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**THE ADSORPTION OF ADSORBABLE ORGANIC HALIDE
ONTO BIOLOGICAL SOLIDS**

A thesis submitted in partial fulfilment
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ABSTRACT

Chlorinated organic molecules may be removed from wastewaters by adsorption onto the biomass present in biological treatment systems. This study assessed the adsorption onto biological solids of Adsorbable Organic Halide (AOX) from two New Zealand kraft pulp and paper mill bleach plant wastewaters.

Batch adsorption studies were carried out to determine the characteristics of this adsorption process, with activated sludge as an adsorbent. Different molecular weight AOX fractions from two bleach plants' wastewaters were studied. The first wastewater was a combined C and E stage effluent from the CEH bleach sequence previously used at the Tasman Pulp and Paper Co. Ltd, Kawerau. The second was a combined D and E₀ stage effluent from the OODE₀D bleach sequence used at New Zealand Forest Products Kinleith Mill, Tokoroa.

For each mill's wastewater, the adsorption isotherms were characterised for four different molecular weight fractions, and the unfractionated wastewater. Adsorption isotherm models used to fit the data for each of the fractions were the Freundlich, Langmuir and Irreversible isotherms. No single model was able to successfully describe the adsorption characteristics for all of the fractions analysed, indicating significant differences in the adsorption processes occurring in the various fractions.

Analysis of the adsorption of the different molecular weight fractions demonstrated that the adsorption affinity of the AOX increased with increasing molecular weight. It appeared that molecules with higher chlorination levels were more effectively adsorbed onto the biomass. Competition for adsorption sites on the biomass by the different molecular weight fractions was a significant factor in the adsorption of the unfractionated wastewater.

Analysis of the adsorption of AOX from the wastewaters at concentrations typical of those expected in different biological treatment systems showed that:

- treatment systems with low biomass concentrations, such as aerated lagoons, would not be expected to remove significant amounts of AOX by adsorption.

- treatment systems utilising higher biomass levels have the potential to remove significant amounts of AOX by adsorption. Conventional activated sludge systems could remove 15-20%, and oxygen activated sludge systems 25-50% of the AOX entering these systems.

The impact of the modernisation of bleach sequences on the adsorption of AOX, by the introduction of oxygen delignification and chlorine dioxide substitution, was assessed. This was carried out by comparison of the adsorption characteristics of the two mills' wastewaters. The Tasman mill's bleach sequence was used as an example of older, conventional bleaching, and the Kinleith mill's sequence an example of modernised bleaching. Significant differences were found in the adsorptive behaviour of the molecular weight fractions, and that of the unfractionated wastewaters, between the two.

From the analysis, adsorption onto biomass in a biological treatment system is predicted to alter the molecular weight distribution of the AOX in wastewaters. The conventional sequence's wastewater should show a decrease in the proportion of high molecular weight AOX due to this adsorptive removal, an effect not as significant in the adsorption of AOX from a modern bleach plant wastewater. Modern bleach sequence wastewaters are expected to reveal a decrease in the proportion of the low molecular weight material, an effect not as notable for the conventional sequence's AOX.

Modernisation was found to decrease the adsorptive affinity of the wastewater, suggested to be due to the lower chlorination levels and average molecular weights of the molecules in the wastewater. It was concluded that the modernisation of bleach sequences has reduced the significance of adsorption onto biological solids as an AOX removal mechanism.

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