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TREATMENT OF CHLORINATED ORGANICS IN BLEACHED KRAFT MILL EFFLUENTS BY ACTIVATED SLUDGE PROCESS

Selale Ataberk and Celal F. Gökçay

Department of Environmental Engineering, Middle East Technical University, Ankara, Turkey

ABSTRACT

Combined effluents from a bleached Kraft pulp mill using annual plants were treated in a lab-scale activated sludge (AS) system. The effects of operating solids retention time (SRT) and concentration of additional carbon source on AOX removal were investigated. Higher AOX removals (30%) were observed with long SRTs, 99% of which was pure metabolization. As SRT was decreased AOX removal efficiency also decreased (4%) and principal AOX removal mechanism changed to adsorption onto wasted biomass. The AOX removal efficiency was lower (10%) on a 20% decrease in the supplemental carbon source, with no apparent effect on the removal mechanism. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Bleached Kraft mill effluents; activated sludge; AOX; biodegradation.

INTRODUCTION

Chlorinated organic compounds, one of the major sources of which is the pulping industry, have become a significant concern for the environment since some of these are known to be often toxic to aquatic organisms. These compounds have a potential to accumulate in fat tissues of organisms and many of them are mutagenic.

As a result of the use of chlorine and/or its derivatives in bleaching of pulp, up to 5 kg organically bound chlorine is produced per tonne of pulp bleached by conventional methods (Eriksson, 1991).

Aerated lagoons and activated sludge plants are most commonly used methods for the biological treatment of spent bleachery effluents. The adsorbable organic halides (AOX) removal efficiencies for such plants is typically around 30-40%. However, AOX removal mechanism in biological treatment is not yet fully understood, though various mechanisms have been proposed.

The aim of this study was to observe AOX removal and to study mechanisms of removal in a lab-scale activated sludge (AS) unit. The effect of additional carbon source on AOX removal was also investigated.

Bryant and Amy (1989) have reported that the major removal mechanism for the organic halides in an aerated stabilization basin (ASB) appears to be biosorption onto settling biomass, followed by anaerobic dehalogenation within the benthal layer. Collins and Allen (1991) also report that most of the soluble AOX removal occurs in the aerobic portion of a bench scale aerated lagoon and that biosorption appears to be an important removal mechanism for AOX.

However, in another study, comparing AOX removal in activated sludge process with aerated and facultative stabilization basins, Hall and Randle (1992) have found that irrespective of process, 66% to 94% of the AOX removed was due to biodegradation. Only 5% was found to be removed with the discarded excess biomass. Further, in a two year survey, it has been reported that (Bryant *et al.*, 1992), although previous laboratory and field work supported biosorption the extent of removal of AOX was not exclusively controlled by biosorption.

Ferguson (1994) reported significant chemical or abiotic AOX degradation occurring after neutralization in bench scale aerobic and anaerobic reactors. However, removal by sorption or insolubilization was found to be relatively minor in contribution.

Stuthridge and McFarlane (1994) have studied the mechanism of AOX removal in an aerated lagoon in New Zealand. A lagoon treating pulp and paper mill wastes removed 65% AOX. Although it was found that settling of AOX containing suspended solids and alkaline dehalogenation are the probable mechanisms, a mass balance of aqueous and solid phases indicated >99% of the removed AOX having been actually mineralized.

MATERIALS AND METHODS

The lab-scale AS plant consisted of a 1 l glass reactor and a 1 l conical flask serving as the settling tank. The influent was fed to the reactor by a variable speed peristaltic pump. The contents of the reactor were pumped to a settling tank by a second peristaltic pump. Air was supplied to the reactor through a diffuser which also provided mixing. A magnetic stirrer and a stir bar supplied additional mixing. The settled biomass was recycled to the reactor periodically at preset time intervals. The temperature of the system was adjusted to 25°C. The SRT of the system was controlled by the amount of daily biomass wastage from the reactor. A composite sample of the combined effluent from SEKA Afyon Mill which produces bleached Kraft pulp from annual plants was obtained periodically every 1 to 2 months in plastic barrels and stored at room temperature. The stock was diluted by 1/2 and nutrients were added to achieve a C:N:P ratio of 106:16:1 prior to feeding to the reactor. Peptone was also added as additional carbon source to attain the desired biomass concentrations. When steady state conditions were reached, two samples were taken from the reactor. One was centrifuged and stored for AOX and total organic carbon (TOC) analysis. The other was vacuum filtered, then washed well with nitrate solution, and dried for AOX analysis. A Euroglas BV Microcoulometer and Ionics 1555B Carbon Analyzer were used for AOX and TOC measurements respectively. Direct determination of organic chlorine in dried biomass provided total Cl-biosorbed and difference between total -Cl input and biosorbed provided Cl-metabolized.

RESULTS AND DISCUSSION

The efficiency of the lab-scale activated sludge unit in removing TOC and AOX is presented in Table 1. Average TOC and AOX removal efficiencies were 83% and 21% respectively. Since the AOX removal was higher at longer SRTs, it is concluded that the operating SRT has a marked effect on the efficiency of the system in the removal of effluent chlorinated organics. The SRT of the system was found also to affect the mechanism of AOX removal, as shown in Figure 1. Material balance indicated that longer SRTs favoured metabolization of AOX, whereas the principal removal mechanism was adsorption onto the wasted biomass in short SRTs.

Table 1. TOC and AOX removal efficiencies of the lab-scale AS system

SRT (d)	TOC removal (%)	AOX removal (%)
24	90	31
19	94	31
11.5	72	21
5.6	79	4
Average	83	21

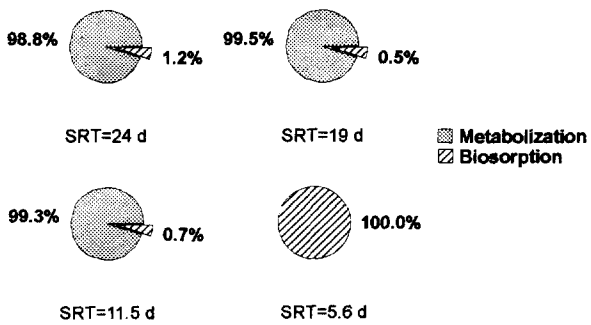

Figure 1. Contributions of metabolization and biosorption in AOX removal.

As for the examination of the effects of the additional carbon source on to the efficiency of AOX removal, similar experiments were performed with reduced amounts of peptone supplemented to the influent.

Table 2. AOX removal efficiencies of the lab-scale AS system operated with 20% less supplemental carbon source

operated with 20% less supplemental carbon source

SRT (d)	TOC removal (%)	AOX removal (%)
20	79	11[¥]
10	80	9[¥]
Average	80	10

[¥] : 100% metabolization

Although complete metabolization was observed, a 20% reduction of supplemented COD in the influent decreased the AOX removal efficiency substantially (Table 2), the reasons for which are not clear. Average TOC removal was comparable to the previous set, though average AOX removal was reduced by half. Further work is necessary to determine the role of additional carbon source in the metabolization of AOX in the activated sludge systems.

More research is also required to verify the relationship between operating solids retention time and mechanism of AOX removal in AS systems.

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