COMBINED CHEMICAL AND BIOLOGICAL TREATMENT OF RECALCITRANT INDUSTRIAL EFFLUENTS: A CASE STUDY ON KRAFT PULP WASTEWATER

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ABSTRACT

The chemical degradation of lignin-rich kraft pulp wastewater was carried out by ozonation process followed by biological treatment using activated sludge. The effects of pH on the degradation of lignin and the production of organic acids were examined experimentally in the ozonolysis of wastewater. The strong alkaline condition enhanced not only the degradation of lignin but also the production of organic acids. The maximum value of BOD_5/COD *obtained after 12 hours of ozonation was 0.41, indicating that ozone treatment improved the biodegradability of the kraft pulp wastewater. The dynamic behaviours of microbial growth and substrate consumption were investigated in the biodegradation of organic acids using activated sludge. Maleic acid and oxalic acid in the ozonized wastewater were degraded completely by the activated sludge in shake-flasks and bench-scale aerated bioreactor experiments. The immobilized activated sludge culture using polyurethane foam (PUF) was most effective in degrading organic acids in continuous culture condition at an optimum hydraulic retention time (HRT) of 14 hours. The study confirmed that consecutive treatments by ozone and activated sludge are effective methods to treat industrial effluents containing recalcitrant environmental pollutants such as kraft pulp wastewater.*

INTRODUCTION

Pulp production from wood, which amounts to more than 10^6 tons per day worldwide, is responsible for discharge of about 200 m^3effluent per metric ton of pulp, making pulp and paper plants the most polluting industries (Leuenberger *et al.* 1985, Gokcay & Dilek 1994). Over 70% of world's pulp production is still made by kraft pulping (Pekarovikova *et al.* 1991). The wastewater from pulp and paper plants pose serious environmental problems when they are discharged into the lakes or oceans without being treated. Rivers receiving pulp and paper mill effluents are characterized by a black colour and a frothy surface and there is no sufficient dissolved oxygen to support aquatic life (Stern & Gasner 1974), Gupta and Battacharya 1985). The dark-brown, odorous effluents derived from the kraft pulping process contain a complex mixture of lignin fragments, resins, tannins, aliphatic carboxylic acids and hydroxyacids originating from polysaccharide degradation (Pekarovikova *et al.* 1991). These high molecular weight constituents of the kraft pulp black liquor account for its high Chemical Oxygen Demand (COD).

The chemical degradation of lignin derivatives contained in pulp wastewater and the recovery of biologically active substances are important subjects not only for the prevention of environmental pollution but also for the manufacture of animal feed, medicines and other useful materials (Nakamura *et al.* 1994). The available methods to treat wastewater such as chemical degradation of lignin in the pulp wastewater and the biological treatments of the products are an important subject of study. However, the treatment of pulp wastewater among the treatments of industrial wastewater is difficult because wastewater from pulp industry contains lignin in quantities as great as 10-100 g/L, and lignin has complex chemical structures (Sawada *et al.* 1995).

Several physical and chemical methods including incineration, lime, and activated carbon have been used to treat pulp and paper mill wastewater but they have proved to be too costly (Stern & Gasner 1974, Gupta & Battacharya 1985, Dancon & Qiting 1993). Biodegradation is a catabolic process in which biologically formed entities convert substrates into less complex intermediates or products (Anderson 1989). Biodegradation is a selective, specific and nontoxic natural process which poses less hazards to human health and the environment, and is more accepted to society than conventional treatment technology (Kamely *et al.* 1990). With the advancement of biotechnology, it is now possible to accelerate this rather slow process to applications of pollution treatment to large-scale decontamination. Although some works have described the biological degradation of lignin by basidiomycetes (Christman & Oglesby 1971), multiple substituted aromatic compounds are generally difficult to degrade by using specific strains of microorganisms.

