A critical review of the ability of biological treatment systems to remove chlorinated organics discharged by the paper industry

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Abstract

One of the principal problems facing the pulp and paper industry is the discharge of chlorinated organics into the environment. The fate of chlorinated organics produced during pulp bleaching with chlorine-based compounds in waste-water treatment systems is critically examined. Aerobic and anaerobic processes are capable of removing chlorinated organics to varying degrees of efficiency. However, the mechanism by which this removal occurs has not been identified precisely.

Nomenclature

AOX	-	adsorbable organic halide
BOD	-	biological oxygen demand
COD	-	chemical oxygen demand
D	-	Dalton
HMM	-	high molecular mass
HRT	-	hydraulic retention time
kD	-	kilodalton
LMM	-	low molecular mass
SRT	-	solids retention time
TOC1	-	total organic chlorine
TOX	-	total organic halide

Introduction

The effect of the pulp and paper industry on the environment is now being closely examined. Mills using chlorine-based compounds for bleaching, discharge chlorinated organics (primarily chlorinated lignin degradation products) into the environment. Some of these compounds may be toxic and mutagenic (Germgard et al., 1984; Kringstad and McKague, 1988) and may bioaccumulate in fish tissue (Renberg et al., 1980). But Craig et al. (1990) reported that the concentration of chlorinated organics discharged could not be related to effluent or sediment toxicity.

An increasingly attractive means to reduce the discharge of chlorinated organics, as measured by adsorbable organic halide (AOX) content, is to modify the bleaching process either by using oxygen delignification or by substituting chlorine dioxide for chlorine (Graves et al., 1993). These techniques serve to reduce chlorinated organics as well as BOD, COD, and toxicity (Germgard et al., 1984; Pryke, 1989; Singh, 1988). However, these process modifications are typically capital-intensive; mills will more likely rely on their presently-installed waste-treatment systems to remove the bulk of the chlorinated organics for the foreseeable future. The most common methods of waste treatment are biological systems such as aerated lagoons, activated sludge, and anaerobic technology.

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In the United States, the only federal regulation by the Environmental Protection Agency for chlorinated organics is for the total amount of the 75 congeners of dibenzo-p-dioxin discharge to be less than 0.013 kg/t (Kinstrey, 1993). Several states have begun monitoring the discharge of AOX. Alabama requires pulp mills to report AOX each quarter when applying for waste- water treatment permit renewals, and Oregon requires discharge of less than 1.5 kg TOCl/t (Kinstrey, 1993).

Other countries have, however, passed regulations regarding the discharge of chlorinated organics into receiving waters. Canada regulates the discharge of AOX to 2.5 kg/t, and plans to decrease this limit to 1.5 kg/t by 1994 (Randle et al., 1991). Sweden will limit the discharge of TOC1 to less than 0.01 kg/t by the year 2010 (Kinstrey, 1993).

With these regulations and concerns in mind, the efficacy of current biological treatment methods, such as aerated lagoons, activated sludge processes, and anaerobic processes, to remove chlorinated organics in the paper industry is critically examined herein. There is much conflict in the literature concerning how much AOX can be removed and what the mechanism may be.

Organic chlorine compound determination

There are several non-specific parameters that can be used to measure the amount of organically bound halogen. In the pulp and paper industry, almost all halogen measured is chlorine, with minor amounts of bromine present due to bromine-containing biocides used on the paper machine. Total organic halide (TOX) is termed a sum parameter test since it measures, without discrimination between specific organic compounds, all organic halogen compounds. In the pulp and paper industry, the bulk of the TOX is lignin degradation products from the pulping process to which chlorine has been added during the bleaching process. Although the carbon/chlorine ratio remains essentially constant through the biological treatment system (Aprahamian and Stevens, 1990), the amount of AOX ultimately discharged depends on many factors including wood source (less AOX is produced when hardwood rather than softwood is bleached; Tomar and Allen, 1991), use of oxygen prebleaching (Graves et al., 1993), and the amount of chlorine dioxide substitution (Barton and Drake, 1993).

Traditionally, TOX measurements involve the combustion of organic compounds dried onto cellulose filter paper in an oxygen atmosphere (Sjöström et al., 1985). The organic halide is con-