier *et al.* 2005; Poznyak & Vivero 2005). The change in pH was

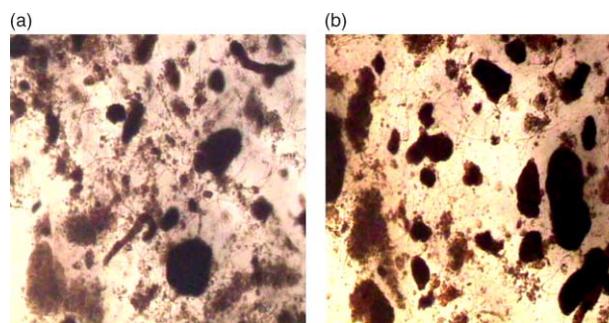


Figure 2 | a) Before ozonation. b) After ozonation.

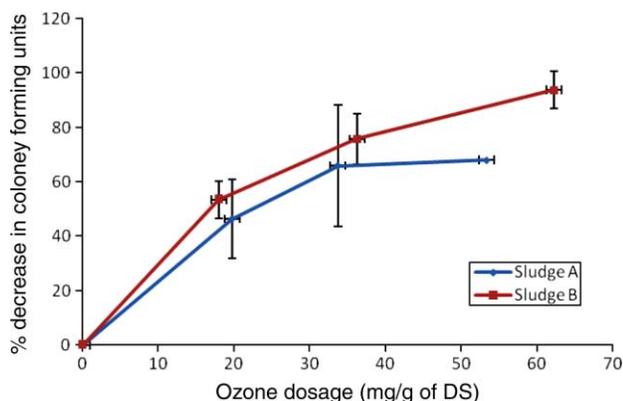


Figure 3 | Effect of ozone on viable count.

0.3–0.4 and 0.5–0.7 unit respectively in sludge A and sludge B at ozone dosage from 30–55 mg/g DS (Figure 4).

With the increase of ozone dosage, solubilisation of biomass increased. Sludge A, which has diffused flocs and excessive filamentous organisms, was more susceptible to ozonation than sludge B. MLSS and MLVSS concentration in return sludge from mill ranged from 4–7.5 and 2.5–4.9 g/l respectively. The sludge was concentrated to 5 to 11 g/l MLSS for ozone application and there is 9–18% solubilisation of MLSS at ozone dosage from 30 to 55 mg O_3 /g DS (Figure 5). Likewise, the MLSS concentration in the lab scale batch reactor varied from 3–4 g/l and was concentrated to 7.5–8 g/l for ozone application. There was lesser solubilisation of biomass than ‘sludge A’ due to presence of a few pin point flocs, filamentous organisms and dominance of compact flocs in sludge B. Biomass solubilisation was 4–6% at ozone dosage of 30–55 mg O_3 /g DS. Ozonation of biomass produced soluble organic

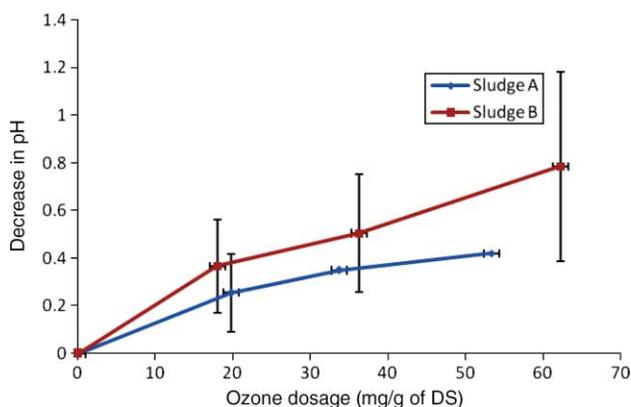


Figure 4 | Effect of ozone on pH.