Studies on combined chemical and biological treatment processes are attractive because of their increased efficiency and cost effectiveness. Ozone is being applied to water supplies and industrial wastes because it offers various advantages, that is, it does not produce sludge; it is effective at relatively low doses and short contact times, and can be generated on site (Walter & Sherman 1974, Joseph & Weber 1976, Heinzle *et al.* 1992, 1995). Furthermore, ozonation process accounts for an appreciable percentage of colour and COD elimination from organic compounds contained in industrial wastewater depending on initial compounds, pH and ozone dose (Gilbert & Zinecker 1980, Brunet *et al.* 1982, Stover *et al.* 1982, Gulyas *et al.* 1994). Toxic or biorefractory substances can be converted, by means of ozonolysis, to biologically active groups of substances, the process which is more cost-effective than their complete destruction (Gilbert 1983, Lin & Lin 1993, Takahashi *et al.* 1994). When the ozone-pretreated wastewater are subjected to microorganisms under aerobic culture conditions, they are completely oxidized to simple, useful and harmless forms (Stern & Gasner 1974, Hoigne & Bader 1983b, Glaser 1990, Kamely *et al.* 1990, Tanaka *et al.* 1992, Gulyas *et al.* 1994). However, the application of ozone should only be to oxidize those steps which can not be accomplished by cheaper biological means.

The microbiologically mediated processes under aerobic conditions hold a possibility of complete degradation of organic macromolecules to harmless end-products such as carbon dioxide and water (Glaser 1990, Kamely *et al.* 1990). Immobilized culture systems possess several advantages over freely suspended cells in both batch and continuous-flow systems. These advantages include better capability of reuse and regeneration of the biomass, easy separation of cells from the reaction mixture, high biomass loading within a given reactor, manipulation of biomass independent of dilution rates, high retention capacity of biomass leading to greater activity and minimum clogging in continuous-flow systems (Rubindamayugi *et al.* 1992, Gulyas *et al.* 1994). Activated sludge is a complex ecosystem consisting of fungi, bacteria, protozoa, viruses and many other types of organisms. The ability of bacteria to induce floc formation thereby facilitating the separation of particles from the treated water accounts for the success of the biotreatment process. The basic aerobic activated sludge process consists of aerating and agitating the effluent in the presence of flocculated suspension of microorganisms on particulate organic matter (Stanbury & Whitaker 1989, Zita & Hermansson 1994). In activated sludge systems, the active biomass incorporates the organic substances through oxidative biodegradation and stores them as energy and carbon sources (Shimizu *et al.* 1993). Activated sludge processes have been well developed as a primary measure of wastewater treatment and are also considered as one of the most reliable methods to treat toxic chemicals. The use of activated sludge is one of the most important biotechnological applications of bacterial attachment and aggregate formation in the treatment of wastewater (Lin & Lin 1993, Blackall 1994, Matsui *et al.* 1994, Moerman *et al.* 1994, Zita & Hermansson 1994).

The present study investigated the applicability of consecutive treatments by ozone degradation and then microbial treatment using activated sludge for improving the treatment of kraft pulp wastewater. A method to increase the degradation rate of lignin was studied by experiments using consecutive treatments under various operational conditions. In addition, the immobilized activated sludge using polyurethane foam was evaluated for its ability to effectively degrade wastewater treated with ozone.

METHODS

The study was carried out at the Biotechnology Laboratories of Kanazawa University, Japan. Kraft pulp wastewater from a pulp manufacturing plant used in this study contained about 40 g/L lignin. A mixture of ozone and air was introduced into a reactor containing 1 L wastewater at a constant flow rate of 0.25 m^3/h. The feed concentration of ozone was 20 g/m^3 at 30°C. Activated sludge from a local municipal wastewater treatment plant was used for the biodegradation of ozonized wastewater throughout this investigation. A basal medium was prepared by dissolving 6.20 g/L KH_2PO_4, 0.50 g/L urea, and 0.67 mL H_3PO_4 in the ozonized wastewater. Activated sludge (1.2 L) was added into a 1.8 L basal medium and all the media were adjusted to pH 7 and at 30^{o}C. The incubation was carried out using a 3 L bioreactor. In a continuous culture, the medium was continuously fed at a rate of 10-360 mL/h to the reactor using a microtube pump. The effluent was withdrawn at a constant rate from the reactor to prevent overflow. Polyurethane foam (PUF - *Inoac Corporation, Japan*) was added to the medium to support and immobilize the activated sludge.