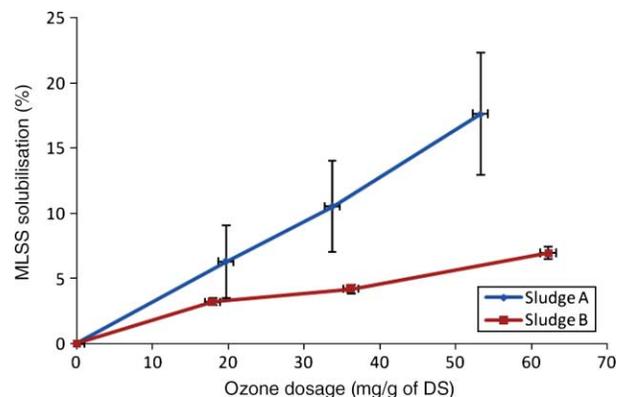


Figure 5 | Effect of ozone on MLSS solubilisation.

compounds and fine suspended particles which resulted in increase of TSS concentration (200–240 mg/l at 55 mg O_3 /g DS) in the supernatant. Finer particles as well as partially disintegrated sludge will be susceptible to biodegradation during aerobic biological treatment.

The colour concentration of aqueous phase was 325 ± 35 Pt-Co unit. Initially ozone reacted less with the sludge and more with soluble and easily oxidisable organic compounds. This resulted in increase in color very slowly. During the disintegration process, presumably due to solubilisation of adsorbed lignin compounds and sludge material, color increased at a faster pace (Figure 6). At dosage of 55 mg O_3 /g DS, there was 1.7–2.4 fold color increase in the supernatant layer.

During disintegration of biomass, refractory organic compounds are converted into easily biodegradable compounds and solubilisation of biomass resulted in an increase of soluble BOD and COD. Initially due to complete

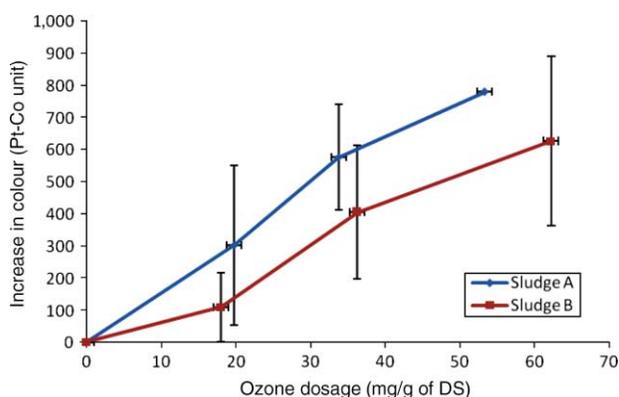


Figure 6 | Effect of ozone on color.

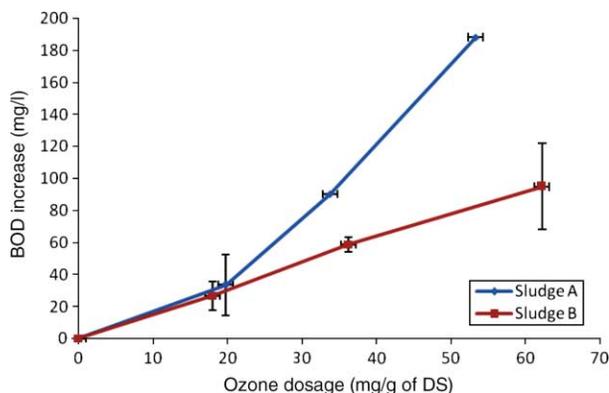


Figure 7 | Effect of ozone on BOD.

oxidation of easily oxidisable compounds, increase in COD and BOD was less and after 10–20 mg O₃/g DS, there was sharp increase (Figures 7 and 8). Initial BOD and COD concentration of supernatant of sludge A were 18.5 ± 1.5 and 280 ± 112 mg/l respectively, whereas those for sludge B were 2.4 ± 1.4 and 125 ± 34 mg/l respectively. Variation of COD in case of mill sample reflects unsteady operation of ETP. In case of sludge A, there was 75–175 mg/l increase in BOD and 300–710 mg/l increase in COD from 30 to 55 mg O₃/g DS, whereas for sludge B, there was 50–85 mg/l increase in BOD and 200–390 mg/l increase in COD from 30 to 55 mg O₃/g DS.

For a 15 litre lab scale aeration tank for ASP having 500 mg/l COD feed (1.5 kg/m³/d COD load) at 8 h HRT, there is 4.7 g excess sludge generation/day. Based on the solubilisation of sludge A (18% at 55 mg O₃/g DS), 4–5 times of excess sludge is to be treated with ozone to maintain sludge balance in ASP and zero sludge discharge. The similar methodology for excess sludge handling in

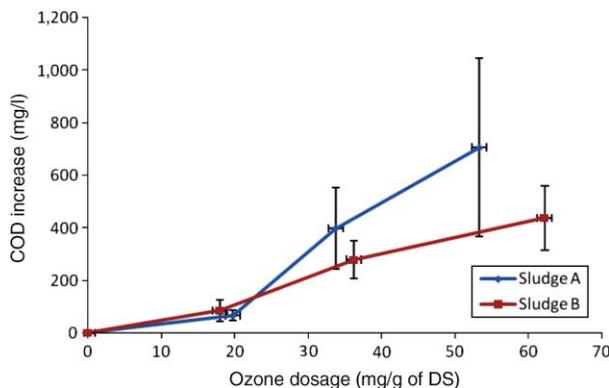


Figure 8 | Effect of ozone on COD.

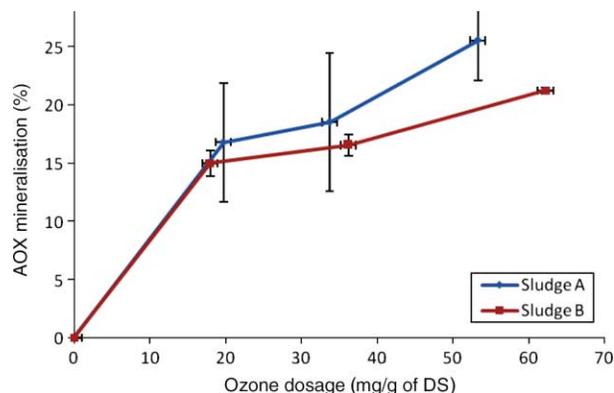


Figure 9 | Effect of ozone on AOX.

municipal wastewater treatment plant has been reported elsewhere (Yasui *et al.* 1996; Lee *et al.* 2005). Considering maximum COD increase (710 mg/l at 55 mg O₃/g DS), only 0.11–0.14 kg/m³/d COD load to ASP will be increased.

The disposal of biosludge generated during treatment of pulp and paper mill wastewater has become a crucial and legal issue due to presence of adsorbable organic compounds. The accumulation of AOX compounds in sludge depends on concentration of the same in influent and nature of sludge. In case of sludge A, the concentration of AOX compounds in sludge and supernatant was 2568 ± 207 mg/kg and 5.51 ± 1.19 mg/l respectively whereas influent AOX concentration was 7.0–9.0 mg/l. Similarly, in case of sludge B, the concentration of AOX compounds in sludge and supernatant was 3282 ± 449 and 5.32 ± 0.31 mg/l respectively and influent AOX concentration was 10–12 mg/l. Initially ozone mineralised the AOX compounds thus reducing the AOX level in liquid phase. In the later stage, AOX compounds from the sludge released in the aqueous phase and concentration of the same increased but remained lower than AOX concentration of initial sample. The mineralization of AOX compounds was 18–26% and 16–20% in sludge A and sludge B respectively at ozone dosage from 30–55 mg/g DS (Figure 9).

CONCLUSIONS

Ozonation of biosludge results in solubilisation and mineralization of biomass and refractory organic compounds. The morphology of flocs has a direct bearing on the solubilisation of the sludge. With a mill sludge having

predominant filamentous organisms, pin point and diffused flocs, 9–18% MLSS was reduced at ozone dosage of 30 to 55 mg O₃/g DS and resulted in 2.5 time increase in COD concentration at an ozone dosage of 55 mg O₃/g DS. Mineralization of AOX compounds in the mill and laboratory sludge was 26% and 20% respectively at the same ozone dosage. For attaining zero sludge discharge from ASP, there will be 7.3–9.3% extra COD load and negligible increase in AOX load to ASP due to solubilisation of biomass. Ozonation can be a potential oxidative pretreatment process for reducing the WAS and paving the way for cost effective overall treatment of WAS.

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