A standard pH meter was used to determine the pH values of test samples. Low molecular weight organic acids were detected by HPLC and identified by comparing them with authentic samples with respect to their retention times. The liquid carrier was 0.1 H_3PO_4%. The amount of muconic acid was calculated by subtracting the value of the UV absorption at 280 nm after the hydrogen reduction, from that of UV absorption at 280 nm in the ozonized wastewater (Mtui *et al.* 1996). Chemical Oxygen Demand (COD in mg O_2/L) test, determined by closed reflux titrimetric method (Anold *et al.* 1992), was used to measure the amount of oxidizable organic matter present in the wastewater samples. A five-day biochemical oxygen demand (BOD_5) test was used to measure the oxygen utilized for the biodegradation kraft pulp wastewater at 20^{o}C. The dissolved oxygen (DO) was determined by using titrimetric (iodometric) method before and after 5 days incubation. The BOD was computed from the difference between initial and final DO (Anold *et al.* 1992). To assess the specific growth and cell mass, the DNA concentration in the activated sludge was measured by using the diphenylamine color reaction method (Liebeskind & Dohmann 1994). The optical density values were correlated to a standard curve drawn from the authentic DNA samples.

RESULTS AND DISCUSSION

The COD value for the raw kraft pulp wastewater was 175 g/L and dissolved solids stood at 229 g/L (Table 1). The high value of optical density of the effluent measured at 280 nm relates to the high concentration of lignin (45%) contained in kraft pulp wastewater. These values are extremely high and, therefore, they emphasize the importance of treatment of such wastewater prior to discharge into the environment.

Table 1: Properties of kraft pulp wastewater used in this study

pH	13.03
Specific gravity	1.11
COD (g/L)	175
Optical density (280 nm) [-]	2230
Total solids (g/L)	230
Suspended solids (g/L)	0.83
Dissolved solids (g/L)	229

Figure 1 shows the rate of decrement of UV absorption (decolourization) at 280 nm with the increase of ozonation time in the ozonolysis of wastewater under various pH values. The ratio of UV absorption at 280 nm represented the total amount of aromatic ring compounds which decreased with the increase of ozonation time (Legube *et al.* 1981, Sawada *et al.* 1995). The colour removal was most rapid at the beginning of the reaction and decreased slowly up to 12 hours of ozonation where it remained constant. From these results, it was found that the rate of decrement of UV absorption increased with the increase of pH value.

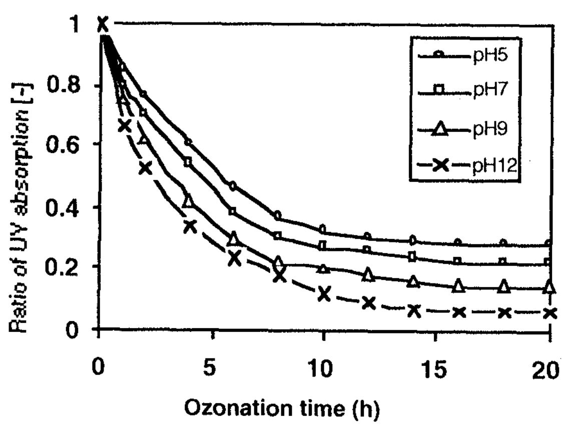

Fig 1: Effect of pH on UV absorption at 280 nm in the ozonolysis of kraft pulp waste water

The higher efficiency of decolourization of kraft pulp wastewater ozonated at high pH values could be due to the fact that ozone degradation is catalyzed mainly by hydroxide ions in aqueous solution to form hydroxyl radicals, thereby facilitating the radical-type oxidation reactions (Stern and Gasner 1974, Joseph and Weber 1976, Gilbert 1982, Hoigne and Bader 1983a, 1983b). Since the ozonolysis in the strong alkaline condition increased both the degradation rate of lignin and the production rate of organic acids, the rest of the of ozonolysis experiments were carried out at pH 12.

Figure 2 shows the rates of production of organic acids during ozonation of kraft pulp wastewater. The oxidation of the aromatic ring of the lignin macromolecules by ozone resulted to production of muconic acid that reached its maximum value of 4.6 g/L at 4 hours of ozonation and then started to decrease. Maleic acid, which was produced next to muconic acid, peaked at 0.22 g/L after 7 hours and then started to decrease to 0.11 g/L after 12 hours while oxalic acid concentration increased steadily up to 5.4 g/L, and then it remained constant after 12 hours of ozonation. The results confirmed that ozonolysis of lignin macromolecule resulted to the formation of lower molecular weight organic compounds in the order of muconic acid, maleic acid and oxalic acid (Mtui 1996). Since by 6 hours of ozonation all organic acids had almost reached their peak values, it was considered economical to terminate the ozonation process after 6 hours and then to carry out consecutive degradation by using microorganisms.

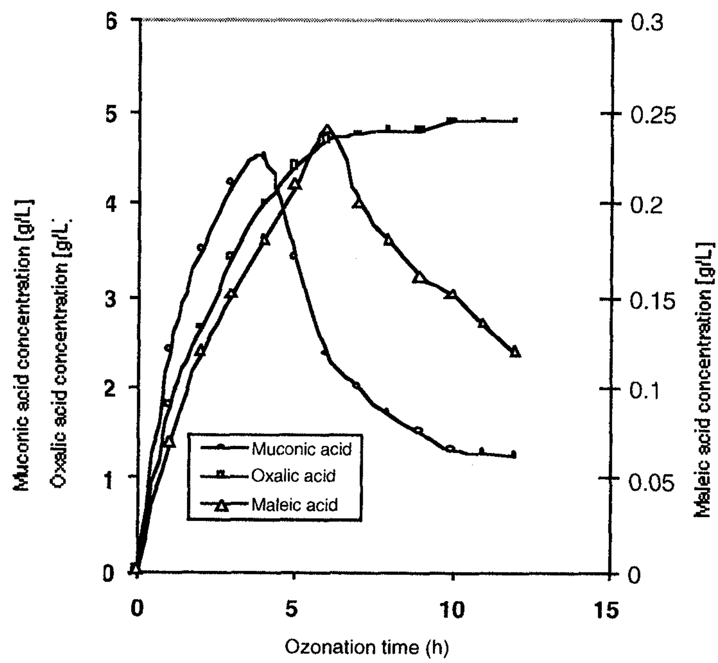

Fig. 2: Production of organic acids in ozonolysis of Kraft pulp wastewater

The time courses of COD and BOD during ozonation of kraft pulp wastewater are shown in Figure 3. The maximum COD reduction of 60% was obtained at pH 12, temperature of 40°C after 16 hours of ozonation. The initial BOD of the wastewater increased from its initial value of 2.53 g/L to 5.88 g/L after 6 hours, and reached its maximum value of 6.1 g/L after 10 hours. When the COD reduction was related to BOD increase, it was found that the BOD_5/COD ratio had increased from 0.05 before ozonation to 0.41 after 12 hours of ozonation. The reduction of COD and increase of BOD during ozonolysis indicated that as ozonation proceeded, biodegradable products were being formed (Tzitzi *et al.* 1994). The improvement of biodegradability caused by ozonation can be attributed to the removal of inhibitory effects due to the changes in molecular structure of the lignin macromolecule (Narkis and Shneider-Rotel 1978). The BOD_5/COD quotient of 0.4 - 0.5 is considered to be an indicator of good biodegradability (Gilbert 1982, 1983, 1986). The maximum value of BOD_5/COD obtained in this study was 0.5, showing that good biodegradability of the kraft pulp wastewater was achieved through ozonation process. Ozone pretreatment of non- or poor biodegradable compounds, mainly lignin and its derivatives, led to the formation of oxidation products such as maleic acids and oxalic acids which can be utilized by microorganisms.

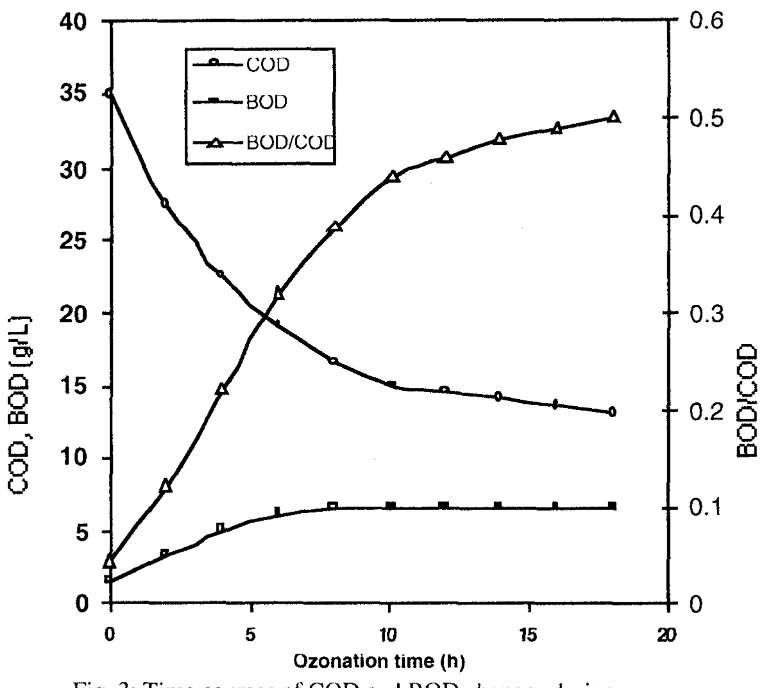

Fig. 3: Time courses of COD and BOD changes during ozonation of kraft pulp wastewater

Figure 4 shows the biological (activated sludge) treatment of maleic acid and oxalic acid in the wastewater preozonized for 6 hours. The dry weight and DNA concentration increased with the incubation time. Initially, the DNA concentration was 2.3 mg/L. After 24 hours of incubation, it then increased exponentially to 6.0 μg/L where it peaked. The increase in DNA concentration corresponded to the decrease in substrate concentration, namely oxalic acid and maleic acid. Maleic acid and oxalic acid were completely degraded by the activated sludge.

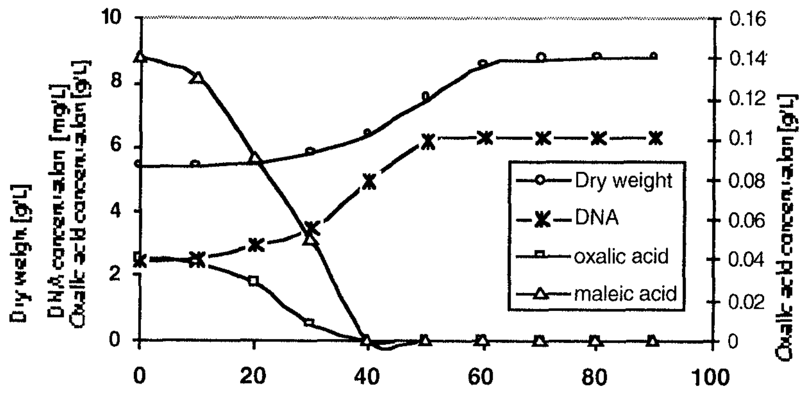

Fig. 4: Time courses of dry weight, DNA and organic acids concentration in the biological treatment of ozonized wastewater using activated sludge.

These results conformed to the assertion by Liebeskind and Dohmann (1994) that there is a proportional factor between DNA concentration and the number of microorganisms present in an activated sludge system. The increase of DNA concentration with time, therefore, represented the proportional increase of biomass.

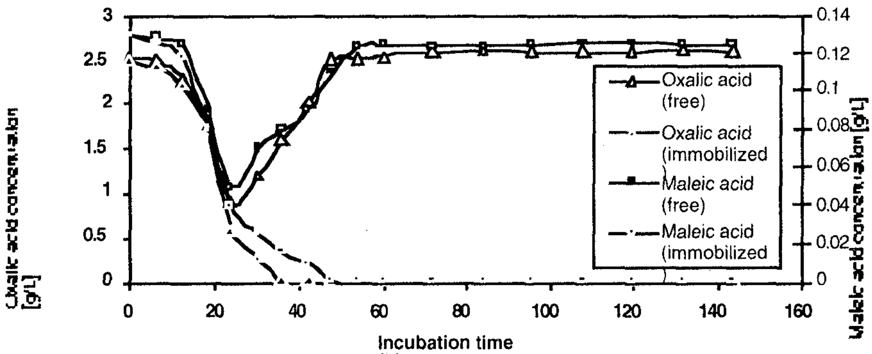

***Fig. 5:* Batch and continuous biodegradation of organic acids contained in kraft pulp wastewater (dilution rate = 0.06/h)**

Figure 5 shows the degradation trends of maleic acid and oxalic acid concentrations under batch culture for 24 h and then under continuous culture at dilution rate of 0.06 h^{-1}. The initial maleic acid concentration, the initial oxalic acid concentration, and the volume of culture, were 0.13 g/L, 2.5 g/L, and 3 L respectively. Under continuous culture condition, the free activated sludge culture showed poor organic acid degradation because of washout of cells in the bioreactor. However, the immobilized activated culture continuously degraded completely both maleic acid and oxalic acid up to the incubation time of 150 h at steady state. It seemed, therefore, that the biodegradability depended on the available surface attachment of the biomass (Rubindamayugi *et al.* 1992).

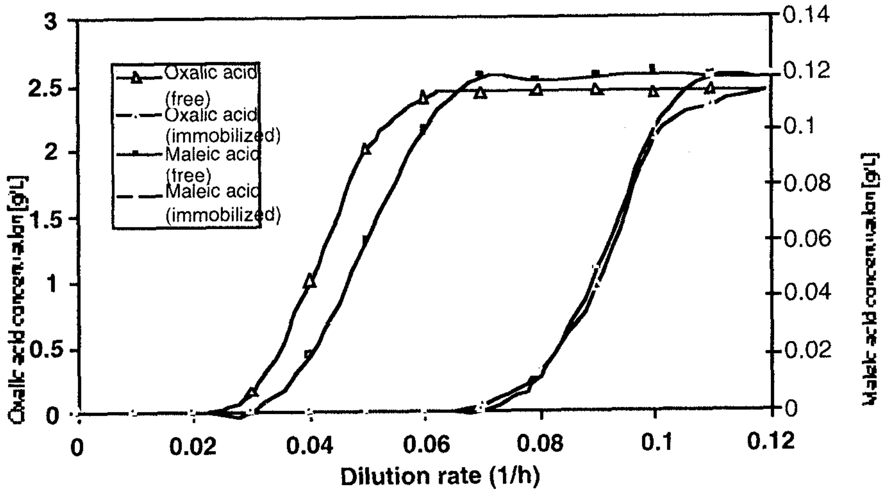

Fig. 6: Concentrations of organic acids in kraft pulp wastewater at steady states in continuous culture of activated sludge under various dilution rates

The effect of dilution rate on the effectiveness of continuous biodegradation of oxalic acid and maleic acid is summarized in Figure 6. The dilution rate was changed from 0 to 0.12 h^{-1}. In the free activated sludge culture, the concentrations of maleic acid and oxalic acid was almost zero up to a dilution rate of 0.02 h^{-1} and then they increased with the increase of dilution rate reaching their feed concentrations at dilution rate of 0.05 h^{-1}. Beyond a dilution rate of 0.05 h^{-1}, no consumption of organic acids was observed and the washout of the cells from the reactor occurred. In immobilized culture by using PUF, maleic acid and oxalic acid were degraded completely up to a dilution rate of 0.07 h^{-1}, but no consumption of organic acids was observed beyond a dilution rate of 0.12 h^{-1}.

The reasons for better degradation of organic acids in immobilized systems compared to conventional free liquid culture systems were due to the fact that the immobilization matrices served as filters to retain the viable biomass throughout the process thereby improving the biodegradation process by preventing cell washout from the bioreactor. This was shown by the drop in the value of mixed liquor suspended solids (MLSS) from 3.5 g/L in suspended liquid culture to 0.2 mg/L in immobilized systems (data not shown). It is therefore suggested that these "biofilter reactors", in which PUF-immobilized microbial systems are continuously cultured, be applied in large-scale biotreatment studies to facilitate their industrial applications.

CONCLUSION

The consecutive treatments by ozone degradation and then activated sludge treatment have been shown to degrade the lignin in the kraft pulp wastewater efficiently. The strong alkaline condition enhanced the degradation of lignin and the production of organic acids in the ozonolysis of wastewater. The maximum value of BOD_5/COD obtained was 0.5, showing that ozone treatment was effective for enhancing the biodegradability of kraft pulp wastewater. Activated sludge could degrade completely the low molecular weight organic acids in the ozonized wastewater. The immobilized activated sludge culture using polyurethane foam (PUF) proved to be more effective for the continuous biodegradation of organic acids rather than the conventional free activated sludge culture, and this study provides the basis for further research on PUF-immobilized bioreactors for their applicability in large-scale operations. The results of this work confirm that consecutive treatments with ozone and microorganisms are effective for the degradation of kraft pulp wastewater and the recovery of biologically active organic acids. The study was able to establish the favourable operational conditions necessary for efficient and cost effective methods of combined chemical and biological treatments of kraft pulp wastewater through ozonation and subsequent activated sludge-induced biodegradation.

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